

AN ABSTRACT OF THE THESIS OF

Jay A. Celorie for the degree of Master of Science in Civil Engineering presented on May 2, 1988.

Title: Modeling Solute Transport by Centrifugation.

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Ted S. Vinson

Measurement of physical and chemical solute transport properties of a soil/waste system is necessary to predict pollutant migration in soils. The adsorption component of solute transport is most often determined in the laboratory by performing column studies and batch equilibrium tests. Both of these methods suffer from disadvantages. Batch equilibrium tests performed with dilute solids concentrations overestimate the sorption distribution coefficient due to the solids effect and column studies with fine grained soils require a long period of time to conduct. An alternate to these methods involves the use of a constant head permeameter that fits in a laboratory centrifuge. Centrifugation testing alleviates the disadvantages of batch equilibrium and column methods by imposing a confining stress in the soil sample at a solids concentration similar to that in the field and producing a greater pore water velocity.

The centrifugal technique was evaluated by conducting

experiments with a kaolinite soil/chloride solute system under different conditions of inertial acceleration and column size. Sorption distribution coefficients, K_d 's, were estimated by modeling the generated solute breakthrough curves with a solute transport curve fitting program. The results produced almost identical K_d values for the range of inertial accelerations and column sizes considered in the program.

Another set of centrifuge experiments was conducted with phenol solute. K_d 's determined in the centrifuge were compared with values measured in batch equilibrium tests performed with the same materials. Although the K_d values determined in the centrifuge were lower than the values predicted by extrapolating the batch sorption data, the results were consistent with the solids effect. The introduction of a parameter which takes into account the surface area of the solids demonstrated a better correlation between the centrifuge and batch data. However, these test techniques are fundamentally different and a strong correlation between the two was not expected.

With the centrifuge technique developed, physical and chemical sorption data can be generated in fine grained soils with respect to: sorption mechanisms of various compounds, sorption kinetics, the solids effect and the effects of pH, ionic strength, and confining stress.

Modeling Solute Transport by Centrifugation

by

Jay A. Celorie

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PREFACE

This thesis is a compilation of two articles written for separate publication and inclusion herein. Each paper is complete by itself. There is some duplication in the background and experimental methods in the papers. Citations in the text refer to references listed at the end of each chapter. These references are collected into a comprehensive bibliography at the end of the report. The co-authors listed in each of the papers contributed their expertise as advisors with respect to the research program; specifically: Ted Vinson - centrifuge theory, Sandra Woods - sorption theory, and Jonathan Istok - solute transport modeling.

Jay A. Celorie

May, 1988

MODELING SOLUTE TRANSPORT BY CENTRIFUGATION

1.0 INTRODUCTION

Predicting the transport of hazardous wastes in soils is a complex problem which requires an understanding and measurement of the physical, chemical and biological mechanisms contributing to the dispersion, retardation and degradation of the wastes. Mathematical models have been developed to predict the transport of pollutants in soils. The physical/chemical properties which are necessary inputs to these models are estimated from field data or measured in laboratory tests.

Present methods of measuring physical/chemical transport properties in the laboratory include column studies and batch equilibrium tests. These methods suffer from disadvantages: column studies with fine grained soils require a long period of time to conduct, and batch equilibrium tests overestimate sorption distribution coefficients. A centrifugation technique alleviates these disadvantages.

The study reported herein consists of two separate papers concerning: (1) the development of the centrifuge method and a comparison of the results obtained in experiments performed under different conditions, and (2) an application of the method by determining sorption distribution coefficients and a comparison of the results with values obtained from batch equilibrium tests.

2.0 MODELING SOLUTE TRANSPORT BY CENTRIFUGATION

Jay A. Celorie, Ted S. Vinson, Sandra L. Woods, and
Jonathan D. Istok

Abstract

Measurement of physical and chemical solute transport properties of a soil/waste system is necessary to predict pollutant migration in soils. The adsorption component of solute transport is most often determined in the laboratory by performing column studies and batch equilibrium tests. Both of these methods suffer from disadvantages. Batch equilibrium tests overestimate the sorption distribution coefficient due to the solids effect and column studies with fine grained soils require a long period of time to conduct. An alternate to these methods involves the use of a constant head permeameter that fits in a laboratory centrifuge. Centrifugation testing alleviates the disadvantages of batch equilibrium and column methods by imposing a confining stress in the soil at a solids concentration similar to that in the field and producing a greater pore water velocity. The centrifuge technique was evaluated by conducting experiments under different conditions of inertial acceleration and column size. Sorption distribution coefficients, K_d 's were estimated by modeling the generated breakthrough curves with a solute transport curve fitting program. The results produced almost identical K_d values for the range of inertial accelerations and column sizes considered in the program.

2.1 INTRODUCTION

Contamination of subsurface water by hazardous wastes may occur by inadequate waste disposal activities or by industrial accidents. Estimating the extent of the contamination requires an understanding of the migration of hazardous wastes through soils. Prediction of solute transport through soils is important for protecting the integrity of groundwater that is threatened by contamination or to restore water quality in a polluted area.

Predicting the transport of hazardous wastes in soils is a complex problem which requires an understanding and quantification of the physical, chemical and biological mechanisms contributing to the dispersion, retardation and degradation of the wastes. Mathematical models have been developed to predict the transport of pollutants in soils. The physical/chemical properties which are necessary inputs to these models are estimated from field data or measured in laboratory tests.

Laboratory column studies of saturated and unsaturated flow through porous media have contributed to the understanding and modeling of solute transport [Bear, 1972; Nkedi-Kizza et al., 1984; Hutzler et al., 1986]. In laboratory column studies, a pulse or continuous input of solute is applied to the top of a soil column. The effluent is collected during the test and analyzed for the compound of interest. The plot of the normalized concentration

(ratio of the concentration of the solute in the effluent to the applied concentration) versus the amount of flow through the porous media expressed as pore volumes is called the breakthrough curve (BTC). The importance of different solute transport mechanisms can be inferred from the shape of the BTC. Figure 2.1 presents the theoretical shapes of BTC's for: (1) plug flow, (2) plug flow with dispersion, and (3) plug flow with sorption and dispersion. Ideal plug flow would produce a step concentration change at one pore volume. Dispersion causes the solute front to spread, and sorption retards the advance of solute. Chemical and biological degradation would be expected to reduce the total mass of solute passing through the soil column.

The size of laboratory soil columns used to characterize solute transport are small and applying results to complex field conditions is difficult. Other problems with column studies include nonuniform flow within the column and the length of time involved when testing fine grained soils (e.g. clay or silty clay soils). However, the tests provide a controlled and accessible soil environment for the study of solute transport mechanisms. BTC's can be fitted with solute transport models to estimate properties of the soil/solute system such as the sorption distribution coefficient, K_d .

Another method used to determine K_d , is to perform batch equilibrium tests. Batch equilibrium tests consist of placing a mixture of soil and solute in a reaction vessel,

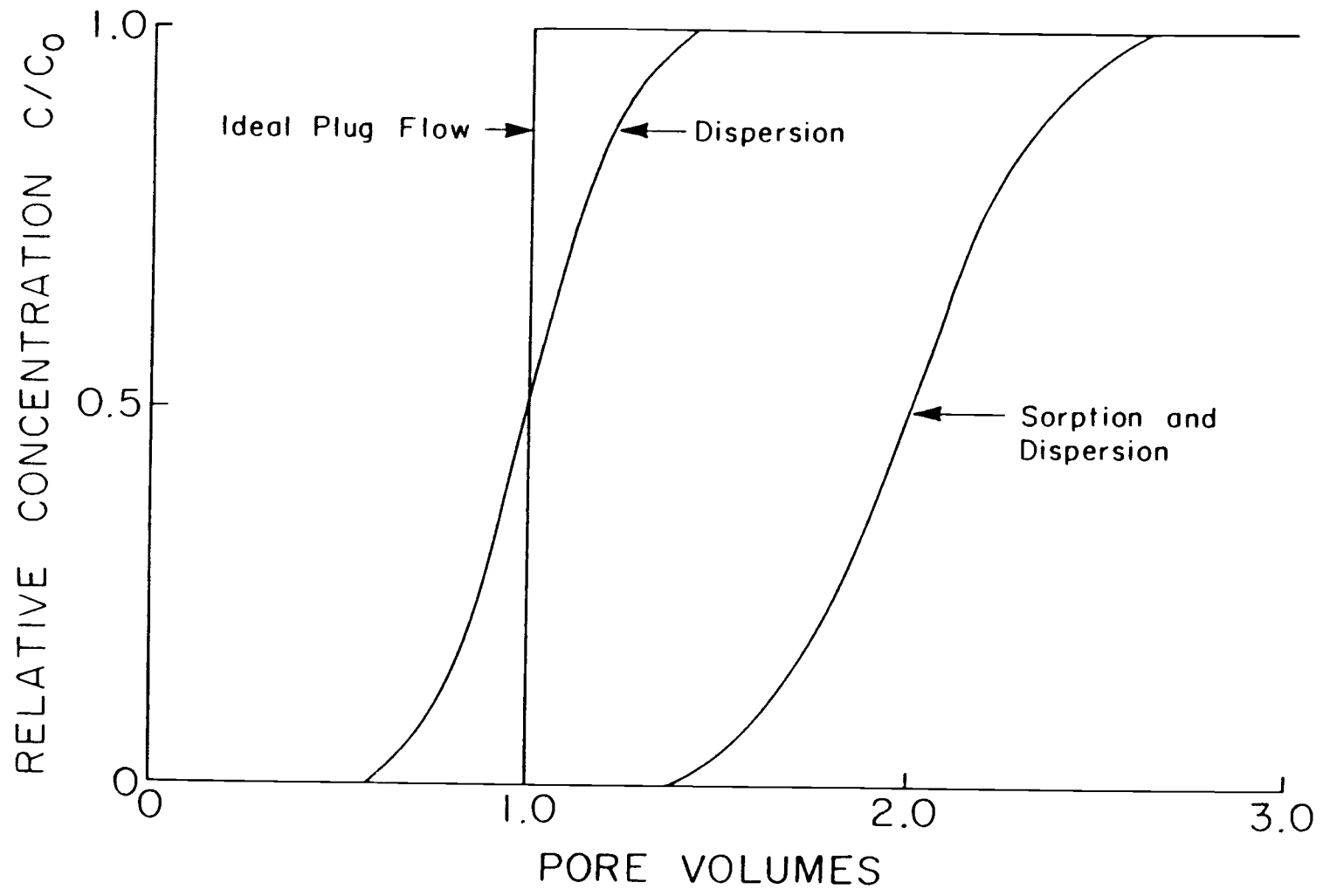


Figure 2.1 Theoretical shapes of breakthrough curves for solute transport.

shaking the vessel at constant temperature for a given time period, and determining the solute concentration in the liquid and solids phases. However, K_d 's obtained by this method depend on the solids (sorbent) concentration; that is, the measured value for K_d decreases with increasing solids concentration (i.e. the "solids effect") [O'Connor and Conolly, 1980; Voice et al., 1983; and Di Toro et al., 1986]. Since the solids concentration for an undisturbed field soil is much greater than that used in batch tests, predicted rates of solute transport using K_d 's from batch experiments will be smaller than may actually occur.

Due to the dependency of K_d on the solids concentration, it would be beneficial to measure K_d values at solids concentrations similar to those in the field. Column studies provide the ability to test at high solids concentrations but require a long period of time to conduct with fine grained soils. Centrifugation can shorten the time required by imposing an acceleration on a soil column substantially greater than one gravity.

Centrifugal modeling has been employed to investigate fluid flow in porous media [Alemi et al., 1976; Goforth et al., 1986; Nimmo et al., 1987]. In centrifugal modeling, a soil column is spun at high rotational speeds in a centrifuge, increasing the gravitational effects (body forces) which simulate an in situ confining stress. The rates at which processes occur in the centrifuge model can be related to the prototype through fundamental principles

of physics [Goodings, 1984]. Centrifugal modeling has recently been used to study solute transport through soil (i.e. advection and dispersion) [Arulanandan et al., 1988]. Centrifuge modeling of solute transport has several advantages: (1) the time for testing soils with a small hydraulic conductivity is reduced, (2) nonuniform flow is negligible due to the lateral stress which results from the inertial acceleration, and (3) the effects of confining stress are included in the method. Modeling solute transport with sorption in a centrifuge apparently has not been considered in previous research.

In recognition of the need to evaluate sorption input parameters for fine grained soils used in solute transport models, a research program was conducted to identify the potential use of a centrifugation technique. In the program, a series of centrifuge experiments were performed using different inertial accelerations and column sizes. The results from the program are presented herein.

2.2 BACKGROUND

Centrifuge Modeling

The technique of centrifuge modeling has been employed intensively over the past 15 years to simulate the stress distribution in earth structures. The technique subjects a small-scale model to an artificial gravitational acceleration in a centrifuge, Ng , simulating the stress distribution in the field. This is accomplished by rotating the soil column (model) in a plane such that the outward radial direction corresponds to the vertical direction in the field (prototype).

The artificial gravitational acceleration contains two components (Figure 2.2): (1) The radial acceleration, A_r , away from the center of rotation:

$$A_r = r\omega^2 \quad [2.1]$$

where r is the radius (m) and ω is the angular velocity

(rad/s), and (2) the tangential acceleration, A_t , perpendicular to the center of rotation and in the direction of rotation:

$$A_t = r\dot{\omega} \quad [2.2]$$

where $\dot{\omega}$ is the angular acceleration (rad/s²) [Clough, 1985].

However, the tangential acceleration can be neglected since its magnitude is small and only exists during the starting and stopping of the centrifuge (usually a short period of time compared to the total test time).

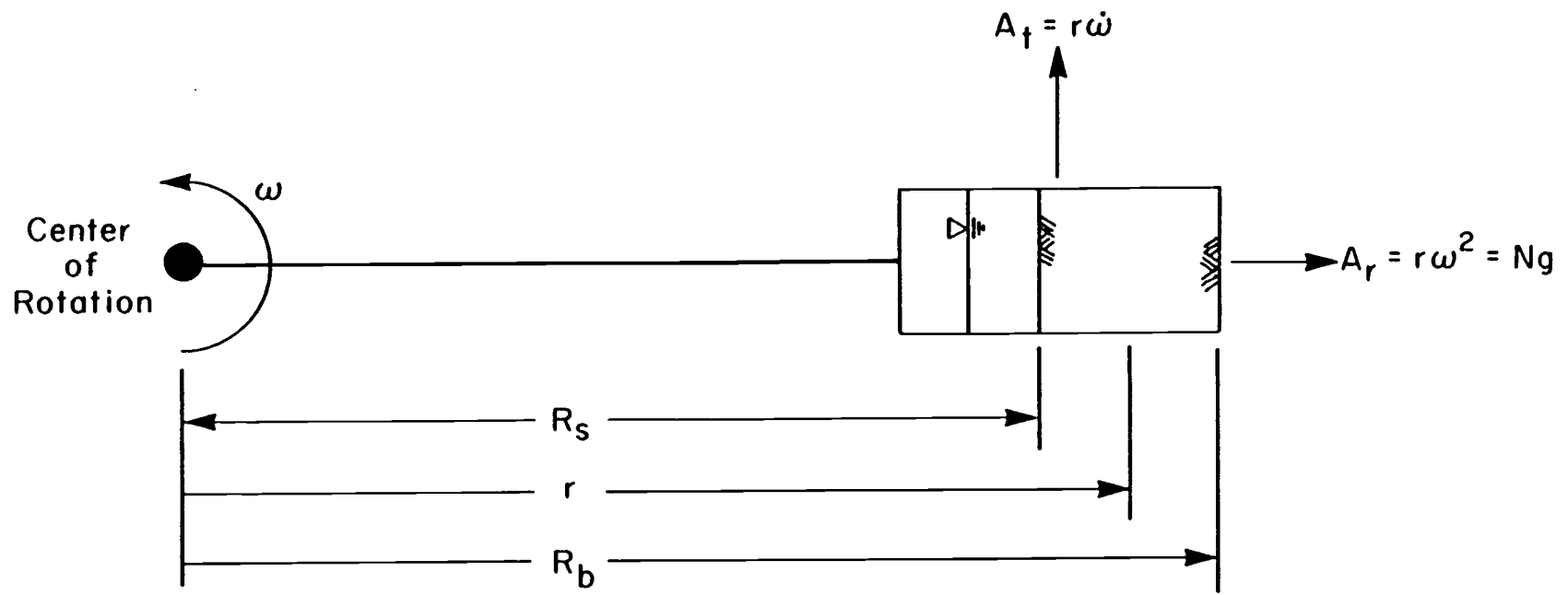


Figure 2.2 Plan view of model rotating in a centrifuge.

In centrifuge modeling, a soil column is constructed at a vertical scale of 1 to N so that a depth L in the model corresponds to a depth NL in the prototype (Figure 2.3).

Thus:

$$L_m = L_p / N \quad [2.3]$$

where L is any vertical dimension and the subscripts m and p denote the model and prototype, respectively. When the model is subjected to an artificial acceleration equal to Ng, where g is the gravitational acceleration, the self weight of the model with length 1/N simulates the stress distribution in the prototype. It follows that the density and void ratio, being stress dependent, will also be simulated as long as the same material in the prototype, subjected to the same stress history, is used in the model. The stress, σ (N/m²), associated with self weight in the model is:

$$\sigma = \gamma_b \omega^2 (R_b^2 - R_s^2) / 2g \quad [2.4]$$

where γ_b is the buoyant unit weight of the soil (N/m³) and R_b and R_s are the radial distance from the center of rotation to the base and surface of the soil (m), respectively [Nimmo et al., 1987]. However, there is a slight distortion of the stress due to the curved field of the centrifugal acceleration as demonstrated by the stress distributions shown in Figure 2.3. The stress in the model is a function of the depth, r, squared so the distribution is not linear. If r is greater than five times the model depth, then the distortion is relatively insignificant.

