AN EVALUATION OF BOUNDARY CONDITIONS FOR
ONE-DIMENSIONAL SOLUTE TRANSPORT, 2,
COLUMN EXPERIMENTS

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by

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MANAGEMENT PERSPECTIVE

This is the second paper in a two-part series in which the boundary conditions for analytical models used to interpret tracer experiments are evaluated. In this paper a number of tracer experiments are conducted in laboratory columns and interpreted using the analytical models developed in the first paper. To conduct the experiments, a new column method was developed which resulted in markedly improved accuracy in estimates of dispersion. This method should prove popular amongst others conducting similar studies. In addition, it was determined that only one particular analytical model is supported by physical evidence. This model is different than any in the literature to date and will provide much more realistic estimates of the dispersion parameters than those currently in use. Having established the correct boundary conditions, a new analytical model must now be developed for radial flow so that these results can be applied to the field case.

PERSPECTIVE GESTION

L'article présenté ici est le second de deux exposés sur
l'évaluation des conditions en zone limitrophe de modèles d'analyse
servant à l'interprétation d'expériences au traceur. On a réalisé un
certain nombre d'expériences au traceur dans des colonnes en
laboratoire et l'on a interprété les résultats au moyen des modèles
d'analyse décrits dans le premier article. Pour la réalisation des
expériences, on a mis au point une nouvelle méthode d'expérimentation
en colonne qui a permis d'améliorer sensiblement la précision de
l'estimation de la dispersion. Cette méthode devrait être appréciée
des autres chercheurs travaillant au même genre d'études. En outre,
on a déterminé que les données physiques n'étaient qu'un seul modèle
d'analyse. Ce modèle est différent de tous les autres décrits
jusqu'ici dans la documentation : il permet d'obtenir une estimation
beaucoup plus réaliste des paramètres de dispersion que les modèles
qu'on emploie actuellement à cette fin. Maintenant que les conditions
en zone limitrophe sont correctement établies, il faut mettre au point
un nouveau modèle d'analyse de l'écoulement circulaire afin de pouvoir
appliquer les résultats obtenus aux conditions sur le terrain.

ABSTRACT

As the result of a theoretical comparison of analytical models for one-dimensional solute transport (Novakowski, this issue), it has been identified that to reconcile the substantial differences observed between the models under conditions of large dispersion, a physical modeling study of the processes of solute transport in the vicinity of boundaries must be undertaken. The physical modeling is conducted using columns ranging in diameter from 76 to 352 mm and length from 300 to 400 mm. Geological materials of either large or small coefficient of dispersion are employed as packing for the columns. Reservoirs of finite volume are located at the inlet and outlet boundaries of each column. Using a conservative flourescent tracer, experiments are conducted to investigate the use of macroscopic continuity in concentration at the boundaries, and the use of the flux-averaged transformation for this boundary value problem. Concentration of the tracer was determined non-invasively from both the inlet and outlet reservoirs and, for some experiments, resident concentration was determined from within interior of the column by excavation. Results of the experiments conducted using different volumes of the outlet reservoir show that the analytical model for flux concentration accounting for macroscopic continuity in concentration at the boundaries only poorly simulates the physical mixing process in the outlet reservoir. In addition, the results of the experiments conducted in which resident concentrations were determined from the interior of the column show that the concept of macroscopic continuity is not supported by physical evidence at either the

inlet or outlet boundary. Thus, the analytical model in which concentration at the boundaries is macroscopically discontinuous, best simulates the solute transport processes for this boundary value problem. Unfortunately, the solutions for resident and flux concentration with these boundary conditions are identical and further distinction between these models can not be undertaken. Analytical inversion of the Laplace domain solution is also presented.

RÉSUMÉ

Au terme de la comparaison théorique de modèles d'analyse du transport en solution unidimensionnel (Novakowski, présent numéro), on déterminé que pour réconcilier les différences considérables observées entre les modèles en conditions de grande dispersion, il faut faire la modélisation physique du processus de transport dans la zone limitrophe. Pour ce faire, on s'est servi de colonnes de 76 à 352 mm de diamètre et de 300 à 400 mm de longueur. Ces colonnes étaient garnies de matériaux géologiques à coefficient de dispersion faible ou élevé. À l'entrée et à la sortie de chaque colonne, on a placé des réservoirs de volume fini. Au moyen d'un traceur fluorescent stable, on a réalisé diverses expériences pour évaluer l'utilisation de la continuité macroscopique de la concentration en zone limitrophe et l'application de la transformation de l'écoulement moyen au problème des valeurs limitrophes. On a déterminé la concentration du traceur par une méthode non invasive dans les réservoirs d'entrée et de sortie et, dans certains cas, on a déterminé la concentration de séjour dans la colonne par excavation. Les résultats des expériences réalisées avec des réservoirs de sortie de différentes capacités montrent que le modèle d'analyse de la concentration d'écoulement où l'on applique la continuité macroscopique de la concentration en zone limitrophe ne reproduit que médiocrement le processus de mélange physique qui se produit dans le réservoir de sortie. En outre, les résultats des expériences dans lesquelles les concentrations de séjour on été mesurées dans la colonne montrent que le principe de la continuité macroscopique n'est pas vérifié par les données physiques et ce, tant à l'entrée qu'à la sortie. Ainsi, c'est le modèle d'analyse dans

lequel la concentration en zone limitrophe est macroscopiquement discontinue qui reproduit le mieux les processus de transport en solution avec ce problème de valeur en zone limitrophe. Malheureusement, les solutions applicables aux concentrations de séjour et d'écoulement sont identiques dans ces conditions limitrophes et il est impossible de pousser davantage la distinction. On présente également la solution d'inversion analytique du domaine de Laplace.

INTRODUCTION

In the previous paper in this series (Novakowski, this issue), analytical solutions are developed for several one-dimensional solute transport problems in which mixing conditions occur in reservoirs attached to the inlet and outlet boundaries of a porous medium. The analytical solutions are derived using the Laplace transform method and are numerically inverted using the De Hoog et al.(1982) algorithm. The solutions were developed using both continuous (first-type) and discontinuous (third-type) conditions at each boundary and the flux-averaged transformation is applied to provide solutions for flux concentration. Comparison of the solutions showed that depending on the coefficient of dispersion there is considerable disimilarity in results for similar boundary conditions, with no obvious recourse through traditional mass balance arguements. In addition, the selection of continuous versus discontinuous conditions at the inlet boundary can lead to the case where concentrations measured in the upstream resevoir may be interpreted to obtain an estimate of the coefficient of dispersion; conceptually an unlikely possibility. Some doubt is also raised with regard to the efficacy of the flux-averaged transformation as it is applied to these problems. To resolve these issues, it was determined that some form of physical modeling is required.

Physical models have been employed in numerous previous studies to investigate the processes of solute transport and can be classified into two general types: 1) column tracer experiments and 2) tracer experiments conducted in glass or acrylic tank

arrangements. A third method whereby the porous medium is constructed so as to be rigid has been employed in at least one study of solute transport (Crider, 1987). For this method, no structural coverings are required and confined and unconfined groundwater flow conditions can easily be simulated by selective application of an external sealant.