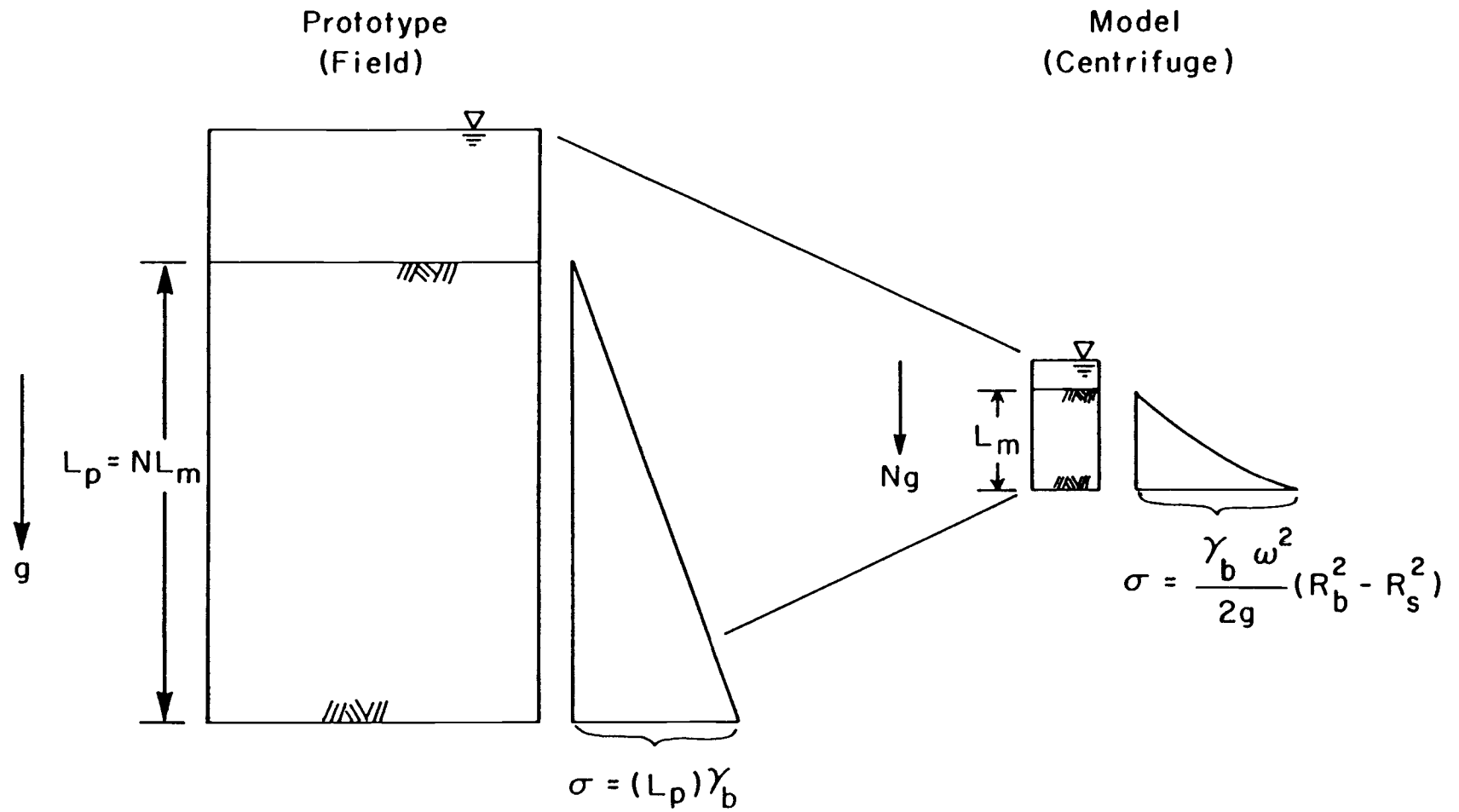


Figure 2.3 Comparison of prototype and model stress distributions.

Flow of water through the soil can also be simulated in a centrifuge model. For most soils, saturated, steady flow is laminar and is characterized by the Reynolds Number:

$$Re = \rho v d / \mu \quad [2.5]$$

where ρ is the density of water (kg/m^3), v is the specific discharge (m/s), d is an effective or average pore diameter (m), and μ is the dynamic viscosity (N s/m^2). When the Reynolds Number is in the range of 1 to 10, then the flow is considered to be laminar [Bear, 1972].

Darcy's law is an empirical equation which describes laminar seepage through soils:

$$v = k i \quad [2.6]$$

where k is the coefficient of permeability (m/s), and i is the hydraulic gradient (m/m) which is the ratio of the total head loss to the distance traveled. The permeability is dependent upon the fluid and the physical characteristics of the porous media:

$$k = K \gamma / \mu \quad [2.7]$$

where K is the intrinsic permeability (m^2), and γ is the unit weight of the fluid (N/m^3). The intrinsic permeability is invariant with respect to the pore fluid, but is dependent on the average particle size and pore diameter (which reflects the void ratio). The permeability in the model will be the same as the prototype ($k_m = k_p$) if the same fluid is used and if similtude of the stress is imposed such that the structure of the soil grains are identical [Goodings, 1984]. The flow regimes in the model and proto-

type are the same except that the distance the fluid travels (vertically) in the model is reduced $1/N$ th of that in the prototype. This implies that the velocity of the model and prototype are identical, but the time required to produce the same specific discharge (flow per unit area) is reduced by a factor of N due to the smaller vertical scale.

However, in the centrifuge, the boundary water pressure is increased due to self weight under the acceleration. This is incorporated in the hydraulic gradient where the total head loss is increased N times. Thus, the velocity in the model is N times that in the prototype ($v_m = N v_p$). The time required for a specified discharge is increased by a factor of N^2 in the model due to the combined effects of the reduced vertical scale and the increased self weight of the water [Goodings, 1984]:

$$L_m = L_p / N \quad [2.8]$$

and
$$v_m = N v_p \quad [2.9]$$

so
$$t_m = L_m / v_m = \frac{L_p / N}{N v_p} = \frac{L_p}{N^2 v_p} = \frac{t_p}{N^2} \quad [2.10]$$

Similitude of other parameters for a centrifugal model maybe evaluated by deriving additional scaling relationships, performing a dimensional analysis, analyzing the governing differential equations or developing experimental evidence. A summary of the scaling relationships for the parameters discussed is presented in Table 2.1.

TABLE 2.1 SCALING RELATIONSHIPS FOR THE CENTRIFUGE MODEL

PARAMETER	RELATIONSHIP
VERTICAL DIMENSION	$L_m / L_p = 1/N$
STRESS	$\sigma_m / \sigma_p = 1$
DENSITY	$\rho_m / \rho_p = 1$
PERMEABILITY	$k_m / k_p = 1$
PORE WATER VELOCITY	$v_m / v_p = N$
TIME FOR EQUIVALENT DISCHARGE	$t_m / t_p = 1/N^2$

Solute Transport Theory

Solute transport occurs by advection and dispersion while sorption reactions are chemical or physical solute/porous media interactions which retard the solute and result in the temporary or permanent storage of solute.

More specifically, advection is the movement of solute attributed to the average linear pore water velocity, v (m/s), where v is the ratio of the Darcian velocity or specific discharge, V (m/s), to the porosity, n (m³/m³).

$$v = V/n \quad [2.11]$$

Hydrodynamic dispersion is the longitudinal mixing and spreading of the solute including mechanical dispersion and molecular diffusion. Mechanical dispersion is velocity dependent and is caused by a variety of physical mechanisms inherent to a fluid passing through a tortuous path [Greenhorn,1983]. Molecular diffusion is the movement of solute from areas of high concentration to low concentration [Freeze and Cherry, 1979].

Adsorption is the accumulation of a solute at the surface of a solid or another phase. Adsorption is a complex phenomena since it is described by a number of mechanisms which are dependent upon the solute, sorbent and solvent system. In this study, only equilibrium adsorption is considered, which exists "when the rate of change of mass due to the microscopic sorption process is much faster than

due to the bulk flow processes" [Valocchi, 1985].

Equilibrium adsorption is described by the equilibrium distribution coefficient, K_d (l/g):

$$K_d = C_s / C_l \quad [2.12]$$

where C_s is the concentration of solute on the solids at equilibrium (mg/g), and C_l is the concentration of solute in the solvent at equilibrium (mg/l).

Solute Transport Model

A linear equilibrium adsorption model is employed in this study to compare BTC's obtained from centrifuge tests. The model is based upon a linearized analytical solution after Lapidus and Amundson (1952) developed for equilibrium adsorption. The BTC's are fitted by a least-squares computer program utilizing the linearized solution [van Genuchten, 1981, Model A:SI-1].

The governing solute transport equation for a sorbing solute with linear equilibrium adsorption in one dimensional, steady state, saturated groundwater flow in homogeneous porous media is:

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad [2.13]$$

where R is the retardation factor, c is the solute concentration (mg/l), t is time (s), D is the coefficient of hydrodynamic dispersion (m^2/s), x is the distance in the direction of flow (m), and v is the average pore water velocity (m/s).

The retardation factor is given by:

$$R = 1 + \frac{\rho K_d}{n} \quad [2.14]$$

where ρ is the bulk density (kg/m^3), K_d is the empirical distribution coefficient (l/g), and n is the porosity (m^3/m^3).

The Peclet number is a dimensionless variable incorporating the coefficient of hydrodynamic dispersion:

$$P = \frac{vl}{D_h} \quad [2.15]$$

where l is the length of the column (m).

The boundary conditions are:

$$c(0,t) = C_0 \quad [2.16]$$

and
$$\frac{\partial c}{\partial x}(\infty,t) = 0 \quad [2.17]$$

where C_0 is the initial concentration. The upper boundary condition, Eq. 2.16, is used for the duration of the solute pulse; after which, the applied concentration is zero. The lower boundary condition, Eq. 2.17, implies a semi-infinite medium.

2.3 MATERIALS AND EXPERIMENTAL METHOD

Materials

Pure kaolinite (code KGa-1, Clay Minerals Society) was chosen for the soil specimen owing to its stability with respect to pH, freedom from microorganisms and workability. Some physical and chemical characteristics of the Kga-1 kaolinite are given in Table 2.2 [van Olphen and Fripiat, 1979]. The coefficients of compression and recompression were 0.34 and 0.045 respectively. Kaolinite has a low cation exchange capacity, but at neutral to low pH, the edges are positively charged and the basal planes are negatively charged [Mitchell, 1976]. The pH of the soil solution of kaolinite and distilled water was 5.0. The surface charge characteristics of the particles at this pH give rise to adsorption of anions as well as cations [Hunter and Alexander, 1963].

Chloride was chosen as the solute for the study because it is nonreactive, nonvolatile, soluble in water and slightly adsorbed by kaolinite. Chloride was added as sodium chloride in distilled water at a concentration of 50 mg/l.

Experimental Apparatus

The centrifuge model container is a constant head permeameter and is constructed of stainless steel (Figure 2.4). It is 3.0 cm in diameter and 15 cm in length and fits into a

TABLE 2.2 PHYSICAL AND CHEMICAL CHARACTERISTICS OF KAOLINITE

PARAMETER	KAOLINITE (KGa-1)
SPECIFIC GRAVITY ¹	2.62
CATION EXCHANGE CAPACITY	2.0 meq/100 g
SPECIFIC SURFACE AREA ²	10.05 m ² /g
THICKNESS ²	0.05 to 2 microns
LENGTH/WIDTH ²	0.1 to 4 microns
CHEMICAL COMPOSITION (% BY WEIGHT)	
SiO ₂	44.2
Al ₂ O ₃	39.7
TiO ₂	1.39
Fe ₂ O ₃	0.13
FeO	0.08
MnO	0.002
MgO	0.03
Na ₂ O	0.013
K ₂ O	0.050
F ₂	0.013
C ¹	0.027
P ₂ O ₅	0.034
LOSS ON HEATING (%)	
550 C ^o	12.6
550-1000 C ^o	1.18

- 1 Experimentally determined.
2 Mitchell, 1976.

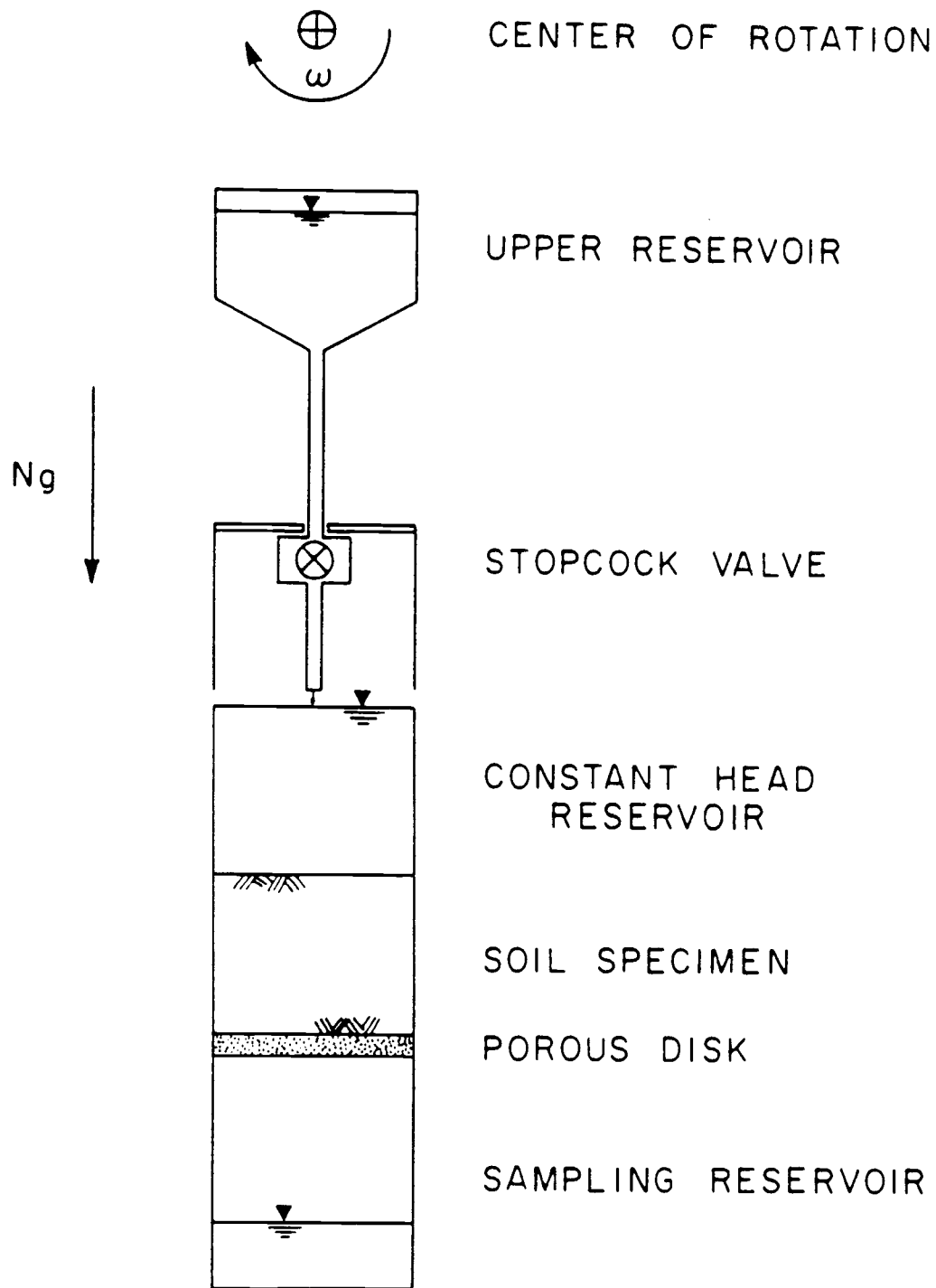


Figure 2.4 Schematic of constant head permeameter.

laboratory centrifuge (International, Model UV). The upper reservoir is constructed from Teflon and is attached to the rotor of the centrifuge. The upper reservoir is connected to the constant head reservoir by Teflon tubing and a stopcock valve. The valve is adjusted so that the flow rate from the upper reservoir is slightly greater than the flow rate through the soil column. The excess fluid overflows the constant head reservoir through slots in the permeameter wall thereby maintaining a constant head of water/solute above the soil column during an experiment. The permeameter can accommodate a soil column 2.5 cm in diameter and 5 cm in length. The soil is retained by a sintered stainless steel disk with 0.5 micron pores. The sampling reservoir collects the effluent from the permeameter and can be removed and replaced with an identical reservoir during sampling.

Experimental Method

At the beginning of each experiment, the permeameter was cleaned by submerging it in detergent and placing it in a sonicator for one to two hours, after which it was thoroughly rinsed with tap and distilled water and air dried. Next, approximately 15 g of distilled, deaired water was placed in the constant head reservoir of the permeameter. The weight of the permeameter and contents was noted. Air dried soil was slowly added to the water. After

the desired amount of soil was added, the permeameter was placed in a glass vessel which was connected to an aspirator to vacuum saturate the soil. The soil was consolidated by: filling the upper and constant head reservoirs with distilled, deaired water, placing the permeameter in the centrifuge, and spinning the centrifuge at the test speed (550 or 900 revolutions per minute). The permeameter was spun until 100% consolidation was achieved. This was determined by measuring soil column length until it remained constant with time. The soil column length is measured by inserting a Teflon disk on top of the soil and noting the distance from the surface of the disk to the top of the permeameter.

Immediately after the soil was consolidated, the water was replaced with solute in the upper and constant head reservoirs. The centrifuge was spun for a specific time period at a prescribed speed, the centrifuge was stopped, the sampling reservoir was replaced with an identical reservoir, and the upper reservoir was refilled to begin another time step. The centrifuge was accelerated to the test speed in 12 to 17 seconds and decelerated in 10 to 15 seconds.

While the centrifuge was spinning, the sampling reservoir (from the previous time step) was weighed to determine the effluent volume. The effluent was withdrawn from the sampling reservoir with a syringe and stored in a 1.5 ml glass vial. The sampling reservoir and syringe were

rinsed with distilled water and dried for the next sample. The speed of the centrifuge was checked with a hand tachometer between each sampling period.

Once a specified number of pore volumes passed through the soil column, the solute was replaced with distilled, deaired water and the test was continued for a specified number of additional pore volumes.

At the conclusion of the test, the soil column was sampled with a tube 2.0 cm in diameter and 12 cm in length. The tube was pushed into the soil column. The soil was retained by connecting an aspirator to the tube. The soil was then extruded in approximately 0.4 cm increments and water contents were determined on each sample. The bulk density and void ratio were then computed for each depth.

Analytical Method

Concentrations of chloride were determined using a Dionex Model 2000i ion chromatograph operated with a conductivity detector. A Dionex HPIC-AS4A column was used for the separation. A solution containing 1.8 mmols/l sodium carbonate and 1.7 mmols/l sodium bicarbonate was used as the eluant at a flow rate of 2.0 ml/min. The detection sensitivity was 0.1 parts per million.

2.4 RESULTS AND DISCUSSION

To evaluate the centrifuge method, four experiments were performed employing kaolinite soil and chloride solute. The tests were performed with columns composed of two different amounts of soil at two inertial accelerations (or centrifuge speeds). In the centrifuge tests, the bulk density and void ratio varied slightly with depth in the model, but average values can be used with negligible error in the results [Selim et al., 1977; De Smedt and Wierenga, 1978].

The tests were performed at two speeds (Table 2.3): 550 and 900 revolutions per minute (RPM). The amount of kaolinite used to construct the soil column was also varied, which changed the length of the column. These parameters directly affect the average void ratio of the soil column and the pore water velocity. The higher speed (in tests 3 and 4) caused a decrease in the void ratio but a faster pore water velocity (with respect to tests 1 and 2). A smaller amount of soil in the column (tests 2 and 4) caused a slight decrease in void ratio and an increase in the pore water velocity (with respect to tests 1 and 3).

The results demonstrate expected trends, since a higher speed (greater inertial acceleration) with the same amount of kaolinite imposes a greater stress on the soil and a smaller void ratio. The greater speed also increases the boundary water pressures, which cause a faster pore water

TABLE 2.3 CENTRIFUGE EXPERIMENT PARAMETERS AND RESULTS

PARAMETER	TEST NO:	1	2	3	4
SPEED (RPM)		550	550	900	900
DRY WEIGHT OF SOIL (g)		13	8	13	8
COLUMN LENGTH (cm)		2.273	1.372	2.146	1.283
AVERAGE VOID RATIO		1.32	1.28	1.19	1.13
PORE WATER VELOCITY ($\mu\text{m/s}$)		2.24	6.11	6.44	11.66
PECLET NUMBER		31.8	38.1	91.0	111.0
D_h ($\text{cm}^2/\text{s} \times 10^{-5}$)		1.60	2.20	1.52	1.35
DISPERSIVITY ($m \times 10^{-4}$)		6.70	3.60	2.36	1.16
RETARDATION FACTOR		1.518	1.563	1.550	1.645
Kd (ml/g)		0.174	0.184	0.172	0.194

velocity. Similarly, a shorter column (smaller amount of soil) at the same speed, is subjected to higher average stress due to the increased radial distance to its center of mass. Therefore, a slightly smaller void ratio was anticipated. Also, the shorter column at the same speed exhibited a larger pore water velocity due to the higher column of water above the soil column (imposing a greater boundary water pressure).

Figures 2.5 through 2.8 show the BTC's generated in the centrifuge. The data are represented by open circles and the line depicts the fitted model. Solute was applied for a period of time from the beginning of the test until a number of pore volumes had passed. The solute was then replaced with water to allow an evaluation of desorption. In test 1, the solute pulse was applied for 2.2 pore volumes. The BTC shows the concentration front was delayed beyond one pore volume demonstrating that the chloride is retarded. Similarly, the desorption of chloride occurs at a pore volume greater than one after the solute pulse was removed. In all tests, there exists some background chloride. This was a result of impure distilled water and chloride leaching from the kaolinite.

The BTC's were fitted with a least-squares curve-fitting program that uses a linearized form of an analytical solution developed for equilibrium adsorption. The program estimates the Peclet number and retardation factor through an iterative process. It calculates a BTC on initial

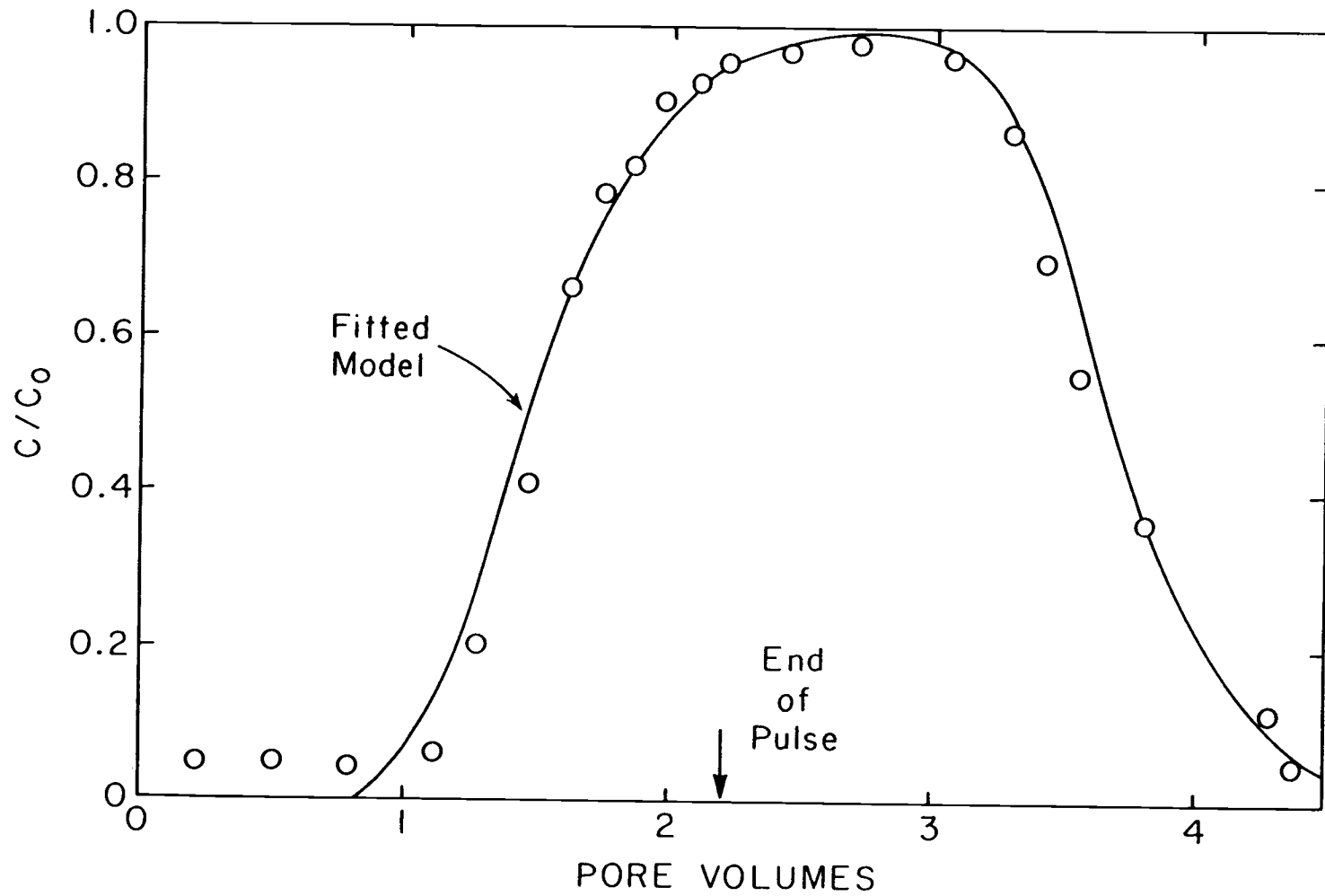


Figure 2.5 Chloride BTC in kaolinite for a 13 gram soil column spun at 550 RPM (test 1).

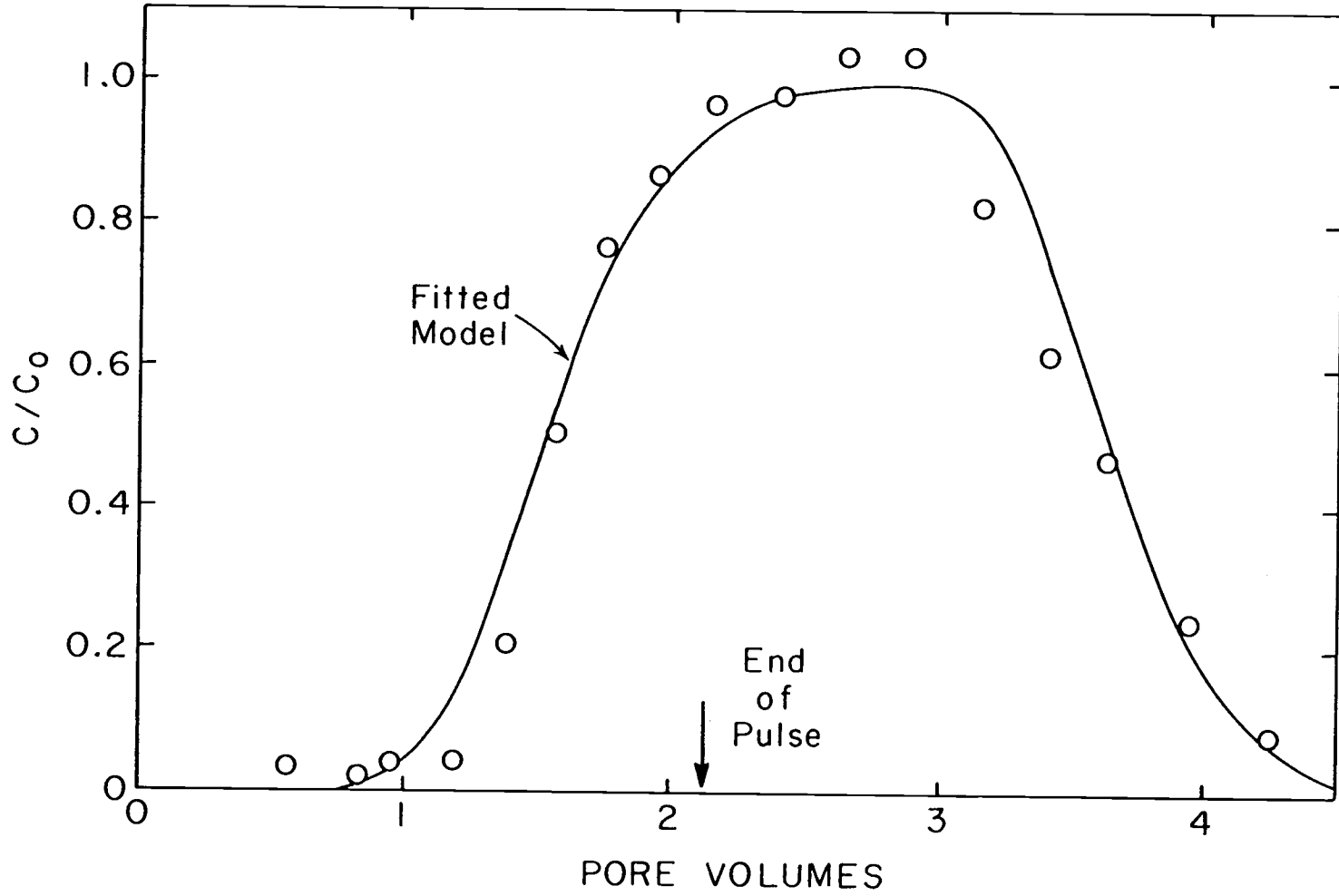


Figure 2.6 Chloride BTC in kaolinite for an 8 gram soil column spun at 550 RPM (test 2).

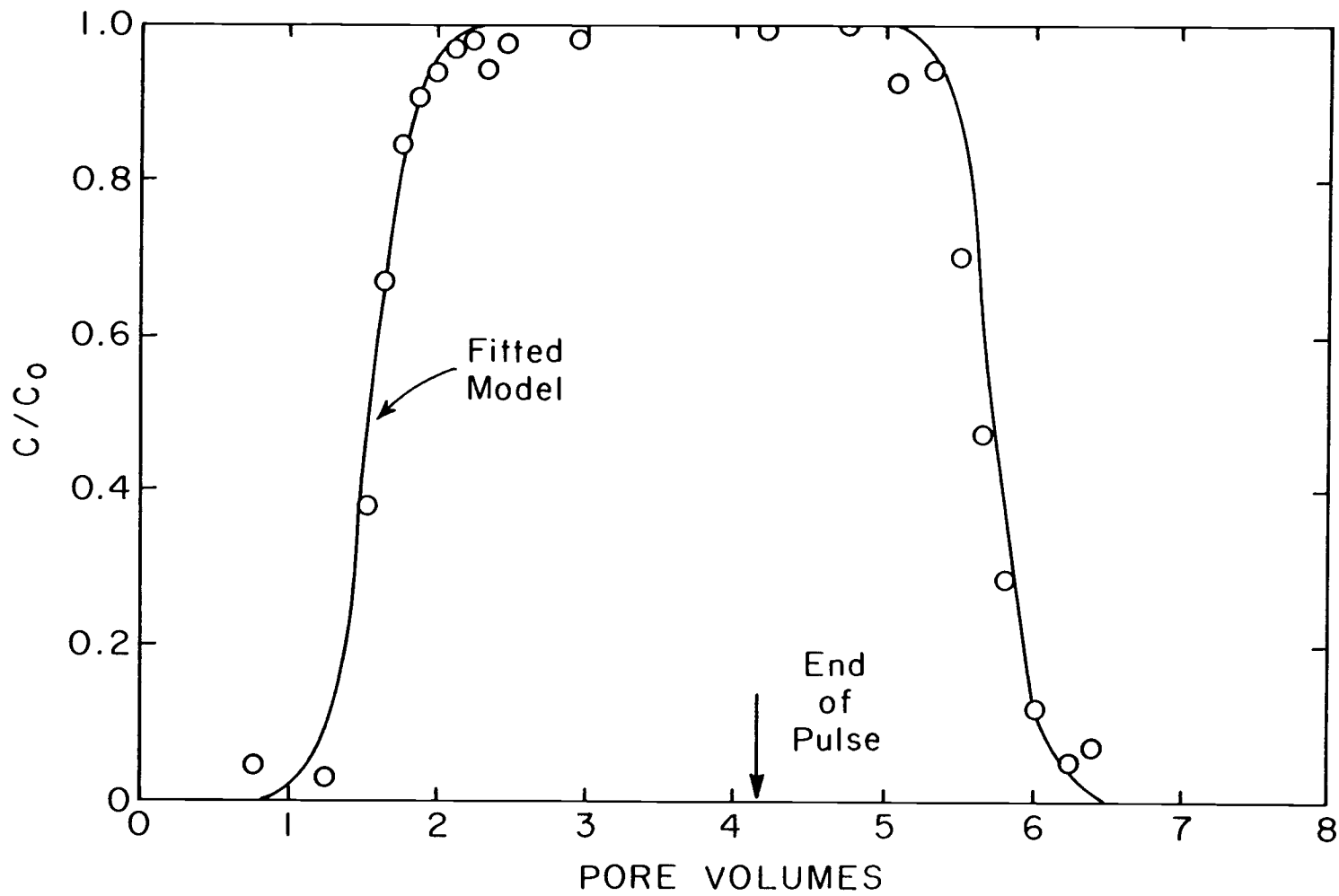


Figure 2.7 Chloride BTC in kaolinite for a 13 gram soil column spun at 900 RPM (test 3).

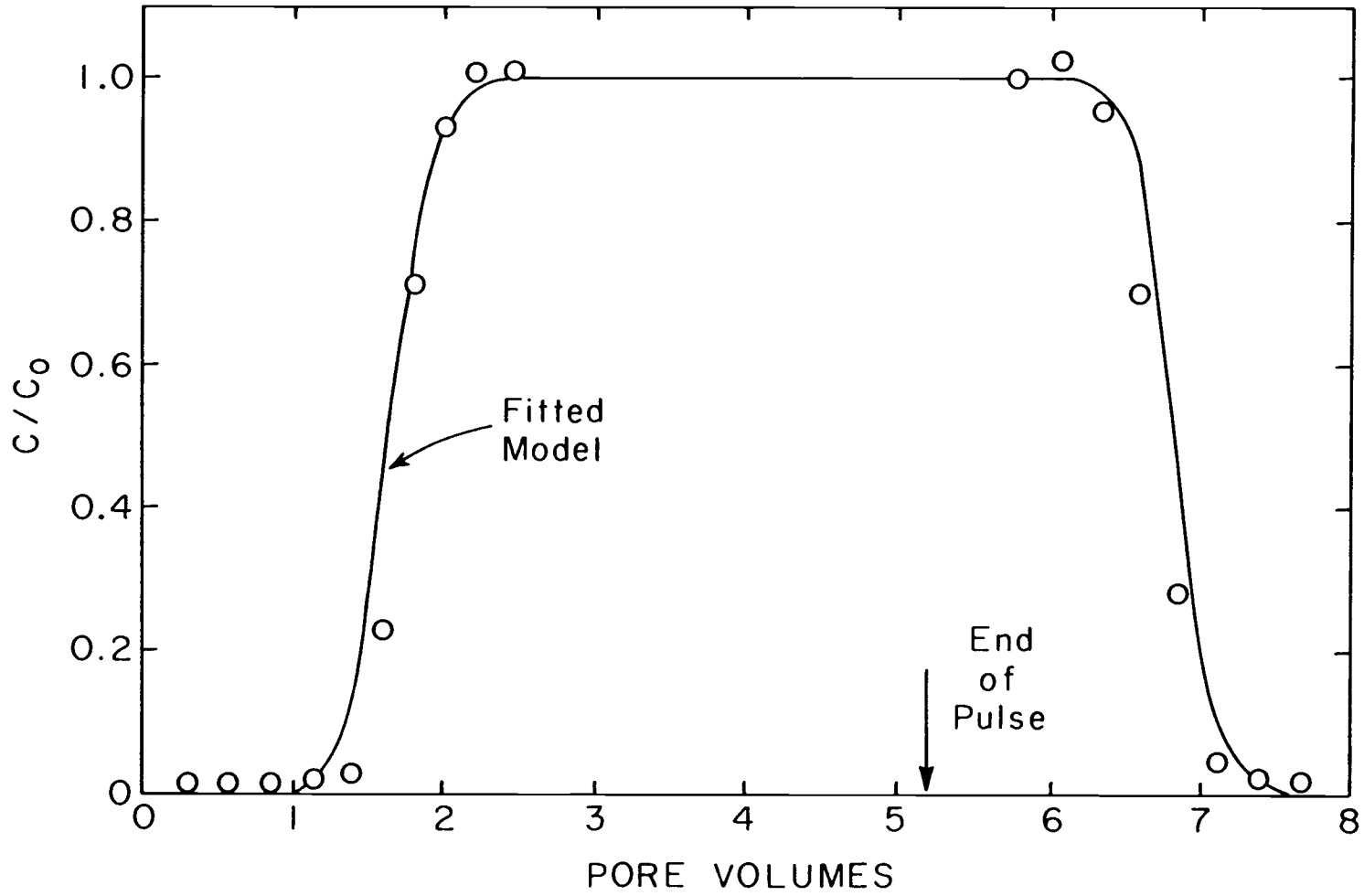


Figure 2.8 Chloride BTC in kaolinite for an 8 gram soil column spun at 900 RPM (test 4).

parameter estimates, calculates the residual error with respect to the experimental data, and then iterates with new parameter estimates until the residuals are minimized.