Solute transport experiments have been conducted using tank arangements for a variety of purposes including evaluation of the two-dimensional nature of dispersion (Simpson, 1962; Lawson, 1971; Silliman et al.,1987), evaluation of non-hydrodynamic transport processes (Sudicky et al.,1985), development of instrumentation methods (Bachmat and Lawson, 1970), investigation of reactive transport processes (Starr et al.,1985) and the study of the behavior of dense or immiscible fluids in porous media (Schincariol, 1988; Kueper et al., 1989). In all cases, the experimental apparatus consists of an acrylic- or glass-walled tank, usually narrow (less than 0.5 m wide) and with a length greater than height. Typical transport scales are on the order of 1.0 to 3.0 m. Concentration is measured using electrodes embedded in the porous medium, by sampling manometers or visually using photographs. Groundwater flow is usually established between reservoirs attached to each end of the tank with the porous medium retained by an arrangement of screen and support rods or through a system of injection and withdrawal ports attached to a manifold (eg. Simpson, 1962).

Column experiments have also been conducted to examine the processes of solute transport in porous media. Shamir and Harleman

(1967) investigated hydrodynamic dispersion through layered media using a column 0.2 m in diameter by 0.90 m in length. The effect of scale and velocity on the magnitude of the dispersion coefficient was studied by Klotz et al. (1980) using columns ranging in diameter from 0.01 m to 0.5 m and length from 0.25 m to 4.0 m. The effects of transverse dispersion have also been investigated using the column method (Robbins, 1989) at a transport scale of about 0.6 m. The dispersive effect of the necessary plumbing and end platens employed for column experiments was studied by James and Rubin (1972). More recently, the column method has been employed to investigate the chemical behavior of groundwater contaminants in geological media (Reynolds, 1978; Bouchard et al., 1988; Brusseau et al., 1989). The results of column tracer experiments have also recently been used to compare to field results obtained at the local scale as a means of assessing the effect of scale on the dispersion coefficient (Taylor et al., 1987).

The only previous physical modeling study that is directly related to the problems considered in this paper is an investigation by Parker (1984) where a column method was employed to investigate the use of the flux-averaged transformation under uniform solute transport conditions with non-mixing boundaries. The column was constructed of PVC pipe 0.19 m long by 0.05 m in diameter and filled with a semi-rigid agglomeration of quartz sand, tile grout and bentonite clay. The conservative tracer Br^- was added to the column, effluent flux concentrations were determined and at the end of the experiment the column was sectioned to obtain

resident concentrations. The results were interpreted using existing analytical solutions for flux and resident concentrations. Unfortunately, a column Peclet number of 0.0023 was obtained, which is several orders of magnitude lower than Peclet numbers obtained from similar experiments conducted in other geological media (c.f. Gelhar et al.,1985). Consequently, the conclusions drawn on the basis of the results of this experiment may be questionable.

For the purposes of this study, the column test method was selected over the use of a tank arrangement or rigid porous medium. The primary reason for this is due to the need to provide a complete mix of the tracer in both the inlet and outlet reservoirs. Although reservoirs have been used in only a few column studies (eg. Robbins, 1989), the likelihood of attaining a complete mix is better in a circular reservoir than in a box-shaped reservoir as would be attached to a tank arrangement. In addition, possible dead space within the medium is less likely in a column, the edge of the column is at a uniform distance from the column axis reducing preferentially located edge effects, a more uniform packing of the geological material can be achieved and a variety of scales can be constructed for relatively little expense.

The purpose of this paper is to examine the theoretical difficulties identified in the previous paper (Novakowski, this issue) using the results of a series of column tracer experiments conducted using geological material having both small and large coefficients of dispersion. The results will be used to define the most appropriate solution for the boundary value problem and to

assess the utility of existing solutions that employ particular continuity conditions and the flux-averaged transformation.

COLUMN EXPERIMENTS

The traditional method by which flowing fluid is introduced or removed from a column requires the use of either an end platen arrangement (Taylor et al., 1987) or a conically shaped diffusive apparatus (Shamir and Harleman, 1967; Robbins 1989). For the purposes of this study the column design is modified to accomodate reservoirs at both the inlet and the outlet of the column. To facilitate the experimental method, the columns are oriented in the vertical position and thus the reservoir attached to the outlet boundary is of fixed volume. Figure 1 shows an example of the column design and the associated apparatus required to conduct an experiment. The fluid flows vertically downward from the upper reservoir to the lower reservoir at a constant rate. The tracer experiments are initiated by instantaneously introducing a spike of tracer in the upper reservoir, ensuring a complete mix. Samples of the tracer concentration are obtained from the upper reservoir and the lower reservoir during the course of the experiment. The fluid in both the upper and lower reservoirs is mixed continually through the duration of the experiment. In addition, several experiments are conducted to investigate resident concentration within the porous medium. In this case, the fluid flow is halted at some time during the experiment and the column is excavated to determine the distribution of resident concentration within the porous medium.

Column Design and Construction

In order to achieve enough variety in scale for each geological material, a range of column diameters and lengths were employed. The length of geological medium employed in each column ranged from 200 to 400 mm. In all cases, approximately 60-80 mm of the column wall was allowed to extend above the porous medium to form the upper reservoir, although the actual volume of the upper reservoir differed for each tracer experiment. The columns were constructed having three different internal diameters, 76, 189 and 352 mm. The largest diameter is required to provide a large surface area of porous medium beneath the upper reservoir for those experiments conducted to investigate the continuity condition at the inlet boundary. For other experiments, the smaller diameter columns (76 and 189 mm) suffice. Tracer experiments conducted in the larger diameter columns require considerably longer to complete.

The 76 and 189 mm diameter columns are constructed of acrylic tubing having a wall thickness of about 7 mm. The porous medium is supported at the lower boundary by a porous acrylic plate covered by a nylon screen of 100 mesh opening (0.149 mm). The porous medium is retained at the upper boundary in all of the columns by a plate of expanded aluminum 3 mm in thickness overlying a sheet of 100 mesh nylon screen. The columns are constructed using silicon sealant and acrylic glue. The 352 mm diameter columns are constructed of rolled steel plate approximately 2 mm in thickness and are assembled in a fashion similar to the above. Silicon putty

was used to seal all seams and connections.

Water flow is established in the column using a constant-head system (Figure 1). Water inflow into the upper reservoir is from a 60-L carbouy configured as a mariotte bottle so that a constant hydraulic head is maintined at the elevation of the bottom of the single air tube installed through the top. The carbouy is positioned with the bottom of the tube approximately 50-100 mm above the desired elevation of the water level in the the upper reservoir. The flow rate of water into the upper reservoir is adjusted to the desired rate using a plastic valve at the base of the carbouy. In this manner a constant flow rate is achieved for the duration of the experiment. The actual volume of water in the upper reservoir is adjusted using the level of the outfall from the lower reservoir. Because the lower reservoir is completely enclosed, the level of the outfall from the lower reservoir defines the hydraulic head and establishes the hydraulic gradient. Thus, by adjusting the flow rate and the level of the outfall, an infinite number of combinations of upper reservoir volume and water velocity can be achieved. The discharge from the outfall is collected in a funnel and routed to a drain. Distilled water was employed for all experiments.

To ensure a complete mix of tracer and water, mechanical mixing is employed in both the upper and lower reservoirs. A rotary mixer is employed in the upper reservoir and a magnetic mixer in the lower. Two rotary mixers were employed in the upper reservoir during some experiments conducted in the 189 mm diameter columns.

A propeller having a diameter of 20 mm was employed on the rotary mixer for the experiments conducted in the 76 mm diameter columns. Both 20 mm and 35 mm diameter propellers were employed for the other experiments. A miniature stirring bar 10 mm in length and 3 mm in diameter was employed during the experiments conducted in the 76 mm diameter columns, a stiring bar of 12 mm length and 6 mm diameter was employed during the tests conducted in the 189 mm diameter columns and two stiring bars of 40 mm length and 6 mm diameter were employed during the experiments conducted in the largest diameter columns. Mixing speed is completely adjustable for both the rotary and magnetic mixers. The speed adjustments were found to significantly influence the test results and thus some experimentation was required to determine the exact rate of mixing for each experiment. This was particularily true for the experiments conducted with an upper reservoir of small volume.

Sampling Procedure and Tracer Selection

Due to the nature of this investigation, the manner in which the concentration of tracer is determined is very important. Considering that measurements of concentration are required from both the upper and lower reservoirs, the sampling method must be as non-invasive as possible. Two possible methods by which to determine concentration non-invasively are 1) by miniature conductivity electrode and 2) by miniature volume samples obtained through a capillary tube. Both methods are subject to experimental difficulties and thus were evaluated simultaneously. However, after

a few preliminary experiments with platinum wire and gold foil electrodes and a review of the existing literature in which experiences with micro-electrodes are discussed in detail (e.g. Lawson, 1972; Robbins, 1989), it was decided that the miniature volume method is probably more appropriate for the experimental configuration considered here.

The primary difficulty with the miniature volume method is that the tracer employed must be detectable in very small volumes of sample, less than 500 μL for example. The obvious candidate tracer for this is therefore the flourescent dye family of tracers which are detectable at concentrations of parts per billion in very small samples (Smart and Laidlaw, 1977; Davis et al., 1985). The green dye tracer Lissamine Flavine FF was selected for these experiments because it is has well known properties, it is very stable in most light, pH and temperature conditions and it is very resistent to adsorptive losses (Smart and Laidlaw, 1977). Analysis of Lissamine concentration is easily conducted using a commercial fluorometer. The fluorometer employed for this study is equiped with a high sensitivity door and an adapter for micro-cuvettes. After some experimentation it was discovered that a sample volume of only 300 μL and a minimum concentration of 10 μg/L of Lissamine are needed for the column tracer experiments. Further discussion of the resistance to adsortion loss is given in the section describing the geological materials.

To obtain a 300 μL sample, a different sampling procedure is employed for each of the upper reservoir and lower reservoir,

respectively. To obtain samples from the upper reservoir, a 500 μL chromatographic syringe is inserted directly into the fluid in the upper reservoir and 300 μL of sample withdrawn. For the samples obtained from the lower reservoir, a capillary tube is employed. The capillary tube (PTFE manufacture) is permenantly inserted in the lower reservoir, and is of 0.8 mm inside diameter. The external end of the tube is capped with a two-way teflon valve (Figure 1). To collect a sample, the valve is opened and a few drops allowed to fall as a means of purging the tube. Three drops are then collected for a total sample volume of approximately 300 μL.

In all cases, the samples are obtained over an instantaneous period of time relative to the duration of the experiment using a relatively non-invasive methodology. Thus, the concentrations measured in this fashion may represent resident values. However, it is possible that reservoir concentrations measured in this way reflect flux-averaged values due to the inherent flux conditions at both the inlet and outlet boundaries. To investigate this possiblity, experiments were conducted using columns of 189 mm diameter, where samples were obtained from the column outfall continuously over time using a fraction collector. During the same experiments, samples were obtained from the lower reservoir in the usual fashion.

For the experiments conducted using geological material of large dispersion coefficient, resident concentrations obtained from within the porous medium are measured by excavating sections of the column perpendicular to the column axis. Sections of approximately

20-30 mm width are employed. The sectioning is aided by layers of 100 mesh nylon screen which are added during the packing of these columns. The prescence of the nylon screens is believed to have a minimal influence on the flow patterns within the columns and greatly facilitates the sectioning process during excavation. Samples are obtained from the uppermost section by first drawing off the water from the upper reservoir and then inserting a syringe from above to the base of the section resting on the nylon screen and withdrawing approximately 0.5 mL of fluid. This process is repeated in a uniform fashion over the area of the section until complete coverage of the resident concentration in the plane of the nylon screen is achieved. Depending on the diameter of the column, up to 50 samples per section are required. Upon completion of the sampling of the uppermost section, the porous medium and excess water are removed until the top of the next section is exposed and the process is repeated. The entire sampling process for four or five sections requires no more than two hours. This procedure works best for determining resident concentration near the inlet boundary.

A similar procedure is employed for obtaining resident concentrations near the outlet boundary except that only a few sections are sampled at and immediately above the outlet boundary and the rest of the column is excavated to obtain these samples. Because the water in these sections may be more disturbed than would be the case for those sections nearer to the inlet boundary, 8 or 9 samples are obtained independently prior to the excavation.

These samples are obtained through capillary tubes (as previously described) inserted into the medium through the wall of the column. The sampling points of these tubes are located at the center of the section and distributed in a random fashion perpendicular to the column axis. Although the capillary tubes constitute considerably fewer sampling points relative to the number of samples obtained from each section, it was found that the average concentration determined by this procedure compared well with the results of the samples obtained during the excavation.

Geological Materials

Two types of material are used to pack the columns for this study. The objective in selecting the material is to obtain two materials having widely different dispersion coefficients. To obtain a material of small dispersivity, glass beads manufactured for sand blasting are employed. The glass beads are uniformly spherical, of uniform size and have a mean grain diameter, d_{50}, of about 420 μm.

For material of large dipersivity, till from a local drumlin is used. The drumlin is part of the Wentworth Till complex of Southern Ontario and is primarily sandy and buff in character. The pebble content is mostly limestone and dolostone with a minor amount of Precambrian material. The carbonate content of the smaller size fractions is leached in some places. Karrow (1963) gives a more thorough description of the till and drumlin fields. Approximately one cubic m of till sample was obtained for the

study.

The ability of the selected tracer to behave in a geochemically conservative manner is critical to the reliable interpretation of the experimental results. The two possible mechanisms by which non-conservative results are possible, when using Lissamine as a tracer, is through adsorption on to organic material and through an exchange process on mineral surfaces (Smart and Laidlaw, 1977). Consequently, the till was prepared to minimize these problems before being packed into the columns. This was done by removing as much as possible of the organic material using a washing process whereby the till is agitated in a large container full of tap water, allowing the organic material to float off. It is estimated that at least 90% of the original organic material was removed in this fashion. In addition, to reduce the amount of mineral surface area, the till was wet-sieved through a 0.5 mm screen to remove the clay, silt and sand fraction. To replace the sand fraction that was lost, an equivalent amount of glass beads of known size (420 μm) were added to the sample. Three combinations of glass and till were manufactured in this way. Figure 2 shows the size distributions in cumulative percent for the four geological materials employed for this study. All of the glass/till samples have a similar bimodal distribution.