Verification and suitability of the model to the experimental data is realized by the good fit. The fitted model generates a Peclet number and retardation factor from which D_h and K_d can be calculated.

The Peclet number is a function of the pore water velocity and the dispersion. The Peclet numbers exhibited a significant increase from the lower to the higher speed. This increase of the Peclet number is a result of a denser soil column and a greater pore water velocity at the higher speed. The values for D_h were inconsistent with the expected results. D_h is expected to vary directly with pore water velocity. Tests 1 and 2 indicate the correct trend showing an increase in D_h with an increase in velocity. However, tests 3 and 4 are not consistent with respect to each other or with respect to tests 1 and 2.

Dispersivity is an intrinsic property of the porous media and is the ratio of the hydrodynamic dispersion to the pore water velocity. The dispersivity is expected to vary directly with the void ratio. The computed values show the expected trend.

A retardation factor equal to one indicates that no sorption has occurred. The model generated retardation factors were between 1.52 and 1.65 demonstrating that chloride is slightly adsorbed by kaolinite. Based on Eq. 2.14,

K_d was calculated from the retardation factor. The range of the K_d values are small with an average of 0.152 ml/g and a standard deviation of 0.012 ml/g (6% of the mean).

Ideally, the K_d values should be identical since its calculation accounts for the bulk density and the volumetric water content. The small variation of the K_d values observed is well within the experimental error and the ability of the model to fit the data accurately. Therefore, these results demonstrate that the level of inertial acceleration and the size of the column does not effect the outcome with equilibrium adsorption.

2.5 SUMMARY AND CONCLUSIONS

The prediction of the movement of hazardous wastes through soils is dependent upon the measurement of the physical and chemical properties of a soil/waste system. Present methods for determining the sorption component of solute transport in the laboratory suffer from disadvantages: (1) batch sorption tests overestimate sorption due to the solids effect, and (2) performing column studies with fine grained soils require a long period of time. This study has demonstrated a new method to evaluate the sorption component of solute transport using a centrifugation technique.

The centrifuge technique was demonstrated by performing experiments with a kaolinite/chloride system in which breakthrough curves were generated and modeled to determine the sorption distribution coefficient. The tests conducted with two different amounts of soil composing the column and under two inertial accelerations demonstrated almost identical results.

The centrifugal technique is advantageous for modeling solute transport in fine grained soils since the method is relatively quick and it is performed under bulk densities and confining stresses encountered in natural soil deposits.

There are many potential applications for this method since physical and chemical data can be generated for fine

grained soils with respect to: sorption mechanisms of various compounds, sorption kinetics, the solids effect, and the effects of pH, ionic strength, and confining stress.

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3.0 A COMPARISON OF SORPTION EQUILIBRIUM DISTRIBUTION COEFFICIENTS USING BATCH AND CENTRIFUGATION METHODS

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Jonathan D. Istok

Abstract

Sorption equilibrium distribution coefficients, K_d 's, are used in solute transport models to predict the movement of hazardous wastes in soils. K_d 's can be determined in the laboratory by performing batch equilibrium tests or column studies. However, these tests suffer from disadvantages, since batch tests overestimate sorption due to the solids effect, and column studies conducted with fine grained soils require a long period of time. Centrifugation testing can alleviate these disadvantages by imposing a confining stress on the soil and producing a greater pore water velocity.

Centrifuge experiments were conducted on a kaolinite/phenol system using a constant head permeameter that fits in a laboratory centrifuge. K_d 's were estimated in the centrifuge by modeling the generated breakthrough curves with a solute transport model. K_d 's obtained in the centrifuge experiments were compared with values measured in batch equilibrium tests. Although the K_d values determined in the centrifuge were lower than the values predicted by extrapolating the batch data, the results were consistent with the solids effect. The introduction of a parameter

which takes into account the surface area of the solids resulted in a better correlation between the centrifuge and batch data.

3.1 INTRODUCTION

The adsorption characteristic of a soil/solute system is an important input parameter to solute transport models used to predict the movement of hazardous wastes in soils. Adsorption is a complex phenomena involving mechanisms occurring through the interactions of the sorbate, sorbent and solvent. Often the equilibrium distribution coefficient is used to quantify the adsorption characteristics of a system because it is simple, both conceptually and computationally [Valocchi, 1984]. The sorption distribution coefficient, K_d (l/g), describes the equilibrium partitioning of a solute between solid and liquid phases:

$$K_d = C_s / C_l \quad [3.1]$$

where C_s is the concentration of the solute in the solid (mg/g) and C_l is the concentration of the solute in the liquid phase (mg/l) at equilibrium. Use of K_d in solute transport models assumes that its value is constant; and that adsorption is linear with liquid concentration; and that the system is at equilibrium.

The sorption distribution coefficient is most often determined in batch equilibrium tests in which a solute is allowed to equilibrate between a solvent and a solid phase. Therefore, K_d is conditional for a given system. The slope of a line describing the sorbate concentration in the solids phase as a function of the liquid phase concentration, is the distribution coefficient. However, research suggests

that the value for K_d is not constant and that it decreases with increasing sorbent concentration (i.e. the "solids effect") [O'Connor and Connolly, 1980; Voice et al., 1983; Di Toro 1985]. This dependency of K_d on the sorbent concentration is non-conservative since the solids concentration in the field is much higher than the solids concentration used in the laboratory to measure distribution coefficients. Although many hypotheses have been proposed to explain this phenomena, controversy still exists concerning the effect of solids concentration on K_d .

Due to the dependency of the sorption distribution coefficient on solids concentration, it would be beneficial to measure K_d values at solids concentrations occurring in the field. The sorption distribution coefficient can be determined from breakthrough curves (BTC) generated in column studies in which a pulse or continuous input of solute is applied to the top of a soil column. The effluent is collected during the test and analyzed for the solute of interest. The plot of the normalized concentration (ratio of the concentration of the solute in the effluent to the applied concentration) versus flow through the column expressed in pore volumes is called the breakthrough curve. Figure 3.1 presents the theoretical shapes of BTC's for a plug flow system, plug flow with dispersion, and plug flow with sorption and dispersion. Ideal plug flow would produce a step concentration change at one pore volume. In a system in which a conservative solute is applied to the top of a

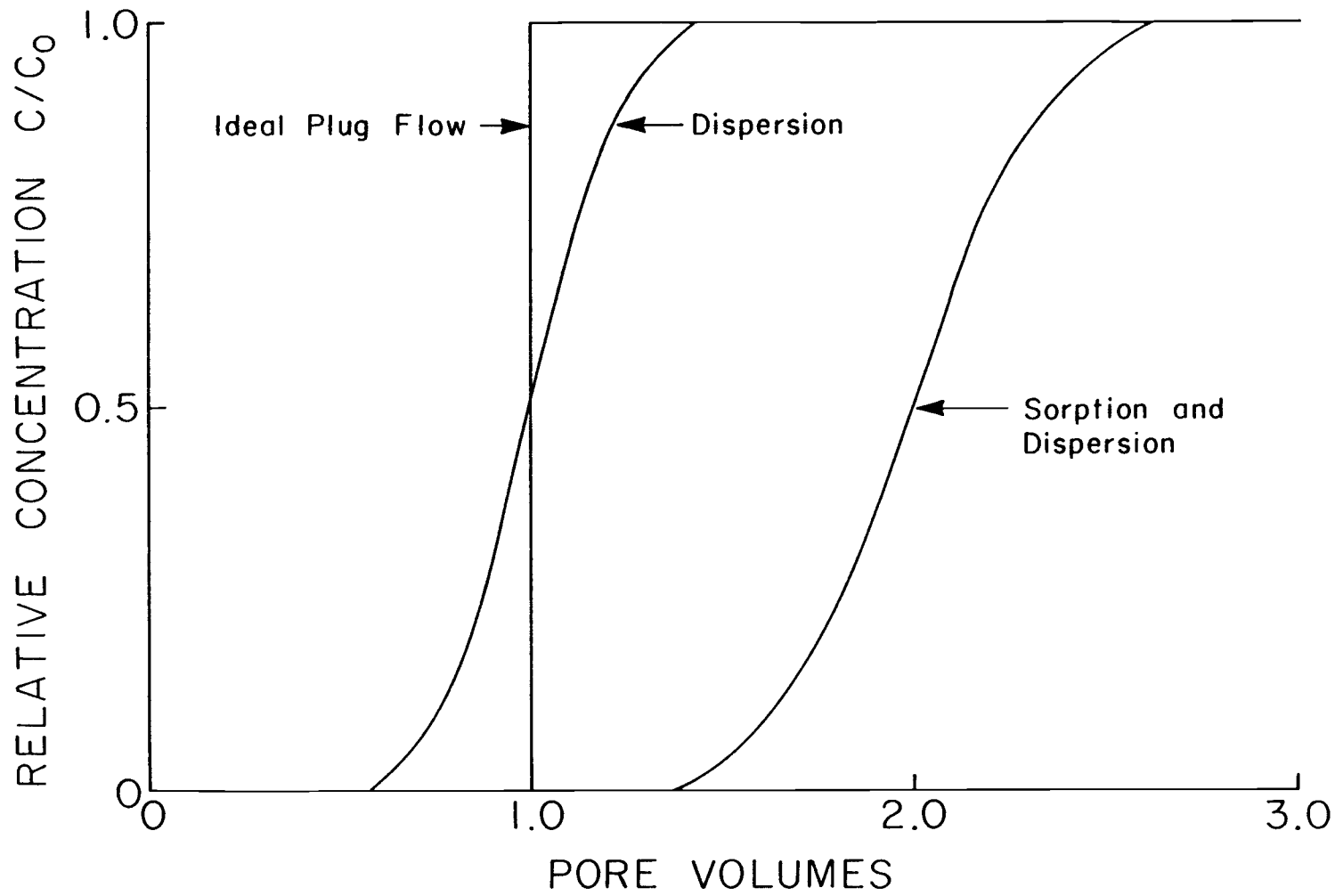


Figure 3.1 Theoretical shapes of breakthrough curves for solute transport.

soil column as a step increase, dispersion distributes the concentration front over a period of time, and sorption retards the solute which delays the breakthrough of the solute. Chemical and biological degradation would be expected to reduce the total mass of solute passing through the soil. Solute transport mechanisms can be inferred from the BTC by applying an appropriate model to fit the data and calculating the desired transport component. Disadvantages of column studies include: nonuniform flow within the column and the length of time involved when testing columns composed of predominantly fine grained soils (soils with a small hydraulic conductivity). Centrifugation can shorten the time required by imposing an acceleration substantially greater than one gravity.

Centrifugal modeling has been employed to describe fluid flow in porous media [Alemi et al., 1976; Goforth, 1986; Nimmo et al., 1987]. In centrifugal modeling, a soil column is spun at high rotational speeds in a centrifuge, increasing the gravitational effects (body forces) which simulate an in situ confining stress. The rates at which processes occur in the centrifuge model can be related to the prototype [Goodings, 1984]. Centrifuge modeling has recently been used to study solute transport through soil [Arulanandan et al., 1988].

A laboratory centrifuge using a constant head permeameter has been used to perform column tests in fine grained soils [Celorie et al., 1988]. This method imposes

confining stresses and a bulk density in the model which are similar to those occurring in the field. The resulting BTC's are analyzed with an appropriate model and can be used to estimate distribution coefficients. There are several advantages to modeling solute transport in a soil column by centrifugation: the time for testing fine grained soils is reduced, nonuniform flow is negligible due to the lateral pressure imposed by the inertial acceleration, and the testing program can incorporate and distinguish the effects of pressure and bulk density on solute transport.

In recognition of the need to develop the centrifuge technique for modeling solute transport and to investigate the solids effect, a laboratory research program was conducted in which K_d 's determined from centrifuge column tests were compared to K_d 's determined in traditional batch equilibrium tests. A kaolinite/phenol system was investigated. The centrifuge technique employed is further described by Celorie et al. (1988).

3.2 BACKGROUND

Adsorption

Adsorption is the accumulation of a solute at the surface of a solid or another phase. This accumulation is caused by a number of mechanisms ranging from van der Waal forces to magnetic bonding [LaPoe, 1985]. The mechanisms of adsorption are dependent upon the solution's ionic strength, pH, temperature, pressure, and the concentration of solids in the system. When these variables are coupled with the many different sorbate and sorbent characteristics present in the environment, adsorption becomes difficult to quantify and to predict in a heterogeneous system.

The traditional method used to characterize adsorption is by performing batch equilibrium tests. However, there is a significant discrepancy in values determined for K_d when the solids concentration is varied. The sorption distribution coefficients measured for a system, decreases as the solids concentration increases (the "solids effect"). Therefore, when a K_d value obtained from the laboratory (tested at a dilute solids concentration) is applied to model solute transport in a real soil deposit under the assumption of local equilibrium, the movement of solute in the field may be underestimated.

Grover and Hance (1970) have suggested that the observed solids effect is due to the dispersion of soil aggregates; and that this dispersion results in a larger

number of colloidal size particles. This effect is greater at low solids concentrations. Thus, in dilute suspensions, more surface area is available for adsorption since the sorption activity and surface area increases as the size of the particle decreases. Another study suggests that sorption equilibrium is approached more quickly in dilute systems which may result in a higher measured value of K_d in systems with lower sorbent concentration [Dolan, 1987]. An alternate explanation suggests that a nonseparable third phase, proportional to solids concentration, complexes with the solute [Voice et al., 1983; Voice et al. 1985; Gschwend and Wu, 1985]. These microparticles in the supernatant are mistaken for free solute in the testing procedure. When the solids concentration is increased, the amount of microparticles is also increased. Since the solute sorbs to the microparticles more readily, the measured supernatant overestimates the free solute concentration, resulting in lower K_d values at high solids concentrations. However, another study performed with quartz and heavy metals suggests that reversible partitioning (desorption) increases with solids concentration [Di Toro et al., 1986]. Di Toro et al. developed a particle-particle interaction model which accounts for a smaller observed K_d value due to collisions of the particles during the shaking procedure in the batch test. Although there are many explanations for the solids effect, it remains an important limitation on the use of K_d values obtained with batch equilibrium tests.

Centrifuge Testing

To avoid errors in predicting solute transport in soils due to the application of K_d values obtained in batch equilibrium tests at low solids concentration, a method using the solids concentration occurring in a natural field soil would be beneficial. Column studies can be employed to generate BTC's from which K_d can be determined; however, breakthrough experiments with columns composed of fine grained soils require a significant period of time to conduct. An alternative to the traditional column test run at one gravity is to place the column in a centrifuge to increase the velocity of the pore fluid flow by imposing a high inertial acceleration (50 to 200g).

The technique of centrifuge modeling has been employed over the past 50 years to simulate the stress distribution of soil deposits and earth structures. The technique subjects a small-scale model to an artificial gravitational acceleration (N_g) in a centrifuge, simulating the confining stress encountered in the field. This is accomplished by rotating the soil column (model) in a plane such that the outward radial direction corresponds to the vertical direction in the field (prototype).