To evaluate the possible adsorptive loss due to the remaining organic material and exposed mineral surfaces in the till samples, comparitive experiments were conducted using Lissamine in conjunction with the known conservative tracer Bromide. The

experiments were conducted using columns of 76 and 189 mm diameter and concentrations were obtained from the column outfall only. This is because the analysis for Br⁻ was conducted using a conductivity electrode which requires a sample of at least 0.005 L in volume.

Figure 3 shows the breakthrough curves for the results of the comparitive experiment conducted using a column 189 mm in diameter. The results are shown plotted relative to the initial concentration of tracer in the upper reservoir. The initial concentration of Br⁻ was about 140 mg/L and the initial concentration of Lissamine was about 1.25 mg/L for this test. As can be observed, the agreement between the results as obtained using the two tracers is very good. Small differences evident in the tail area are probably within the combined analytical error for the instrumentation or may possibly be due to a minor density effect on the more concentrated Bromide tracer. The mass recovery determined for this experiment was approximately 100%. Results obtained from the smaller columns were identical. Therefore, in consideration of these results it is safe to assume that Lissamine behaves as a conservative tracer for the experiments described herein.

Table 1 summarizes the physical and hydraulic properties of the four materials. Although all of the glass/till samples are manufactured from the same parent, they each have a unique and quite different mean grain diameter and uniformity coefficient. The uniformity coeffecient is probably the best indicator as to the magnitude of the dispersivity of the material. Thus, the glass/till #2 and #3 should have the largest dispersivity as they have the

largest uniformity coefficient.

The hydraulic conductivity of the materials was determined during the column tracer experiments, and the values are probably most reflective of the manner in which the columns were packed. Hence, the difference between the average hydraulic conductivity of each glass/till sample. Hydraulic conductivity is calculated using the Darcy equation, $Q = KiA$ where Q is volumetric flowrate, K is hydraulic conductivity, i is hydraulic gradient and A is the cross-sectional area of the column.

Porosity was also determined for each material just proir to being packed into the columns. Porosity is estimated by dividing the wieght of a known volume of dry sample by the bulk density of rock (2.65 g/cm^3) and subtracting from one. At least 5 replicate samples were taken and the volume of each was determined after the material had settled using a method similar to the way it was to be packed in the columns. The samples were oven dried at 165°C for several hours prior to conducting the porosity measurements. The replicate porosity estimates for the glass beads varied by less than 1%, while those for the glass/till samples varied by as much as 10%. Therefore, the values of porosity as given Table 1 for the glass/till samples are probably only accurate to ± 0.02. Porosity is also determined independently using the results of the column experiments.

Experimental Method

Prior to conducting an experiment, the column was packed with

geological material and saturated with water. For each column, the material was oven dried at 165°C overnight before the packing commenced. The packing was conducted with the material dry and with the use of periodic mechanical compaction. In addition, the column was mechanically agitated during the entire packing procedure to ensure settling and the proper filling of the large-scale pores. On the basis of visual observation, this procedure resulted in a very uniform packing, free of layering.

After the columns were packed, CO_2 was flushed through the column from bottom to top for several minutes. Immediately after saturation with CO_2, the column was filled with de-ionized water. Although the de-ionized water was not de-aired, no entrapment of air or CO_2 was observed to occur, at least along the column walls. De-ionized water was employed to prevent the possibility of co-precipitation of the tracer with major cations or anions. A minor amount of disolution of the carbonate in the till material resulted from the use of de-ionized water. This was observed using a conductivity cell, immediately following the initial displacement of pore water. However, after the dispacement of a few pore volumes, the disolution appeared to cease.

Prior to the injection of tracer, the fluorometer was calibrated using standard concentrations of Lissamine ranging between 0.25 and 1.5 mg/L. When Bromide was also employed as a tracer, the conductivity cell was calibrated using standards ranging between 25 and 150 mg/L. Before any experiment, measurements of the background fluorescence and conductivity were

collected. In all cases, the background concentration of the tracers were negligible prior to the start of an experiment.

Depending on the specific purpose of each experiment, the flowrate is adjusted to the desired value and the elevation of the column outfall adjusted to achieve the desired volume for the upper reservoir. The flowrate is measured volumetrically at the drain or the column outfall over a time span typically in the order of 10-15 min. The flowrate is measured at least two times or more prior to the injection of tracer and at least twice during the course of each experiment. The flowrate is assumed to be constant prior to tracer injection when two measurements differ by no more than 1-2%. The average velocity of the water through the porous medium is then calculated using the displacement equation, $v_D = Q/(n \times A)$ where v_D is the velocity for plug flow through the column, and n is the porosity. A typical velocity for each experiment was in the order of 10^{-4} to 10^{-6} m/s.

When constant flow conditions are established, the hydraulic gradient is determined by measuring the difference in water level between the manometer attached to the lower reservoir and the surface of the water in the upper reservoir (Figure 1). The volume of the upper reservoir is also determined at this time by measuring the height of the water column above the porous medium. All measurements are made using a machinist's micrometer and are accurate to 0.1 mm.

For the experiments in which the volume of the upper reservoir is large, the Lissamine was injected directly into the standing

water column at a concentration of 1 g/L (stock solution) using either a 500 or 1000 μL syringe depending on the desired initial concentration. The injection was conducted in a manner such that the tracer was distributed quickly and evenly about the reservoir. For the experiments in which the volume of the upper reservoir is small, the stock solution is diluted into 15-30 mL of water and then poured into the upper reservoir. This is done to prevent density effects during tracer injection. The Br^- tracer was introduced into the upper reservoir in a similar fashion, using approximately 15-20 mL of stock 1 g/L solution of NaBr. The initial concentration, C_0, of Lissamine ranged form 1.0-1.5 mg/L for most experiments. The C_0 of Br^- ranged from 100-150 mg/L.

During the course of the experiment, samples were obtained frequently, particularly at early time, and stored in test tubes for subsequent analysis. The frequency of the sampling is determined by the estimate of the number of points required to clearly define a concentration curve. For the experiments where the volume of the upper reservoir was large or the water velocity very slow, the samples were analysed directly. Analysis for Br^- concentration was only conducted on large volume samples obtained from the column outfall.

For those experiments in which resident concentrations are determined from the interior of the column, the column flow is halted by capping the outfall and by closing the inflow valve, simultaneously. The column is immediately removed from the ancillary apparatus and excavation commenced.

RESULTS AND DISCUSSION

Over 45 column experiments were conducted during the course of this study. Many of these were conducted to develop a consistent experimental method and a few were conducted to evaluate the conservative nature of the Lissamine tracer. The balance of the experiments were conducted to investigate the boundary conditions at the inlet and outlet of the column and the use of the flux-averaged transformation.