With the imposed acceleration equal to N_g , a depth L in the model corresponds to a depth NL in the prototype (Figure 3.2). In this way, when the model employs the same material as the prototype, identical confining stresses are

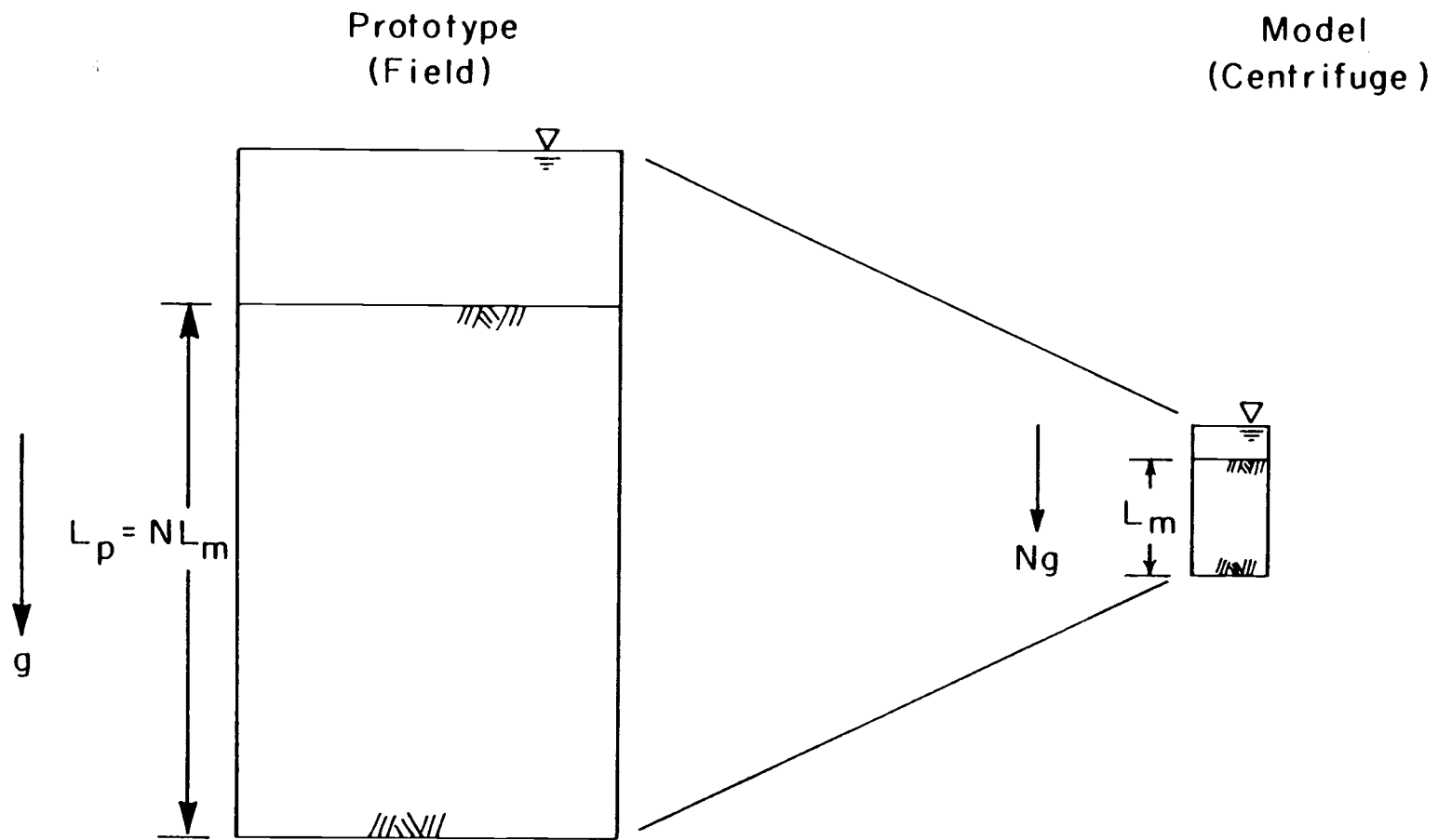


Figure 3.2 Comparison of prototype and model configurations.

imposed, in addition to density, void ratio, permeability and flow geometry [Goodings, 1984]. However, due to the reduced vertical dimension and increased self weight of the boundary water pressures in the model, the time required to produce the same specific discharge (flow per unit area) as in the prototype is decreased N^2 times. For example, for a physical model subjected to a radial acceleration of 120 g in a centrifuge, the time required for the specific discharge will be reduced from one year in the field to only 36 minutes in the physical model.

The time savings in performing a centrifuge column test on fine grained soils is a great advantage. This method provides the ability to test soils with small hydraulic conductivities while still simulating the structure, confining stress and flow regime of that in a the field. Although in a centrifuge test the bulk density varies with depth in the model, an average value can be used with negligible error in the results [Selim et al., 1977; De Smedt and Wierenga, 1978].

Solute Transport Model

A linear equilibrium adsorption model is employed in this study to determine K_d values from the BTC's obtained from the centrifuge column tests. The BTC's are fitted by a least-squares method that uses a linearized analytical solution developed for equilibrium adsorption after Lapidus and Amundson (1952) [van Genuchten 1981, Model A:SI-1].

The governing solute transport equation for a sorbing solute with linear equilibrium adsorption in one dimensional, steady state, saturated groundwater flow in a homogeneous porous media is:

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad [3.2]$$

where R is the retardation factor, c is the solute concentration (mg/l), t is time (s), D is the coefficient of hydrodynamic dispersion ($\frac{m^2}{s}$), x is the distance in the direction of flow (m), and v is the average pore water velocity (m/s).

The retardation factor is expressed as:

$$R = 1 + \frac{\rho K_d}{n} \quad [3.3]$$

where ρ is the bulk density ($\frac{g}{cm^3}$), K_d is the empirical distribution coefficient (l/g), and n is the porosity.

The boundary conditions are:

$$c(0,t) = C_0 \quad [3.4]$$

and $\frac{\partial c}{\partial x}(\infty,t) = 0 \quad [3.5]$

where C_0 is the applied concentration (mg/l). The upper boundary condition, Eq. 3.4, is used for the duration of the solute pulse; after which, the applied concentration is zero. The lower boundary condition, Eq. 3.5, implies a semi-infinite medium in the direction of flow.

3.3 MATERIALS AND EXPERIMENTAL METHOD

Materials

Kaolinite (code KGa-1, Clay Minerals Society) was chosen for the soil because of its purity, stability with respect to pH, freedom of microorganisms and workability. Some physical and chemical characteristics of KGa-1 kaolinite are presented in Table 3.1 [van Olphen and Fripiat, 1979]. Kaolinite has a low cation exchange capacity, but at neutral to low pH, the edges are positively charged and the basal planes are negatively charged [Mitchell, 1976].

Phenol was chosen as the solute because it is nonreactive, relatively nonvolatile, soluble in water and it is a known groundwater contaminant. The pK_a and water solubility are 9.9 and 93 g/l, respectively [Morrison and Boyd, 1983]. Solutions were prepared with reagent grade phenol and glass distilled water. The pH of the soil solution of phenol and kaolinite was 5.0. Therefore, little phenol was present as the phenolate ion and the sorption was almost solely by the phenol molecule. The solute solution contained 200 mg/l of phenol and 400 mg/l of sodium chloride.

Experimental Apparatus

The centrifugal method of modeling solute transport employs a constant head permeameter which allows solute to

TABLE 3.1 PHYSICAL AND CHEMICAL CHARACTERISTICS OF KAOLINITE

PARAMETER	KAOLINITE (KGa-1)
SPECIFIC GRAVITY ¹	2.62
CATION EXCHANGE CAPACITY	2.0 meq/100 g
SPECIFIC SURFACE AREA	10.05 m ² /g
THICKNESS ²	0.05 to 2 microns
LENGTH/WIDTH ²	0.1 to 4 microns
CHEMICAL COMPOSITION (% BY WEIGHT)	
SiO ₂	44.2
Al ₂ O ₃	39.7
TiO ₂	1.39
Fe ₂ O ₃	0.13
FeO	0.08
MnO	0.002
MgO	0.03
Na ₂ O	0.013
K ₂ O	0.050
F	0.013
C ¹	0.027
P ₂ O ₅	0.034
LOSS ON HEATING (% BY WEIGHT)	
550 C ^o	12.6
550-1000 C ^o	1.18

1 Experimentally determined.

2 Mitchell, 1976.

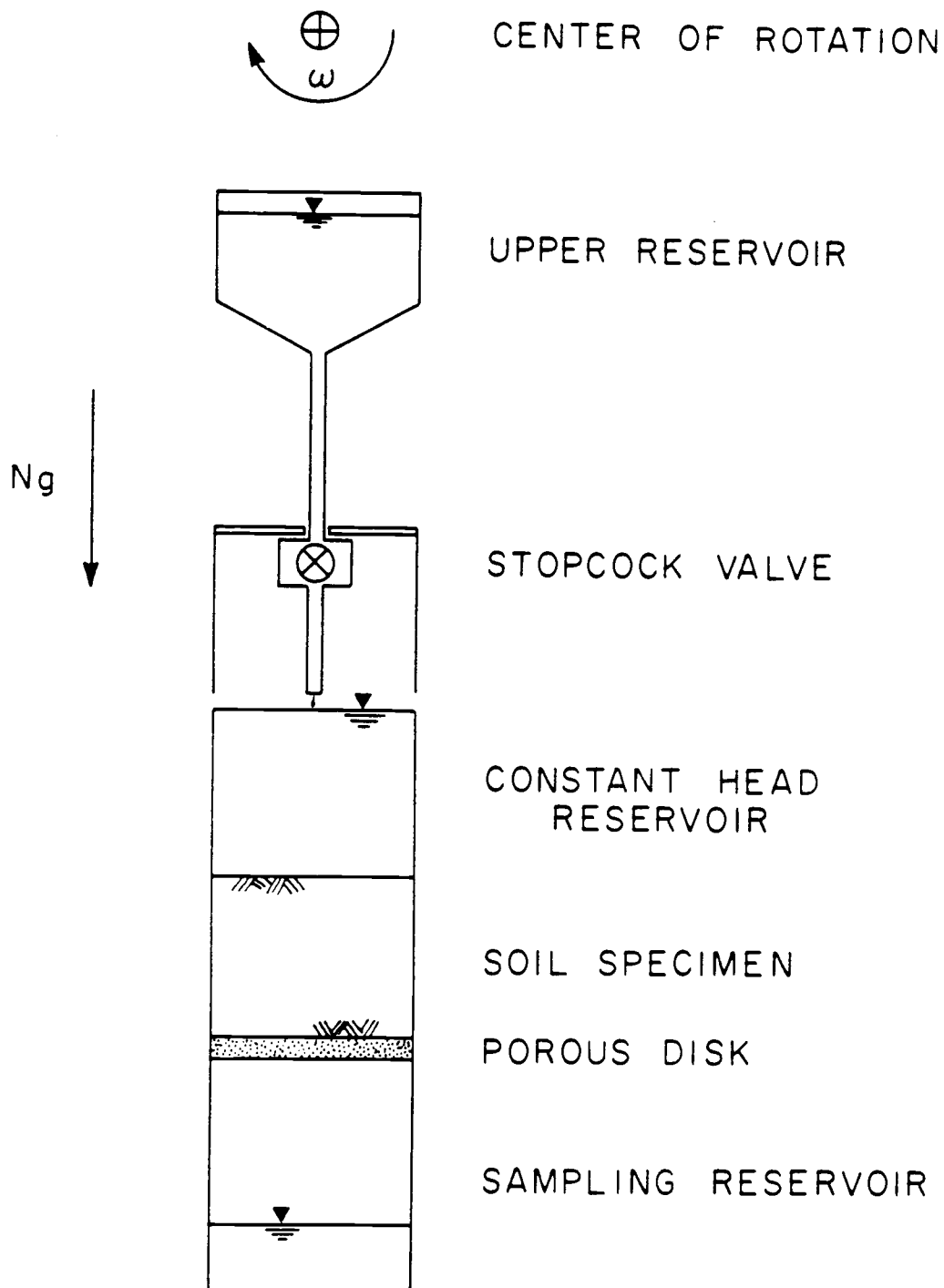


Figure 3.3 Schematic of constant head permeameter.

flow at a steady state (constant velocity) through a soil column (Figure 3.3). The permeameter is constructed of stainless steel. It is 3.0 cm in diameter and 15 cm in length, and fits into a laboratory centrifuge. The upper reservoir is constructed from Teflon and is attached to the rotor of the centrifuge. The upper reservoir is connected to the constant head reservoir by Teflon tubing and a stopcock valve. The valve is adjusted so that the flow rate from the upper reservoir is slightly greater than the flow rate through the soil column. The excess overflows the constant head reservoir through openings in the permeameter wall, thereby maintaining a constant head of water above the soil column during the experiment. The permeameter can accommodate a soil column 2.5 cm in diameter and up to 5 cm in length. The soil is retained by a sintered stainless steel disk with 0.5 micron pores. The sampling reservoir collects effluent from the permeameter and can be removed and replaced with an identical reservoir during sampling.

Experimental Method

At the beginning of each experiment, the permeameter was cleaned by submerging it in detergent and placing it in a sonicator for one to two hours, after which, it was thoroughly rinsed with tap and distilled water and then air dried. Next, approximately 15 g of consolidating solution (8.55 mmol/l NaNO₃) was placed in the constant head reservoir of the permeameter. The weight of the permeameter

and contents was noted. Air dried soil was slowly added to the permeameter to allow the soil to saturate and settle into the water. After the desired amount of soil was added, the permeameter was placed in a glass vessel which was connected to an aspirator to vacuum saturate the soil. The soil was consolidated by: filling the upper and constant head reservoirs with consolidating solution, placing the permeameter in the centrifuge, and spinning the centrifuge at the testing speed. The permeameter was spun until 100% consolidation was achieved. This was determined by measuring the soil column length until it remained constant with time. The soil column length was measured by inserting a Teflon disk on top of the soil and noting the distance from the surface of the disk to the top of the permeameter.

Immediately after the soil was consolidated, the consolidating solution was replaced with solute in the upper and constant head reservoirs. The centrifuge was spun for a specific time period at a prescribed speed. Then the centrifuge was stopped; the sampling reservoir was replaced with an identical reservoir; and the upper reservoir was refilled to begin another time step. The centrifuge was accelerated to the test speed in 12 to 17 seconds, allowed to spin for a specified time period, and decelerated in 10 to 15 seconds.

While the centrifuge was spinning, the sampling reservoir (from the previous time step) was weighed to determine the effluent volume. The effluent was withdrawn

from the sampling reservoir with a glass syringe and stored in a 1.5 ml glass vial. The sampling reservoir and syringe were rinsed with distilled water and dried for the next sample. The speed of the centrifuge was checked with a hand tachometer between each sampling period.

Once a specified number of pore volumes passed through the soil column, the solute solution was replaced with the consolidating solution and the test was continued for a specified number of additional pore volumes.

At the conclusion of the test, the soil column was sampled with a sampling tube 2.0 cm in diameter and 12 cm in length. The tube was pushed into the soil column. The soil was retained by connecting an aspirator to the tube. The soil was then extruded in approximately 0.4 cm increments and water contents were measured on each sample. These results were used to compute the porosity and bulk density at each depth.

The batch reactors used in the batch equilibrium tests consisted of 25 ml glass vials with Teflon lined screw caps. Air dried kaolinite soil was weighed and placed into glass vials. 20 ml of the solute solution was placed into each vial and shaken manually to saturate the solids. The concentration of kaolinite in each vial was varied between 0.01 and 270 g/l. The vials were allowed to equilibrate for 12 hours in a constant temperature shaker bath set at 150 oscillations per minute and at a temperature of 25 C. The amount of time for equilibrium to be established was

determined to be less than one hour.

At the end of the test time, the vials were removed individually and sampled immediately to avoid a redistribution of the solute between phases as the kaolinite settled. Samples were collected with a glass syringe. A glass fiber filter between the needle and syringe body served to separate the liquid phase from the kaolinite. The samples were stored in 1.5 ml glass vials.

Analytical Method

Concentrations of phenol were determined by extracting samples into hexane and analyzing the hexane extract using a Hewlett Packard Model 5890A gas chromatograph operated with a flame ionization detector. The instrument was equipped with a Hewlett Packard Model 3392A integrator and a Hewlett Packard Model 7673A autosampler. A 2 mm glass column, 0.38 m long and packed with 100/120 Supelcoport with 1% SP 1240-DA, was used for the separation. Nitrogen, flowing at a rate of 40 ml/min, was used as the carrier gas. Hydrogen and air flows to the flame ionization detector were 20 ml/min and 200 ml/min, respectively. The oven temperature was held at 120 °C for 8 minutes runs. The injection port and flame ionization detector temperatures were 250 °C. The detection sensitivity was 1 part per million.

3.4 RESULTS AND DISCUSSION

Equilibrium partition coefficients were measured in two ways: by performing batch sorption tests and centrifuge column tests. Both experiments used the same kaolinite soil and solute solution.

The results of the batch sorption tests are shown as open circles in Figure 3.4. As the solids concentration increased from 0.01 g/l to 270 g/l, the K_d decreased four orders of magnitude, demonstrating the solids effect. A regression on the data gives a slope of -0.95 with a correlation coefficient equal to 0.998. The slope of the sorption line is consistent with similar data for heavy metal sorption to quartz and montmorillonite (-0.67 to -0.91) [Di Toro et al., 1986], sorption of chlorinated aromatic compounds sorption to lake sediments (-0.68 +/- 0.26) [Di Toro and Horzempa, 1982] and the sorption of many hazardous wastes to sediments, sludge and standard clay soils [O'Connor and Connolly, 1980]. The results presented here are from a system with little or no organic matter (total carbon in the kaolinite is 0.027 percent by weight).

Typical BTC's generated in the centrifuge are shown in Figures 3.5 and 3.6 (tests 1 and 2). The data are represented by open circles and the line shows the fitted model incorporating the retardation factor. The solute was applied during the period between zero and 0.7 pore volumes. The pulse of solute was applied as a step addition to

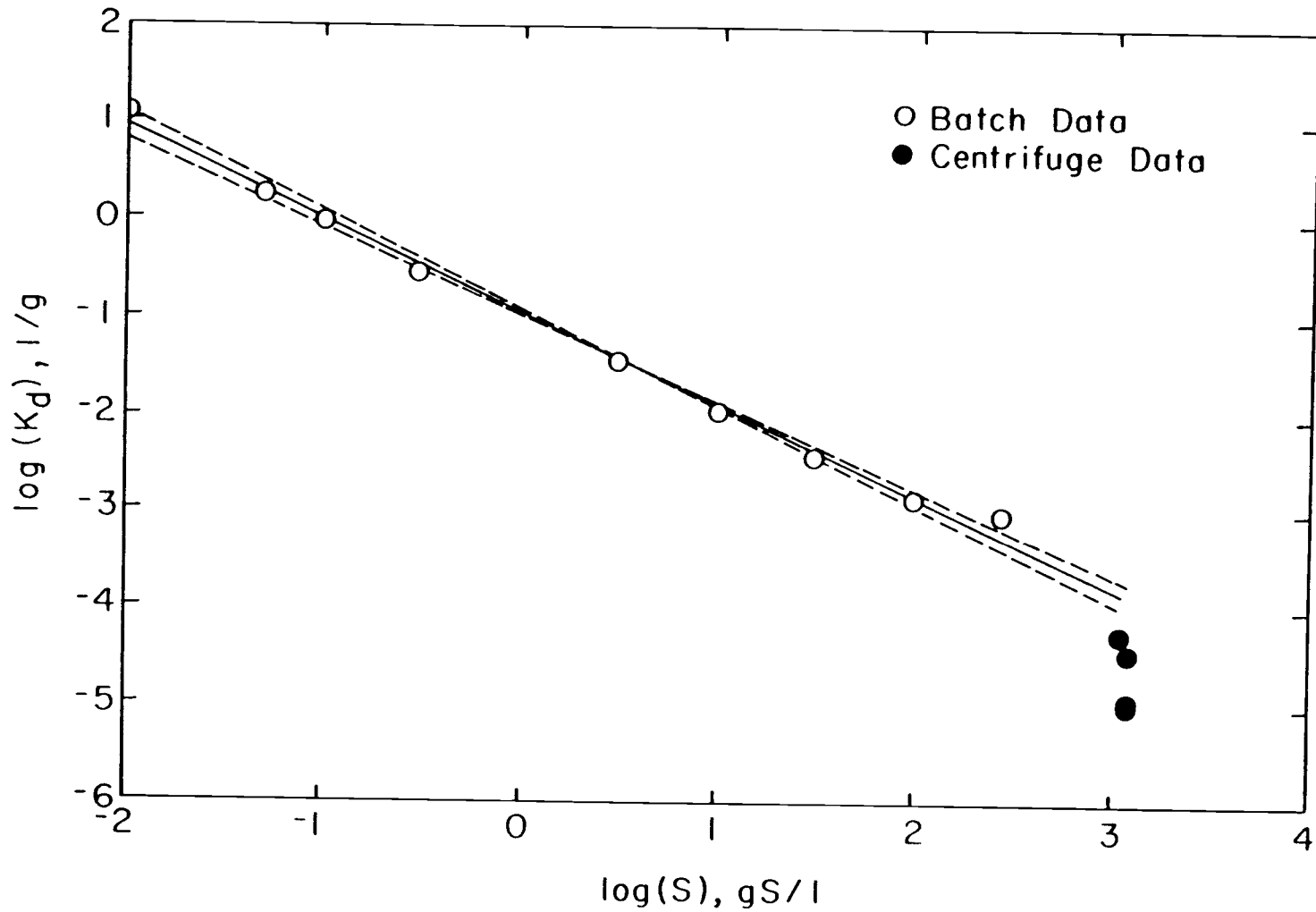


Figure 3.4 Batch equilibrium and centrifuge sorption distribution coefficients versus the solids concentration for phenol and kaolinite with 95% confidence intervals.