The raw results for each experiment are entered into a spreadsheet and manipulated to obtain concentrations using the calibration curve specific to the experiment. Time is entered as elapsed time where t=0 is the exact time of tracer injection. The concentrations are converted to dimensionless quantities by dividing by C_0 in the spreadsheet program and are then exported to an external ASCII file for plotting and interpretation.

To determine an independent measure of the water velocity, an analysis of the relative concentrations obtained from the upper reservoir is conducted using the point dilution method. This is done by transforming the C/C_0 logarithmically and conducting a regression analysis on the semi-log concentration-time curve using the spreadsheet program. Using the equation of the regression line, a value of time, $t_{0.5}$, is obtained for the point where C/C_0 equals 0.5. The water velocity, v_p, is then calculated from the equation (Grisak et al.,1977):

$$V_p = \frac{0.693 \times V_i}{n \times A \times t_{0.5}}$$ [1]

where V_i is the volume of the upper reservoir and the other parameters are as defined previously.

Because the analytical solutions developed for this boundary value problem are derived using dimensionless variables for time and distance (Novakowski, this issue), the simulation of the results of the column tests as obtained from the lower reservoir, are conducted using a type curve method. To provide a consistent time scale for matching the results to the type curve, the results and type curve are plotted with time on a logarithmic x-axis. The x-axis of the type curve is expressed in t_D/Pe where Pe is the dimensionless length of the column of porous media, Lv/D_L, and L is the length of the column. Dimensionless time, t_D, is defined as tv^2/D_L where D_L is the coefficient of hydrodynamic dispersion. The experimental data is plotted with time in seconds on the x-axis.

Fitting the data to the type curves is conducted visually by sliding the column data along the x-axis of the type curve. Once a match is obtained, a match point is determined from the real and dimensionless time axes. As can be observed from the graphical representation of some of the type curve matches (see Figure 4 for an example), the quality of the fit obtained using this method is very good. It is estimated that the values of the parameters

obtained from the match are probably accurate to within 2%, meaning that adjustment of the type curve by more than 2%, results in a fit that is visually unacceptable. Because of the high quality of the fits, a least squares fitting algorithm could be employed. However, it is unlikely that such an approach will improve the reliability of the measured parameters by any significant degree or improve the speed at which the analysis is conducted and thus is not employed.

In the case where results are obtained from the lower reservoir, velocity, v_t, is determined from the match point data using the expression:

$$v_t = \frac{L(t_D/Pe)_m}{t_m} \qquad\qquad [2]$$

where $(t_D/Pe)_m$ is the match point from the t_D/Pe axis and t_m is the match point from the real time axis. Once the velocity is determined, it is a straightforward calculation to determine dispersivity from the Peclet number employed to generate the type curve.

Unfortunately, the type curves are unique for each volume of upper and lower reservoir. Thus, a new set of type curves are generated to analyse the results of each experiment. The computer program developed for the previous paper is employed to generate the curves. With practise it was found that only two or three type curves were required to find a suitable fit. Each type curve is generated in approximately 10-20 s on a 386 based PC.

For the case where resident concentration is obtained from the medium, the results are presented by plotting C/C_0 with respect to real distance and type-curve fitting is not employed. The porosity and dispersivity are determined directly from the parameters employed to obtain the model fit.

In the following discussion of the experimental results, several experiments having different experimental conditions are presented. Table 2 provides a summary of the experimental conditions and the results as obtained using the solution for macroscopically discontinuous concentrations at the boundaries. The reason this solution is employed will become evident during the course of the discussion.

The Use of the Flux Transformation

To investigate the use of the flux transformation, experiments were conducted in columns of 76 mm diameter having lower reservoirs of both large and small volume. Recalling that the solution for flux concentration in a finite domain accounting for macroscopic continuity at the inlet and outlet boundaries is insensitive to the volume of the lower reservoir, these experiments will determine the utility of this boundary value configuration. The experiments are conducted using the glass beads for a packing material. As shown in the previous paper of this series, for this case ($D_L \sim 0$), there is no distinction between macroscopically continuous and macroscopically discontinuous concentrations.

Figures 4a and 4b show the results of the experiments

conducted using large volume and small volume reservoirs, respectively. Note the difference in scale on the y-axis. Also shown on these Figures are the type curve fits as obtained using the solution(s) for resident concentration. A Pe number of 600 is obtained from the results of both experiments. By dividing Pe into the length of geological material in the column (300 mm), a dispersivity (α_L) of 0.5 mm is obtained. This value is in good agreement with what might be expected for the results of a tracer experiment conducted in a uniform material of approximately 0.5 mm mean grain diameter.

To illustrate what might happen if these experiments are interpreted using the solution for flux-averaged concentration, Figure 5 shows a comparison of the flux and resident type curves using the parameters as obtained from the resident type curves for each experiment. In the case of test no. 2 (small lower reservoir), the distinction between the solutions is evident but small. However, for test no. 1 (large lower reservoir), the distinction is substantial, with the simulation using the solution for flux concentration exhibiting a peak value of more than twice that of the case for resident concentration. In fact, by employing the solution for flux concentration to analyse the results of test no. 1, a poor quality of fit is obtained and a value of 10 mm is determined for α_L. This value is almost two orders of magnitude greater than that obtained using the solution for resident concentration and is completely unrealistic for the media employed in these experiments.

As a further means of evaluting the distinction between flux and resident concentrations, an additional experiment was conducted using a column packed with glass/till #1 in which concentration was measured at the column outfall continuously over time (a flux type measurement) and discretely with respect to time (a resident type measurement). Figure 6 shows the flux and resident measurements plotted together with respect to time. As is evident, there is complete overlap of the results suggesting no difference between the sampling methods. However, according to the type curves shown in Figure 7, which were plotted using the parameters obtained from a fit determined with the third-type solution, some distinction between flux and resident measurements should be observed.

Thus, in consideration of these observations, the solution for flux concentration having macroscopic continuity at both the inlet and outlet boundaries appears to have no significant physical meaning. This is probably due to the effect of the application of the flux transformation on the particular boundary value problem. In a finite domain where continuity conditions are imposed at the inlet and outlet boundaries, the flux transformation results in a redundant description of dispersive flux at these boundaries. Conversely, when the flux transformation is applied to the solution having discontinuous resident concentrations at the boundaries, the dispersive flux terms are directly eliminated in the boundary conditions. This is similar to the solution of this BVP for resident concentrations, where the dispersive flux terms cancel each other out during the solution procedure. Thus, dispersive flux

is eliminated by the solution method in both cases and the solutions are identical.

However, because the solution for continuous flux concentration fails and due to the inherent expression of flux conditions at the boundaries, resident concentration is most likely determined in the upstream and downstream reservoirs, irrespective of the manner in which the samples are obtained. Alternatively, if the dimensionless mixing coefficient for the outlet reservoir is set to zero in the solution for discontinuous concentrations, the solution is reduced to that for the semi-infinite case in which flux rather than resident concentrations are determined (equation [35] in the previous paper). This suggests that the solution for a finite domain may represent flux concentrations. In addition, because the application of continuity conditions at the boundaries is responsible for the failure of the flux transformation in this case, some uncertainty must be placed on the physical meaning of the use of continuity here.

The Inlet Boundary Condition

To investigate the use of continuous versus discontinuous conditions at the boundaries, dilution experiments were conducted in the upper reservoir of the larger diameter columns. Recall that if continuity conditions apply, the concentration in an inlet reservoir attached to a medium of large dispersivity should decline according to components of both advective and dispersive mass flux. This results in a non-linear curve when logarithmic concentration

is plotted against time as compared to a linear curve for the case where discontinuity is employed.

Figures 8 and 9 show the results of the experiments conducted using glass/till #2 in the 189 mm column and glass/till #3 in the 352 mm column, respectively. The 189 mm column was also packed with glass beads for one experiment so as to compare the results for small dispersion coefficient to that for large dispersion coefficient. As is evident, the semi-logarithmic decline in concentration for each experiment is linear. A regression analysis was conducted on the concentration curves and the correlation coefficients were found to range from 0.998 to 0.999.

A measure of dispersivity was also obtained for each of the columns using concentration measurements obtained from the lower reservoir. Values of dispersivity for columns containing glass/till #2 and #3 were determined to be 25 mm and 150 mm, respectively, using the solution for discontinuous concentration. Figures 8 and 9 also show the results of a simulation in which the solution having continuous resident concentration is employed for the inlet reservoir using the corresponding value of dispersivity to account for the dispersive flux. In both cases, the simulations show significant departure from the experimental data at both early and late time. Thus, if we can assume that D_L is valid near the boundary and the REV defined within the diameter and length of the column (discussion to follow), the use of macroscopically continuous concentrations at the inlet boundary is not supported by this physical evidence.

There has been considerable discussion in the literature regarding the validity of the macroscopic variables describing flow and transport in the neighborhood of boundaries (Dagan, 1979; Parker and van Genucthen, 1984; Dagan and Bresler, 1985; Parker and van Genucthen, 1985). Dagan and Bresler (1985) suggest that due to the Lagrangian nature of dispersion, the dispersion coefficient is only defined once it has attained its asymptotic value (i.e. travelled many integral scales of the hydraulic conductivity distribution). They estimated that the asymptotic value is attained after the criterion $v_D\tau/x_p > 10$ is exceeded (x_p is the longitudinal integral scale and τ is the travel time from the source boundary). Thus, because $v_D\tau$ is often less or approximately equal to x_p, it is more common for practical field and laboratory measurements to be obtained at less than the asymptotic limit. Consequently, the general application of the advection-dispersion model as a tool for simulation or prediction, is questioned by this criteria.

Furthermore, it can be argued that by this definition, D_L must start at or near zero at the inlet boundary and grow progressively with travel distance. Hence, continuity is implied for concentration at the inlet boundary and thus, with respect to the column experiments, because D_L is approximately zero at the inlet boundary, a non-linear semi-logarithmic decline for the concentration in the upper reservoir would not be observed. Consequently, the results of the dilution experiments conducted in the upstream reservoir are inconclusive with respect to defining the selection of the inlet boundary condition.

Alternatively, if it is presumed that resident concentration can be defined in an infinitesimaly thin plane perpendicular to the axis of the column (i.e. within an areal REV), then it is intuitive that after travel distances of only a few pore lengths downstream from the inlet boundary in dispersive media (a transition zone where D_L is ill-defined macroscopically), the averaging process in the plane will lead to resident concentrations that appear discontinuous when measured. This occurs as a result of the distribution of pore velocities in the plane and may not be observed were the resident concentrations defined on a volumetric basis within a three-dimensional REV. Thus, the physical conditions accounting for discontinuity in concentration at the inlet boundary are concievable at travel distances many times less than integral scale in the direction of flow and, in fact, could be dependent on the integral scale of the properties of the medium perpendicular to the flow direction. This process would also have no "backmixing" effect on the concentration in the upstream reservoir.

To investigate further the condition at the inlet boundary, several experiments were conducted in the 189 mm and 352 mm columns, both packed with glass/till #3. During these experiments, concentration was measured in the upper reservoir and resident concentration determined by sectioning the columns as previously described. The experiments were conducted using an upper reservoir of large volume so as to create a substantive difference between the reservoir concentration and the concentration immediately inside the medium (provided discontinuity can be measured). The

experiments were halted after a decay in concentration in the upper reservoir of about 15-20%. The experiments were repeated several times using slightly different flowrates so as to insure reproducibility of the results. Prior to these experiments, independent measurements of α_L were determined from concentration measurements obtained from the lower reservoirs and interpreted using the solution for third-type resident concentrations.

Figures 10 and 11 show the results from the experiments conducted in the 189 mm and 352 mm columns, respectively. Only 3 to 4 experimental points were obtained downstream from the inlet boundary thus only this portion of the column length is presented. Also shown are the results of the simulations conducted using both the first- and third-type solutions for resident concentration. It is clear that in both cases, the solution accounting for discontinuous inlet boundary conditions provides a better fit to the experimental data. In particular, the quality of the fit obtained for the larger diameter column is very good, almost exactly overlying all three points.

The best fit shown in Figure 11 (curve no. 2) is obtained using a dispersivity of 80 mm. This is almost half of the value obtained from the independent determination. However, note that, as shown in both Figures 10 and 11, the solutions are relatively insensitive to α_L, thus, larger or smaller values of dispersivity are equally possible. Conversely, the simulations using the solution for continuous resident concentration do not remotely approximate the experimental data in either case, except farther

downstream in the smaller diameter column. For the results obtained from the larger diameter column, a fit can be forced using this solution by adjusting the porosity to an unrealistic value of 0.75. However, this, in turn, forces a poor fit to data obtained concurrently from the upstream reservoir. Therefore, the solution for continuous resident concentrations can not be employed to simulate resident concentration in the neighborhood of a source boundary where $D_L >> 0$.

Based on the observed increase in α_L obtained from the smaller to larger columns and assuming that the longitudinal and transverse integral scales are related (i.e. a statistically isotropic medium), then the integral scale for this medium is probably quite large, i.e. hundreds of mm or greater. Thus, the advection-dispersion equation will not meet the criteria for the asymptotic limit as defined previously anywhere in either column. However, because the solution for discontinuous resident concentration does very well to predict resident concentration within the medium, even, as shown in Figure 11, quite near to the inlet boundary, some doubt is raised as to the validity of this criteria as applied to one dimensional transport in a two-dimensional heterogeneous field. Further explanation of this problem will require additional study and is beyond the scope of the present investigation.

Furthermore, based on the results obtained from different diameter columns, it is suggested that the use of the discontinuous boundary condition allows for the application of the advection-

dispersion model independently of scale. However, for experiments conducted where the tranverse scale (i.e. diameter of column) is substantially less than the longitudinal scale and also less than the transverse integral scale, it must be recognized that the results are appropriate for this transverse scale only. Therefore, in practical applications where determination of the true macroscopic dispersivity is desired at a given scale, the transverse scale used experimentally must approach the longitudinal scale or at least exceed the transverse integral scale. Thus, for field experiments, injection and withdrawal wells having long uninterupted screen lengths are required.