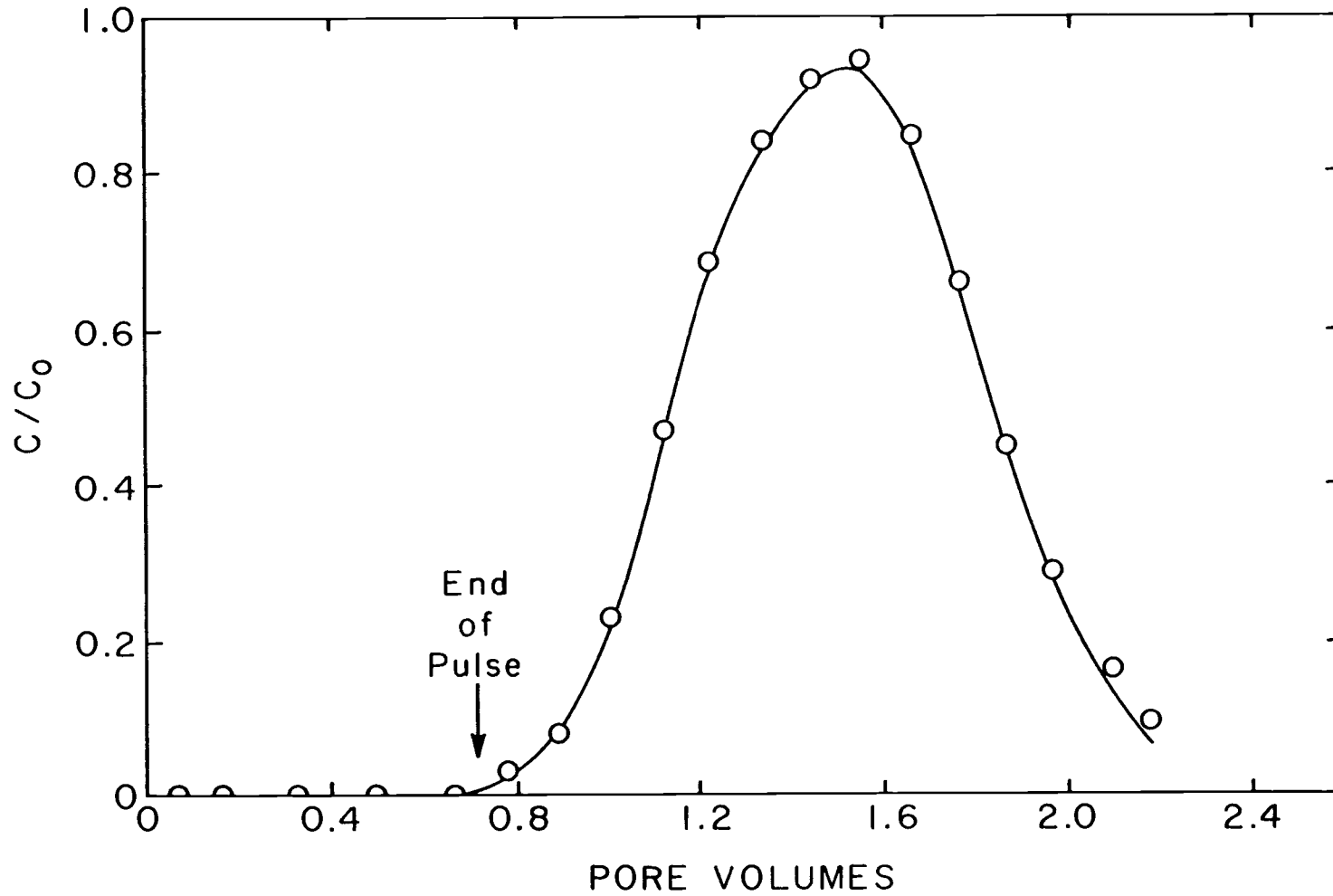


Figure 3.5 Phenol BTC in kaolinite spun at 400 RPM (test 1).

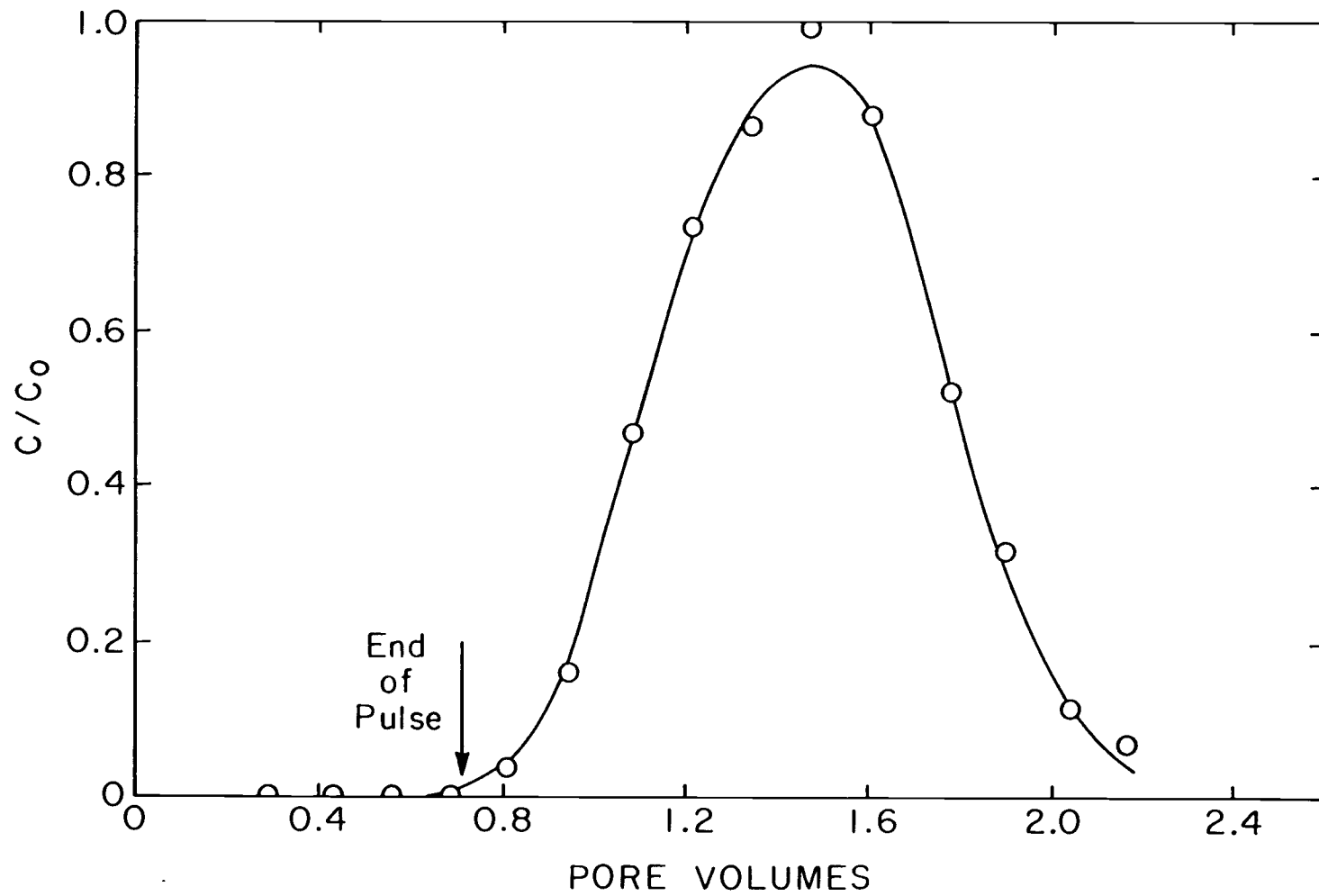


Figure 3.6 Phenol BTC in kaolinite spun at 900 RPM (test 2).

evaluate both sorption and desorption of the phenol. The BTC shows the concentration front was delayed beyond one pore volume demonstrating that phenol is slightly retarded. Similarly, the desorption of phenol occurs at a pore volume greater than one after the pulse was removed. The symmetrical shape of the breakthrough curve suggests the reversibility of the sorption reaction and suggests that sorption is in equilibrium. Non-equilibrium is characterized by asymmetrical or tailing breakthrough curves. Asymmetry is caused by insufficient residence time for the solute to transfer to and from the solid surface through immobile water [Nkedi-Kizza et al., 1982]. In addition, a timed batch equilibrium test demonstrated the phenol solute to be at equilibrium in less than one hour. Therefore, sorption equilibrium was expected since all of the centrifuge tests were conducted with the phenol solution in contact with the soil column, for more than one hour.

The test parameters for the centrifuge tests are presented in Table 3.2. Centrifuge tests were conducted at two speeds: 400 and 900 revolutions per minute (RPM). The increase in speed resulted in a decrease in the porosity from 58 to 54 percent, as expected. Similarly, the solids concentration calculated as the ratio of the dry weight of solids to the total volume of the soil column, increased with the increase in speed. The velocity of the fluid is also a function of the inertial acceleration, and the tests

TABLE 3.2 CENTRIFUGE EXPERIMENT PARAMETERS AND RESULTS

PARAMETER	TEST NO:	1	2	3	4
SPEED (RPM)		400	900	900	900
POROSITY		0.58	0.54	0.54	0.54
SOLIDS CONCENTRATION (g/l)		1106	1204	1204	1210
PORE WATER VELOCITY ($\mu\text{m/s}$)		2.24	5.50	5.30	5.61
RETARDATION FACTOR		1.157	1.1136	1.035	1.032
K_d (ml/g)		0.054	0.035	0.011	0.010

demonstrated a greater than two-fold increase in velocity between the two speeds.

The BTC's from the centrifuge tests were fitted with a least-squares curve-fitting algorithm that uses a linearized form of an analytical solution developed for equilibrium adsorption. The program estimates the retardation factor and the Peclet number through an iterative process. It calculates a BTC with initial parameter estimates; finds the residual error with respect to the experimental data; and then iterates with new parameter estimates until the residual errors are minimized. Verification and suitability of the model is achieved by the good curve fit to the experimental data. The fitted model generates a retardation factor and a Peclet number from which K_d and the coefficient of hydrodynamic dispersion can be computed.

A retardation factor equal to one indicates that no sorption occurred. The observed retardation factors were less than 1.15 demonstrating that phenol is only slightly adsorbed by kaolinite. Based on Eq. 3.3, K_d was calculated from the retardation factor. Values for K_d varied between 0.010 and 0.054 ml/g. The variation of K_d values is partially due to the decreased sensitivity of the fitted model when the retardation factor is very close to one. For example, a change in the retardation factor from 1.10 to 1.05 produces a 50 percent decrease in K_d .

The K_d 's determined from four centrifuge tests are presented in Figure 3.4 and are represented by four solid

circles. The dotted lines show the 95 percent confidence intervals based on the linear regression for the batch data. The K_d 's calculated from the centrifuge tests were approximately 3 to 13 times lower than the values estimated by extrapolation of the regression line. Although the K_d 's determined in the centrifuge varied, these values are smaller than the K_d at the highest solids concentration in the batch test which is consistent with the solids effect.

Fundamentally, the batch equilibrium and centrifuge tests are different. The former tests a dilute soil suspension while the latter is conducted with a soil matrix. Therefore, a linear correlation was not expected. Intuitively, the centrifuge technique is more representative of a natural soil deposit and the results may be more realistic.

A possible explanation for the difference between the tests may be that as the soil particles become packed closer together, less surface area is accessible by the solute for adsorption. An adsorbed water layer exists on the kaolinite soil particles. Adsorption of the phenol most likely occurs at the interface of the pore water and adsorbed water layer. Therefore, phenol adsorption would be dependent upon the surface area of adsorbed water in contact with the pore water. Some of the particles may be close together such that the adsorbed water layers are in contact and these areas would be less accessible to the solute causing the observed decrease in adsorption. In comparison, batch tests

are performed in soil solution suspensions where soil contact is momentary in the form of collisions. Di Toro (1985) developed a particle-particle interaction model suggesting that the collisions cause desorption. Thus, a particle contact mechanism is a plausible explanation for the observed decrease in K_d in a soil matrix.

Since it would be impossible to measure the effective surface area available for adsorption, an alternative model for interactions between sorbent concentrations and K_d would be to calculate the average water thickness (AWT) on a soil particle surface. The calculation of AWT (m) is described by [Mitchell, 1976]:

$$AWT = V_l / (W_s A_s) \quad [3.6]$$

where V_l is the volume of liquid (l), W_s is the dry weight of solids (g), and A_s is the specific surface area (m^2/g).

A plot of the experimental data is shown in Figure 3.7 using the AWT. The 95 percent confidence intervals based on the regression for the batch data are included and the centrifuge data demonstrates a closer fit. Therefore, the AWT which includes surface area may be a better model for the solids effect.

If adsorption is dependent upon the effective surface area accessible to the solute, then confining stress becomes an important parameter to consider during testing. The centrifuge technique is the only method which provides the opportunity to simulate confining stresses similar to a natural soil deposit.

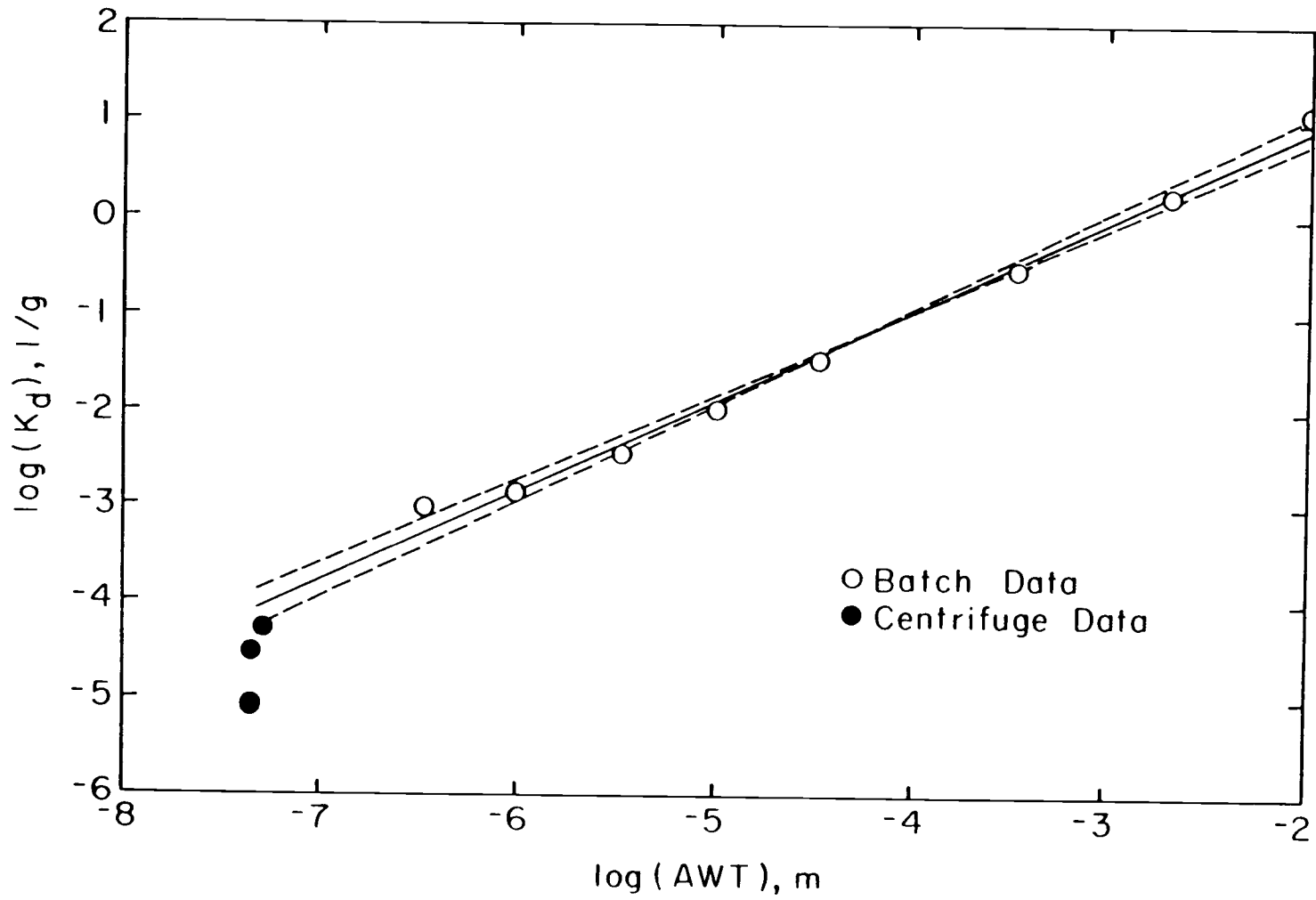


Figure 3.7 Batch equilibrium and centrifuge sorption distribution coefficients versus the average water thickness for phenol and kaolinite with 95% confidence intervals.