In the case where the transverse scale is small relative to the longitudinal scale, the role of the transition zone adjacent to the inlet boundary becomes significant. When enough information regarding the true macroscopic dispersivity is available, it would be possible to define a local dispersivity particular to the transition zone and use the solution for discontinuous concentration to simulate solute transport at this scale. The local dispersivity would be that employed for the inlet boundary condition. The solution to this BVP would be different than that previously obtained for the same boundary conditions. Unfortunately, for most practical applications, the required information is not available and this method can not be employed.

The Outlet Boundary Condition

As suggested earlier, having mixed continuous and

discontinuous conditions at respective inlet and outlet boundaries, is difficult to conceptualize. Therefore, having established that the inlet boundary condition should be of third-type, it follows that the outlet boundary condition should be of the same nature. Furthermore, if continuity in concentration is assumed at the outlet boundary, a "backmixing" effect similar to that postulated for the inlet boundary for continuous conditions would influence the concentration in the medium upstream from the outlet boundary. It is difficult to invision how such a process could take place, physically.

As a means of demonstrating these arguements, several experiments were conducted using the 189 mm column packed with glass/till #3 in which 2-3 sections were isolated in the nieghborhood of the outlet boundary using the previously described method. A lower reservoir of approximately 1.5 L was employed for these experiments so as to provide a large influence for possible "backmixing" effects. Due to experimental difficulties in properly mixing lower reservoirs of large volume, the columns of 352 mm diameter were not employed. The flow in each experiment was halted after decay in the concentration in the upper reservoir of 80-85%.

Figure 12 shows the results of one experiment conducted in a column having 230 mm of geological material. Although only three experimental points were obtained from the medium during this experiment, a very good fit to the solution having discontinuous boundary conditions is observed. The fit, as shown by curve no. 1 in Figure 12, is obtained using a velocity determined from the

decline in concentration in the upper reservoir and a dispersivity of 40 mm which was determined from the results of previous experiments where concentrations were obtained from the lower reservoir. Furthermore, using these same parameters, a good fit is also obtained to the few points obtained from the lower reservoir prior to the ceasation of this experiment. Similar results were obtained from other experiments.

As with the case for the inlet boundary, the solution is relatively insensitive to dispersivity and shows a substantial discontinuity at the outlet boundary interface. Conversely, the solution accounting for continuous concentrations (curve no. 2 in Figure 12) does poorly in simulating the experimental results, showing a substantial decline in resident concentration adjacent to the boundary due to the influence of the presence of the lower reservoir. In fact, a reasonable fit to the experimental data can not be found using this solution. Again this is similar to the case for the inlet boundary and supports the contention that third-type conditions must be used consistently at both boundaries.

The Solution

Thus, the solution for one-dimensional solute transport in a finite domain accounting for macroscopic discontinuity in concentration between the medium and finite volume reservoirs located at the boundaries, best approximates the physical processes of solute transport for this particular boundary value problem. The solution is given as (Novakowski, this issue):

$$\overline{C}_{De}(p) = \frac{\beta_{Di} \exp\{\xi Pe\}}{(\beta_{Do}p+1)(\beta_{Di}p+1)}$$

[3]

where b_{Di} and b_{Do} are dimensionless mixing coefficients for the upstream and downstream reservoirs, respectively, n is equal to $1/2-(p+1/4)^{1/2}$ and p is the Laplace variable (see previous paper for a more complete definition of all the dimensionless variables). This solution can only be used for concentration in the downstream reservoir but should be suitable for almost all practical problems for which these boundary conditions apply. It is doubtfull that the equivalent solution for resident concentration in a semi-infinite domain (equation [17] previous paper) would have any practical application and is discussed no further.

Because the form of the solution, equation [3], is relatively simplistic, analytical inversion is possible using a combination of the shift and convolution theorems for the Laplace domain. The following expression is the analytical inversion of equation [3]:

$$C_{De}(t_D) = \frac{\beta_{Di}}{2(\beta_{Do}-\beta_{Di})} \exp\left\{\frac{Pe}{2}\right\}\Bigg[$$

$$\exp\left\{\frac{-t_D}{\beta_{Do}}\right\}\left[\exp\left\{Pe\left(\frac{1}{4}-\frac{1}{\beta_{Do}}\right)^{\frac{1}{2}}\right\} \mathrm{erfc}\left\{\frac{Pe}{2\sqrt{t_D}}+\left(\frac{1}{4}-\frac{1}{\beta_{Do}}\right)^{\frac{1}{2}}\sqrt{t_D}\right\}\right.$$

$$\left.+\exp\left\{-Pe\left(\frac{1}{4}-\frac{1}{\beta_{Do}}\right)^{\frac{1}{2}}\right\} \mathrm{erfc}\left\{\frac{Pe}{2\sqrt{T_D}}-\left(\frac{1}{4}-\frac{1}{\beta_{Do}}\right)^{\frac{1}{2}}\sqrt{t_D}\right\}\right]\quad\quad [4]$$

$$-\exp\left\{\frac{-t_D}{\beta_{Di}}\right\}\left[\exp\left\{Pe\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}\right\} \mathrm{erfc}\left\{\frac{Pe}{2\sqrt{t_D}}+\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}\sqrt{t_D}\right\}\right.$$

$$\left.+\exp\left\{-Pe\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}\right\} \mathrm{erfc}\left\{\frac{Pe}{2\sqrt{t_D}}-\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}\sqrt{t_D}\right\}\right]\Bigg]$$

Due to the nature of the inversion for the general case, an additional inversion is required for the special case where β_{Di} is equal to β_{Do}. This is given as:

$$C_{De}(t_D) = \frac{1}{2\beta_{Di}} \exp\left\{\frac{Pe}{2}-\frac{t_D}{\beta_{Di}}\right\}$$

$$\Bigg[\left(t_D-\frac{Pe}{2\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}}\right)\exp\left\{-Pe\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}\right\}\mathrm{erfc}\left\{\frac{Pe}{2\sqrt{t_D}}+\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}\sqrt{t_D}\right\}$$

$$+\left(t_D+\frac{Pe}{2\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}}\right)\exp\left\{Pe\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}\right\}\mathrm{erfc}\left\{\frac{Pe}{2\sqrt{T_D}}+\left(\frac{1}{4}-\frac{1}{\beta_{Di}}\right)^{\frac{1}{2}}\sqrt{t_D}\right\}\Bigg]$$

$$[5]$$

Therefore, because equations [4] and [5] consist of combinations of the exponential and complementary error functions, computer coding is straightforward and the general utility is enhanced relative to

having the solution in the Laplace domain only.