3.5 SUMMARY AND CONCLUSION

The sorption distribution coefficient used in solute transport models is difficult to measure in fine grained soils. Present methods suffer from disadvantages: (1) batch sorption tests overestimate sorption distribution coefficient values in natural soils due to the solids effect, and (2) column studies with fine grained soils require a long period of time to conduct. This study has demonstrated a centrifugation technique, useful in determining K_d values in fine grained soils at a solids concentration representative of those occurring the field.

The results from four centrifuge column experiments demonstrated the solids effect on a kaolinite/phenol system. The K_d 's determined in the centrifuge were consistent with batch sorption tests performed with the same materials, although the results were lower than expected when based on an extrapolation of the batch data. The batch data were compatible with similar published data for sorption of solutes to soils and clays. While the cause of the solids effect is not well understood, this study suggests a possible mechanism may be the decrease in effective surface area accessible to the solute due to the particle contact when the soil is packed in a matrix. Therefore, an average water thickness surrounding the particle was calculated to approximate the surface area dependency. When K_d was plotted versus the average water thickness, the centrifuge

data demonstrated a closer fit to the batch data. If adsorption is dependent upon the effective surface area (due to soil contact) available, then confining stress becomes an important parameter to consider during testing. The centrifuge technique is the only method which provides the opportunity to simulate confining stresses similar to a natural soil deposit.

In centrifuge column experiments, the solids concentration, confining stress, and flow regime imposed are similar to those in the field. The ability to model a field situation closely, is important in evaluating solute transport. The BTC's generated from centrifuge experiments may also be useful in determining sorption/desorption kinetics constants. Since the method is relatively rapid, it lends itself to evaluating other aspects of solute transport in fine grained soils with respect to: the effects of pressure, bulk density, pH, temperature, ionic strength, and heterogeneities.

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5.0 APPENDICES

5.1 APPENDIX A: Chloride Centrifuge Data

DATE 3-9-88

RUN CL #1

SPEED = 550.000 RPM 57.618 RAD/S 69.39593 G'S
 THICKNESS 2.273 CM
 VOLUME = 11.518 CM³
 SOIL WT = 13.000 GRAMS
 PULSE = 2.2 POR VOLUMES
 AVE VEL = 0.000224 CM/S

CONSOL STK WATER
 STK SOLN NACL

DEP	INC	W/C	INC	AVE W/C	AVE VOID	CAL SAT
0.1	69.0	53.0	THICKNS=	2.27	1.32	105.16
0.17	58.5		Vt=	11.52		
0.17	52.0		Ws=	13.00		
0.15	48.7		Gd=	1.13		
0.15	47.3					
0.15	47.4					
0	37.0					

	CL	NA
VOID RAT=	1.32	RETARD = 1.5183 1.7255
AVE W/C=	53.03	
POROSITY=	0.57	Kd = 0.1738 0.2432 CM ³ /G
POR VOL =	6.81	
BULK DEN=	1.70 G/CM ³	PECLET NO 31.80 8.32
SOL CON =	1128.7 G/L	

CONC (CL)	C/CO (CL)	EFF VOL	PORE VOL	PROGRAM (CL)	CONC (NA)	C/CO (NA)	PROGRAM (NA)
2.5	0.048	1.438	0.211		9.03	0.26	
2.6	0.050	3.404	0.500		7.29	0.21	
2.4	0.046	5.348	0.786		7.24	0.21	
3.2	0.062	7.546	1.109	0.126	6.56	0.19	0.24
10.5	0.202	8.670	1.274	0.280			
21.3	0.410	9.984	1.467	0.494	13.71	0.39	0.46
34.4	0.662	11.074	1.627	0.656	19.87	0.57	0.544
40.8	0.785	11.859	1.743	0.751			
42.6	0.819	12.622	1.855	0.824			
46.9	0.902	13.413	1.971	0.880			
48.3	0.929	14.327	2.105	0.925	26.34	0.75	0.743
49.6	0.954	15.067	2.214	0.950	28.09	0.80	0.776
50.2	0.965	16.650	2.446	0.980	27.3	0.78	0.834
50.8	0.977	18.482	2.716	0.994	28.4	0.81	0.876
49.9	0.960	20.873	3.067	0.983	28.94	0.83	0.819
44.9	0.863	22.389	3.290	0.887	25.88	0.74	0.716
36.2	0.696	23.279	3.421	0.774	22.56	0.65	0.644
28.5	0.548	24.164	3.551	0.635	18.96	0.54	0.572
18.6	0.358	25.950	3.813	0.357	12.46	0.36	0.436
6	0.115	29.129	4.280	0.082	6.8	0.19	0.251
2.4	0.046	29.738	4.370	0.059	15.5	0.44	

DATE 3-31-88

RUN CL #2

SPEED = 550.000 RPM 57.618 RAD/S 69.39593 G'S
 THICKNESS 1.372 CM
 VOLUME = 6.952 CM³
 SOIL WT = 8.000 GRAMS
 PULSE = 2.1 POR VOLUMES
 AVE VEL = 0.000611 CM/S

CONSOL STK WATER
 STK SOLN NACL

DEP	INC	W/C	INC	AVE W/C		AVE VOID	CAL SAT
0.18		45.1		43.4	THICKNS=	1.37	89.07
0.13		51.3			Vt=	6.95	
0.19		36.4			Ws=	8.00	
0		48.7			Gd=	1.15	
0		47.3					
0		47.4					
0		37.0					

	CL	NA
VOID RAT= 1.28	RETARD = 1.5625	1.9565
AVE W/C= 43.41		
POROSITY= 0.56	Kd = 0.1843	0.3134 CM ³ /G
POR VOL = 4.15		
BULK DEN= 1.71 G/CM ³	PECLET NO 38.10	6.66
SOL CON = 1150.7 G/L		

CONC (CL)	C/CO (CL)	EFF VOL	PORE VOL	PROGRAM (CL)	CONC (NA)	C/CO (NA)	PROGRAM (NA)
1.7	0.033	2.317	0.558	0.00	3.80	0.11	
1.3	0.025	3.435	0.828	0.00	4.29	0.12	
2.1	0.040	3.889	0.937	0.02			
2.3	0.044	4.895	1.180	0.13	5.73	0.16	
11	0.212	5.719	1.379	0.33	5.83	0.17	0.343
26.2	0.504	6.459	1.557	0.54			
39.9	0.767	7.221	1.741	0.722	17.74	0.51	0.516
45.1	0.867	8.017	1.932	0.853	18.02	0.52	0.593
50.2	0.965	8.881	2.141	0.934	26.14	0.75	0.666
50.9	0.979	9.934	2.395	0.977	25.56	0.73	0.739
53.8	1.035	10.932	2.635	0.993	27.41	0.78	0.786
53.8	1.035	11.972	2.886	0.996	26.39	0.76	0.777
43	0.827	13.066	3.149	0.95	22.62	0.65	0.704
32.2	0.619	14.133	3.407	0.749	22.06	0.63	0.6
24.4	0.469	15.040	3.625	0.497	18.54	0.53	0.509
12.5	0.240	16.329	3.936	0.205	10.32	0.30	0.39
4.4	0.085	17.626	4.249	0.064	3.01	0.09	0.291

DATE 3-14-88 RUN CL #3

SPEED = 900.000 RPM 94.284 RAD/S 185.8205 G'S
 THICKNESS 2.146 CM
 VOLUME = 10.874 CM^3
 SOIL WT = 13.000 GRAMS
 PULSE = 4.2 POR VOLUMES
 AVE VEL = 0.000644 CM/S

CONSOL STK WATER
 STK SOLN NACL

DEP	INC	W/C	INC	AVE W/C	AVE VOID	CAL	SAT
0.18	55.2	44.0	THICKNS=	2.15	1.19	96.74	
0.16	45.1		Vt=	10.87			
0.16	41.2		Ws=	13.00			
0.16	38.9		Gd=	1.20			
0.15	37.8						
0	47.4						
0	37.0						

	CL	NA
VOID RAT=	1.19	
AVE W/C=	44.00	
POROSITY=	0.54	
POR VOL =	6.16	
BULK DEN=	1.74 G/CM^3	
SOL CON =	1195.5 G/L	
RETARD =	1.5493	1.6986
Kd =	0.1717	0.2184 CM^3/G
PECLET NO	91.00	12.30

CONC (CL)	C/CO (CL)	EFF VOL	PORE VOL	PROGRAM (CL)	CONC (NA)	C/CO (NA)	PROGRAM (NA)	PORE VOL
2.2	0.042	4.676	0.759	0.00	4.48	0.13		0.759
1.6	0.031	7.679	1.246	0.08	3.11	0.09	0.277	1.246
4.3	0.083	8.699	1.412	0.29	5.10	0.15	0.393	1.412
19.7	0.379	9.388	1.523	0.48	18.71	0.54	0.539	1.634
34.8	0.669	10.071	1.634	0.67	21.42	0.61	0.608	1.752
43.9	0.844	10.794	1.752	0.82	24.58	0.70	0.669	1.869
47.1	0.906	11.520	1.869	0.911	27.01	0.77	0.768	2.099
48.8	0.938	12.238	1.986	0.961	27.77	0.79	0.807	2.215
50.4	0.969	12.936	2.099	0.984	27.66	0.79	0.841	2.331
50.9	0.979	13.652	2.215	0.994	27.82	0.80	0.87	2.449
48.9	0.940	14.361	2.331	0.998	38.53	1.10	0.892	2.560
50.7	0.975	15.091	2.449	0.999	27.46	0.79	0.923	2.750
51	0.981	18.079	2.934	1	28.22	0.81	0.944	2.934
51.6	0.992	25.947	4.211	1	28.7	0.82	0.971	3.288
52	1.000	29.233	4.744	1	29.47	0.84	0.984	3.632
48.1	0.925	31.276	5.075	1	30.59	0.88	0.992	3.959
49	0.942	32.81	5.324	0.982	42.12	1.21	0.994	4.120
36.5	0.702	33.895	5.501	0.866	29.32	0.84	0.996	4.744
24.6	0.473	34.868	5.658	0.632	29.71	0.85	0.934	5.075
14.8	0.285	35.861	5.820	0.354	28.82	0.82	0.804	5.324
6.3	0.121	37.123	6.024	0.119	23.04	0.66	0.684	5.501
2.6	0.050	38.499	6.248	0.025	17.22	0.49	0.575	5.658
3.5	0.067	39.406	6.395	0.007	11.33	0.32	0.47	5.820
					6.69	0.19	0.353	6.024
					3.67	0.11	0.252	6.248
					7.7	0.22		6.395

DATE 3-17-88

RUN CL #4

SPEED = 900.000 RPM 94.284 RAD/S 185.8205 G'S
 THICKNESS 1.283 CM
 VOLUME = 6.501 CM^3
 SOIL WT = 8.000 GRAMS
 PULSE = 5.2 POR VOLUMES
 AVE VEL = 0.001166 CM/S

CONSOL STK WATER
 STK SOLN NACL

DEP	INC	W/C	INC	AVE W/C	AVE VOID	CAL SAT
0.14	58.2	44.4	THICKNS=	1.28	1.13	103.05
0.19	41		Vt=	6.50		
0.2	38.0		Ws=	8.00		
0	48.7		Gd=	1.23		
0	47.3					
0	47.4					
0	0.0					

CL NA

VOID RAT= 1.13 RETARD = 1.6450 2.3060
 AVE W/C= 44.41
 POROSITY= 0.53 Kd = 0.1943 0.3933 CM^3/G
 POR VOL = 3.70
 BULK DEN= 1.76 G/CM^3 PECKET NO 111.00 9.67
 SOL CON = 1230.6 G/L

CONC (CL)	C/CO (CL)	EFF VOL	PORE VOL	PROGRAM (CL)	CONC (NA)	C/CO (NA)	PROGRAM (NA)	POR VOL
0.95	0.018	1.124	0.304	0.000	8.500	0.24		0.304
0.9	0.017	2.154	0.583	0.000	6.630	0.19		0.583
0.85	0.016	3.144	0.850	0.000	7.020	0.20		0.850
1.1	0.021	4.142	1.120	0.002	6.350	0.18	0.074	1.120
1.5	0.029	5.111	1.382	0.108	8.660	0.25	0.265	1.588
11.9	0.229	5.873	1.588	0.422	18.160	0.52	0.364	1.794
36.9	0.710	6.634	1.794	0.763	24.630	0.70	0.458	1.997
48.4	0.931	7.386	1.997	0.935	26.980	0.77	0.636	2.443
52.3	1.006	8.095	2.189	0.986	28.710	0.82	0.775	2.927
52.6	1.012	9.035	2.443	0.999	29.260	0.84	0.877	3.497
52	1.000	21.352	5.774	1.000	30	0.86	0.934	4.057
53.3	1.025	22.43	6.066	1.000	31.18	0.89	0.965	4.624
49.6	0.954	23.4	6.328	0.997	31.17	0.89	0.981	5.201
36.3	0.698	24.369	6.590	0.883	31.51	0.90	0.963	5.499
14.5	0.279	25.396	6.868	0.432	33.09	0.95	0.899	5.774
2.3	0.044	26.385	7.136	0.099	33.62	0.96	0.663	6.328
1.2	0.023	27.354	7.398	0.013	25.83	0.74	0.542	6.590
1.1	0.021	28.34	7.664	0.001	17.6	0.50	0.425	6.868
					9.19	0.26	0.331	7.136
					8.46	0.24	0.255	7.398
					6.94	0.20	0.194	7.664
					6.51	0.19	0.117	8.132

5.2 APPENDIX B: Phenol Centrifuge Data and
Supplemental Breakthrough Curves

DATE 11-3-87

RUN PH #1

SPEED = 400.000 RPM 41.904 RAD/S 36.70528 G'S
 THICKNESS 2.320 CM
 VOLUME = 11.756 CM³
 SOIL WT = 13.000 GRAMS
 PULSE = 0.7 POR VOLUMES
 AVE VEL = 0.000224 CM/S

CONSOL STK NANO3
 STK SOLN PHENOL/NACL/HCL

DEP	INC	W/C INC	AVE W/C	AVE VOID
0.365	62.8	53.1	THICKNS=	2.32
0.15	52.7		Vt=	11.76
0.15	43.3		Ws=	13.00
0.12	43.7		Gd=	1.11
0.13	46.1			
0	37.0			
0	37.0			

VOID RAT= 1.37 RETARD = 1.1568
 AVE W/C= 53.07
 POROSITY= 0.58 Kd = 0.0538 CM³/G
 POR VOL = 7.04
 BULK DEN= 1.68 G/CM³ PECLET NO 68.50
 SOL CON = 1105.8 G/L

CONC	C/CO	EFF VOL	PORE VOL	FITTED MODEL
0	0.000	0.440	0.062	0.00
0	0.000	1.110	0.158	0.00
0	0.000	2.260	0.321	0.00
0	0.000	3.470	0.493	0.00
0	0.000	4.660	0.662	0.00
6.56	0.034	5.490	0.779	0.012
16.16	0.083	6.260	0.889	0.071
44.44	0.229	7.070	1.004	0.227
90.99	0.469	7.880	1.119	0.456
132.73	0.684	8.61	1.222	0.658
162.91	0.840	9.41	1.336	0.824
178.38	0.919	10.160	1.442	0.911
183.34	0.945	10.910	1.549	0.923
164.49	0.848	11.730	1.665	0.824
127.92	0.659	12.410	1.762	0.657
87.31	0.450	13.110	1.861	0.456
55.65	0.287	13.860	1.968	0.266
31.48	0.162	14.730	2.091	0.121
18.38	0.095	15.320	2.175	0.065

DATE 10-26-87

RUN PH #2

SPEED = 900.000 RPM 94.284 RAD/S 185.8205 G'S
 THICKNESS 2.130 CM
 VOLUME = 10.793 CM³
 SOIL WT = 13.000 GRAMS
 PULSE = 0.71 POR VOLUMES
 AVE VEL = 0.000550 CM/S

CONSOL STK NANO3
 STK SOLN PHENOL/NACL/HCL

DEP	INC	W/C	INC	AVE W/C	AVE VOID
0.17	61.0	44.2	THICKNS=	2.13	1.18
0.15	44.2	Vt=	10.79		
0.16	39.6	Ws=	13.00		
0.16	37.4	Gd=	1.20		
0.14	36.6				
0	37.0				
0	37.0				

VOID RAT= 1.18 RETARD = 1.1136
 AVE W/C= 44.16
 POROSITY= 0.54 Kd = 0.0352 CM³/G
 POR VOL = 6.08
 BULK DEN= 1.74 G/CM³ PECLET NO 73.80
 SOL CON = 1204.5 G/L

CONC	C/CO	EFF VOL	PORE VOL	PROGRAM
0	0.000	1.790	0.294	0.00
0	0.000	2.620	0.431	0.00
0	0.000	3.400	0.559	0.00
0	0.000	4.180	0.687	0.00
7.22	0.037	4.930	0.811	0.03
31.71	0.161	5.760	0.947	0.182
92.42	0.469	6.570	1.080	0.458
144.71	0.734	7.370	1.212	0.725
170.25	0.864	8.160	1.342	0.888
195.42	0.991	8.93	1.468	0.948
173.43	0.880	9.74	1.602	0.875
103.07	0.523	10.800	1.776	0.549
62.29	0.316	11.540	1.898	0.299
22.6	0.115	12.420	2.042	0.111
13.39	0.068	13.190	2.169	0.038

DATE 10-20-87

RUN PH #3

SPEED = 900.000 RPM 94.284 RAD/S 185.8205 G'S
 THICKNESS 2.130 CM
 VOLUME = 10.793 CM³
 SOIL WT = 13.000 GRAMS
 PULSE = 0.92 POR VOLUMES
 AVE VEL = 0.000530 CM/S

CONSOL STK NANO3
 STK SOLN PHENOL/NACL/HCL

DEP	INC	W/C	INC	AVE W/C	AVE VOID
0.12	52.2	41.8	THICKNS=	2.13	1.18
0.08	45.1		Vt=	10.79	
0.16	43.0		Ws=	13.00	
0.15	39.2		Gd=	1.20	
0.15	37.6				
0.15	37.0				
0	37.0				

VOID RAT= 1.18 RETARD = 1.0351
 AVE W/C= 41.76
 POROSITY= 0.54 Kd = 0.0109 CM³/G
 POR VOL = 6.08
 BULK DEN= 1.74 G/CM³ PECLET NO 101.90
 SOL CON = 1204.5 G/L

CONC	C/CO	EFF VOL	PORE VOL	PROGRAM
0	0.000	2.260	0.372	0.00
0	0.000	2.930	0.482	0.00
0	0.000	3.690	0.607	0.00
5.34	0.027	4.530	0.745	0.01
25.04	0.127	5.410	0.890	0.16
102.88	0.521	6.280	1.033	0.522
166.35	0.843	7.160	1.177	0.839
184.03	0.933	8.110	1.334	0.971
194.8	0.987	9.090	1.495	0.997
197.35	1.000	10.14	1.667	0.981
150.03	0.760	11.1	1.825	0.769
59.39	0.301	12.100	1.990	0.33
18.8	0.095	13.080	2.151	0.077
10.06	0.051	14.200	2.335	0.008
7.67	0.039	15.170	2.495	0.001
7.18	0.036	16.100	2.648	0

DATE 10-13-87

RUN PH #4

SPEED = 900.000 RPM 94.284 RAD/S 185.8205 G'S
 THICKNESS 2.120 CM
 VOLUME = 10.742 CM³
 SOIL WT = 13.000 GRAMS
 PULSE = 1.73 POR VOLUMES
 AVE VEL = 0.000561 CM/S

CONSOL STK NANO3
 STK SOLN PHENOL/NACL/HCL

DEP	INC	W/C	INC	AVE	W/C	AVE	VOID
0.13		64.0		42.9	THICKNS=	2.12	1.16
0.07		44.7			Vt=	10.74	
0.15		41.7			Ws=	13.00	
0.15		38.2			Gd=	1.21	
0.15		36.4					
0.15		36.3					
0		37.0					

VOID RAT= 1.16 RETARD = 1.0321
 AVE W/C= 42.92
 POROSITY= 0.54 Kd = 0.0099 CM³/G
 POR VOL = 6.03
 BULK DEN= 1.75 G/CM³ PECLET NO 76.90
 SOL CON = 1210.2 G/L

CONC	C/CO	EFF	PORE	PROGRAM
		VOL	VOL	
0	0.000	2.520	0.418	0.00
0	0.000	3.290	0.546	0.00
0	0.000	4.130	0.685	0.01
8.07	0.042	4.970	0.824	0.09
70.04	0.361	6.040	1.002	0.46
149.7	0.772	6.880	1.141	0.759
169.89	0.876	7.710	1.279	0.922
177.86	0.917	8.530	1.414	0.98
187.19	0.965	9.360	1.552	0.996
193.09	0.995	10.17	1.686	0.999
181.2	0.934	11.02	1.827	1
193.41	0.997	11.830	1.962	1
181.16	0.934	12.650	2.098	1
179.53	0.925	13.470	2.234	1
184.53	0.951	14.290	2.370	0.996
175.01	0.902	15.100	2.504	0.93
126.6	0.653	15.920	2.640	0.692
55.5	0.286	16.720	2.773	0.374
22.61	0.117	17.550	2.910	0.142
12.9	0.066	18.360	3.045	0.042

BATCH WITH SOLIDS CONCENTRATION

S (g/l)	LOG S (g)	Cl (mg/L)	Cs (mg/g)	Kd (L/g)	LOG Kd (L/g)	S (g)	REGRESSION	SOLIDS ANALYSIS	
								CI +	CI -
1106.00	3.04	183.81	0.00	0.00005	-4.26922	#8	-3.85426	-3.72077	-3.98775
269.18	2.43	145.57	0.14	0.00093	-3.03030	6	-3.27055	-3.16941	-3.37170
96.32	1.98	164.29	0.22	0.00134	-2.87295	2	-2.84607	-2.76827	-2.92387
29.66	1.47	168.75	0.59	0.00347	-2.45997	0.6	-2.35953	-2.30800	-2.41106
9.96	1.00	168.78	1.75	0.01038	-1.98377	0.2	-1.90887	-1.87999	-1.93775
3.00	0.48	168.62	5.89	0.03496	-1.45643	0.06	-1.41266	-1.39526	-1.43005
0.30	-0.52	171.85	48.17	0.28031	-0.55236	0.006	-0.46198	-0.40198	-0.52198
0.10	-1.00	170.23	160.67	0.94380	-0.02512	0.002	-0.00822	0.076472	-0.09292
0.05	-1.30	170.54	315.20	1.84823	0.26676	0.001	0.278075	0.378541	0.177608
0.01	-2.00	165.87	2042.70	12.31469	1.09042	0.0002	0.942860	1.080178	0.805541
1204.00	3.08	183.81	0.00	0.00004	-4.45346	#7	-3.88933		
1204.00	3.08	183.81	0.00	0.00001	-5.00436	#5	-3.88933		
1210.00	3.08	183.81	0.00	0.00001	-4.96257	#6	-3.89138		

Regression Output:

Constant -0.95934
Std Err of Y Est 0.115628
R Squared 0.995532
No. of Observations 10
Degrees of Freedom 8

X Coefficient(s) -0.95110
Std Err of Coef. 0.022526

STATISTICS FOR SOLIDS CONCENTRATION

LOG S (g)	LOG Ks (L/g)	LOG s +5 (X)	LOG Kd +5 (Y)	X^2	SYc	CONF INT +/-
2.43	-3.03029	7.430039	1.969704	55.20548	0.042766	0.101142
1.98	-2.87294	6.983732	2.127050	48.77251	0.032895	0.077798
1.47	-2.45996	6.472176	2.540030	41.88907	0.021788	0.051530
1.00	-1.98377	5.998345	3.016225	35.98014	0.012210	0.028878
0.48	-1.45642	5.476624	3.543570	29.99341	0.007355	0.017396
-0.52	-0.55236	4.477071	4.447639	20.04416	0.025371	0.060003
-1.00	-0.02512	3.999983	4.974879	15.99986	0.035813	0.084699
-1.30	0.266755	3.698961	5.266755	13.68231	0.042480	0.100466
-2.00	1.090423	2.999998	6.090423	8.999990	0.058062	0.137318
3.04	-3.87752	8.043755	1.122479	64.70199	0.056444	0.133492

MEAN 5.558068
SUM SQRD 3089.212

SUM X^2 335.2689

BATCH WITH THICKNESS LAYER

S (g/l)	LOG S (g)	Kd (L/g)	LOG Ks (L/g)	S (g)	TL	VL	LOG TL	REGRESSION	TL ANALYSIS	CI +	CI -
		0.000049	-4.30627	#8	0.000005	6.7942	-5.28397	-4.03952	-3.87005	-4.20899	
269.1780	2.43	0.000932	-3.03029	6	0.000033	20	-4.47928	-3.28255	-3.13758	-3.42753	
96.32352	1.98	0.001339	-2.87294	2	0.000099	20	-4.00216	-2.83372	-2.71956	-2.94789	
29.66037	1.47	0.003467	-2.45996	0.6	0.000331	20	-3.47928	-2.34185	-2.26104	-2.42266	
9.961977	1.00	0.010380	-1.98377	0.2	0.000995	20	-3.00216	-1.89302	-1.84161	-1.94443	
2.996568	0.48	0.034959	-1.45642	0.06	0.003316	20	-2.47928	-1.40114	-1.37609	-1.42620	
0.299965	-0.52	0.280310	-0.55236	0.006	0.033167	20	-1.47928	-0.46044	-0.40289	-0.51799	
0.099996	-1.00	0.943798	-0.02512	0.002	0.099502	20	-1.00216	-0.01161	0.075665	-0.09889	
0.049999	-1.30	1.848228	0.266755	0.001	0.199004	20	-0.70113	0.271565	0.378056	0.165073	
0.009999	-2.00	12.31469	1.090423	0.0002	0.995024	20	-0.00216	0.929089	1.080695	0.777483	
1204	3.08	0.000028	-4.54060	#7	0.000004	5.8312	-5.35035	-4.10197			
1204	3.08	0.000007	-5.10237	#5	0.000004	5.7802	-5.35416	-4.10556			
1210	3.08	0.000008	-5.07572	#6	0.000004	5.8312	-5.35035	-4.10197			

Regression Output:

Constant	0.931126
Std Err of Y Est	0.133684
R Squared	0.992895
No. of Observations	9
Degrees of Freedom	7

X Coefficient(s)	0.940704
Std Err of Coef.	0.030076

STATISTICS FOR THICKNESS LAYER

LOG TL (g)	LOG Ks (L/g)	LOG TL +5 (X)	LOG Kd +5 (Y)	X^2	SYc	CONF INT +/-
-4.47928	-3.03029	1.520712	2.969704	2.312567	0.049273	0.116532
-4.00216	-2.87294	1.997833	3.127050	3.991340	0.037176	0.087921
-3.47928	-2.45996	2.520712	3.540030	6.353992	0.024182	0.057191
-3.00216	-1.98377	2.997833	4.016225	8.987008	0.013253	0.031344
-2.47928	-1.45642	3.520712	4.543570	12.39541	0.008725	0.020636
-1.47928	-0.55236	4.520712	5.447639	20.43684	0.030032	0.071025
-1.00216	-0.02512	4.997833	5.974879	24.97834	0.042025	0.099390
-0.70113	0.266755	5.298863	6.266755	28.07795	0.049676	0.117484
-0.00216	1.090423	5.997833	7.090423	35.97401	0.067550	0.159757
-5.35416	-4.30627	0.645833	1.693726	0.417100	0.071657	0.169470
MEAN		3.401888				
SUM SQRD		1157.284				
				SUM X^2	143.9245	

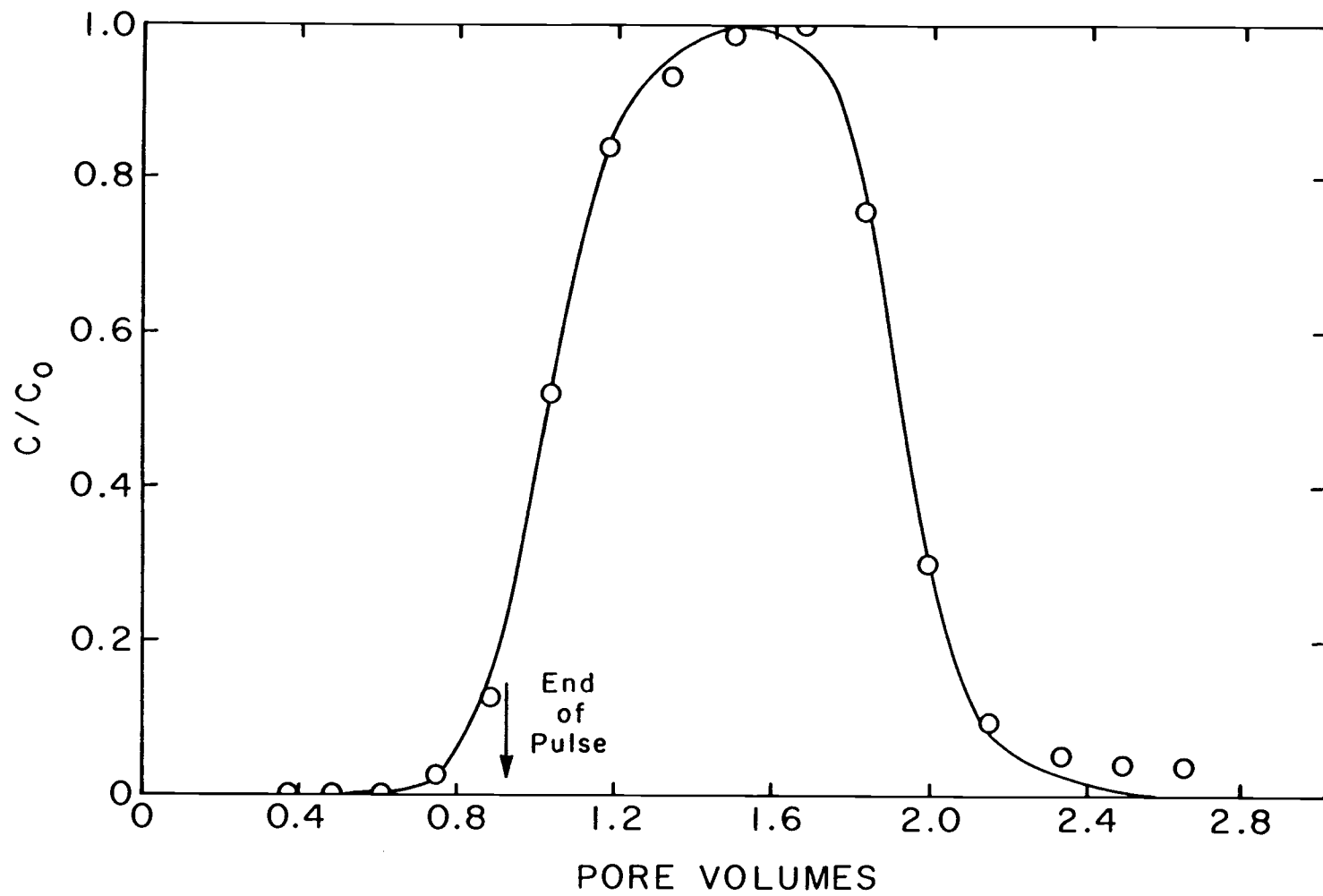


Figure B.1 Phenol BTC in kaolinite spun at 900 RPM (test 3).

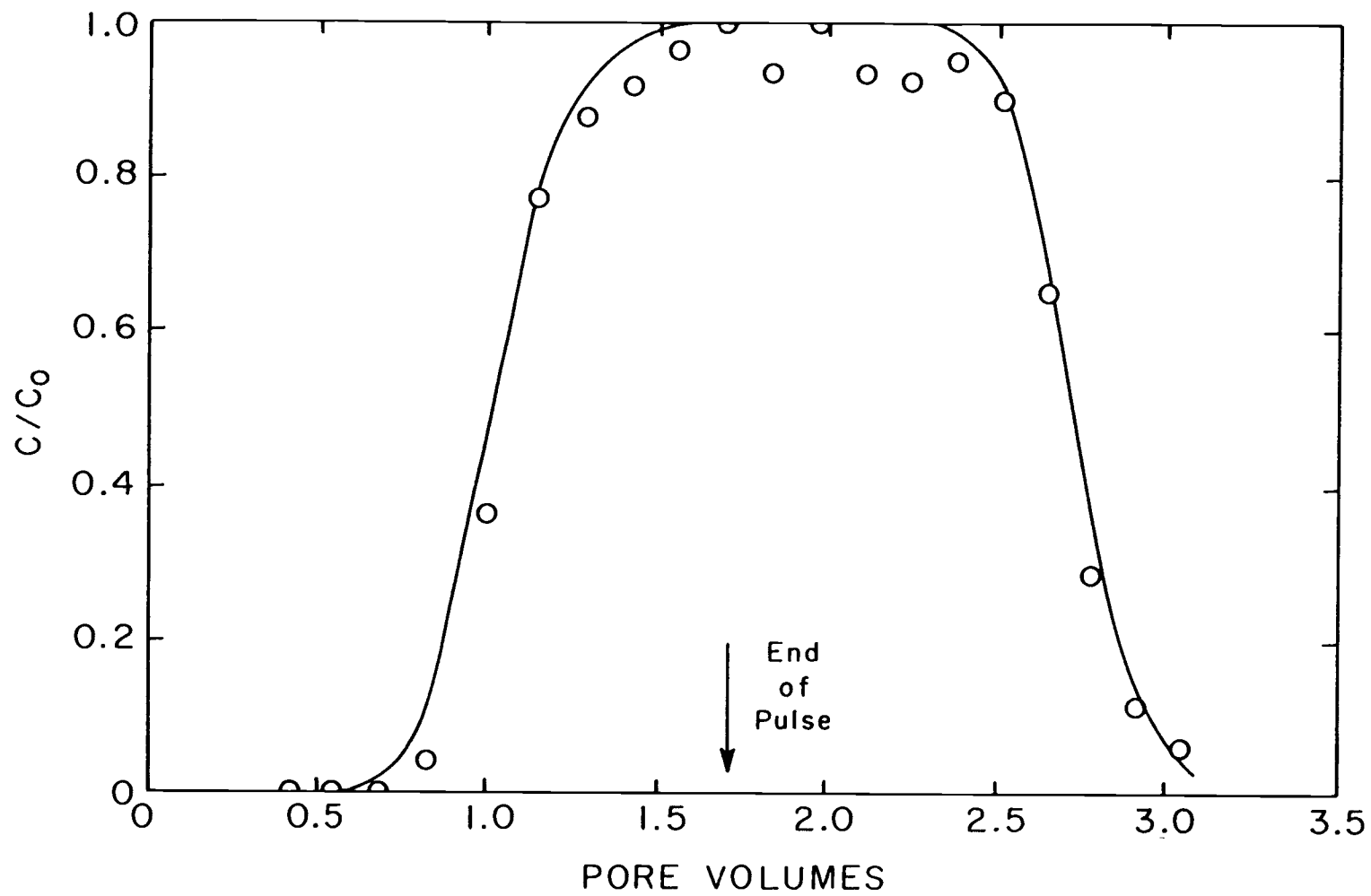


Figure B.2 Phenol BTC in kaolinite spun at 900 RPM (test 4).