Futhermore, the experimental method developed for this study is generally applicable for the study of solute transport in unconsolidated media. Specifically, this method provides advantages over standard methods with respect to the unknown effects of mixing in the diffusive or platen apparatus required to introduce and withdraw fluids from a standard column. By using reservoirs of a known size and providing continual and consistent mixing in these reservoirs, the effects of unknown mixing is eliminated and very accurate estimates of α_L and velocity are obtained. This is evidenced by the measurement of the dispersivity of the glass beads (Figure 4) which was found to be 0.5 mm. To the author's knowledge this is the smallest value of dispersivity ever reported from the results of a column experiment. The experimental method and concomitant analytical solution are therefore recomended for all column experiments irrespective of the purpose for which they are conducted.

The only failure with respect to the objectives of this study is that distinction between resident and flux concentrations can not be undertaken for this solution. In consideration of the equivalent solution for radially convergent tracer experiments, this may be a problem due to the fact that the governing equation for resident and flux-averaged concentrations are not the same as is the case for uniform flow (Chen, 1987). Thus, it is unlikely that the solutions for flux and resident third-type concentration in the radial case will be equivalent.

The final concern with respect to this solution is that a formal mass balance within the solution domain, can not be conducted successfully (Novakowski, this issue). The reason for this is not entirely clear but may be due to the way in which the formal mass balance is developed. For example, it is possible that because the macroscopic equations are developed using the concepts of a volumetric REV which implies continuity at the inlet boundary, the mass conservative solution which applies to the domain in which this concept is supported, must include at least one continuous boundary condition. This was observed from mass balance discussions undertaken in the previous paper of this series. However, because it has been shown in this paper, that the volumetric concept of the REV fails at the inlet boundary, the fact that the theoretical mass balance is also found to fail for the solution that is more physically justifiable, is probably of no concern.

CONCLUSIONS

In the previous paper in this series (Novakowski, this issue), several analytical models were developed for the boundary value problem in which solute transport is uniformly one-dimensional. Inlet and outlet boundary conditions were derived for the case where reservoirs of a finite volume are attached to each boundary. Conditions of macroscopically continuous or macroscopically discontinuous concentration were accounted for and the flux transformation employed to obtain flux-averaged concentrations. Comparison showed that substantial differences between the models

were possible under conditions of large dispersion. It was determined that these differences could only be resolved using the results of physical modeling experiments.

The results of tracer experiments conducted in columns ranging in diameter from 76 to 352 mm and length from 300 to 400 mm were employed to reconcile the differences between the models. The columns were packed with either a course grained material of large dispersivity or a uniformly small grained material of small dispersivity. Because the columns were oriented vertically so that fluid fluid flow was in the downward direction, each column was manufactured with a lower reservoir of fixed volume. The volume of the upper reservoir was allowed to vary according to the flowrate of the fluid and the hydraulic gradient. The fluid in both reservoirs was mechanically mixed throughout the duration of each experiment. To conduct an experiment, a conservative tracer was introduced into the upper reservoir instantaneously and the decay in concentration measured in the upper reservoir with time. Breakthrough of concentration in the lower reservoir was monitored using a non-invasive method. During some experiments the flow of fluid was halted and the column was excavated and sampled to obtain resident concentrations from within the interior of the medium.

Several experiments were conducted using the smallest diameter columns packed with the material of uniform grain size and having a lower reservoir of either small or large volume. the results showed that the solution for flux concentration in which continuity in concentration is required at both the inlet and outlet

boundaries can not be used to interpret the concentration history in the lower reservoir for these experiments. Therefore, this solution has no physical meaning and suggests that use of the flux transformation may be redundant for this boundary value problem. Unfortunately, further distinction between flux and resident concentration for the case where concentration is macroscopically discontinuous, can not be undertaken due to the fact that the solutions are identical.

Experiments were conducted in the large diameter columns packed with the material of large dispersion coefficient to investigate the inlet boundary condition. It was found that the decline in concentration in the upper reservoir did not exhibit a concentration history that could be predicted by the solution for resident concentration having a continuous inlet boundary condition. Therefore, the point dilution method can not be employed to determine a dispersion coefficient as has been suggested in the literature. Additional experiments conducted to investigate the resident concentration in the immediate vicinity of the inlet boundary, provided further evidence to suggest that macroscopic discontinuity is the best approximation of the physical processes here. This contradicts traditional REV arguements and must be investigated further.

Likewise, solute transport at the outlet boundary was also found to be better approximated by conditions of macroscopic discontinuity. The solution for macroscopic continuity predicted a "backmixing" effect upstream from the outlet reservoir that was not

observed in the results of experiments conducted in which resident concentrations were obtained adjacent to the outlet boundary.

Therefore, the solution for resident (or flux) concentration having discontinuous inlet and outlet boundary conditions was found to be the most suitable solution for this boundary value problem. Because the solution in the Laplace domain is non-complex, analytical inversion was achievable. Inversions for the general case and for the special case in which the volumes of the inlet and outlet reservoirs are the same, were presented.

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LIST OF FIGURES

flux concentration. Experimental conditions employed are the same as for the previous Figure.

Figure 8. The decline in concentration in the upper reservoir for two experiments conducted in the 189 mm columns. One experiment was conducted using the packing material of large dispersivity and the other with the material of small dispersivity. Also shown is the poorly-fitting type curve produced by the solution for first-type resident concentration.

Figure 9. The decline in concentration in the upper reservoir for an experiment conducted in a column of 352 mm diameter packed with glass/till #3. As in the previous Figure, the solution for resident concentration having first-type boundary conditions simulates the results very poorly.

Figure 10. The results of an experiment conducted in a column of 189 mm diameter using glass/till #3 as compared to the fits obtained using the solutions for resident concentrations having first- and third-type boundary conditions. Concentration in the upper reservoir is shown in the upper left of the diagram.

Figure 11. The results of an experiment conducted in a column of 352 mm diameter using glass/till #3 as compared to the model fits. Only the results from the portion of the column

which was excavated are shown. Note the concentration in the upper reservoir as shown in the upper left of the diagram.

Figure 12. Resident concentration in the vicinity of the outlet boundary as compared to solutions having having first- and third-type boundary conditions. The concentration in the lower reservoir is shown in the lower right of the diagram.

Table 1. Description of the physical and hydraulic properties of the geological materials used in the column experiments.

Geological Material	Mean Grain Diameter d_{50} (mm)	Uniformity Coefficient d_{60}/d_{10}	Hydraulic Cond. (m/s)	Porosity
glass beads	0.42	1.2	1.1×10^{-3}	0.40
glass/till #1	1.44	8.7	7.0×10^{-4}	0.27
glass/till #2	3.97	17.6	1.4×10^{-4}	0.25
glass/till #3	3.20	14.3	4.5×10^{-4}	0.27

Table 2. Summary of the experimental conditions and results for the experiments presented in Figures 4-12.

Figure #	Column Diameter (mm)	Packing	Volume Upper Res. (L)	Volume Lower Res. (L)	Length of Geol. Material (mm)	Velocity (m/s)	α_L (mm)	n
4a	76	glass beads	0.136	0.197	300	1.0×10^{-4}	0.5	0.40
4b	76	glass beads	0.205	0.037	300	1.3×10^{-4}	0.5	0.40
6	189	glass till #1	0.955	0.701	246	3.2×10^{-5}	15	0.29
8	189	glass till #2	0.332	0.632	252	2.5×10^{-5}	-	0.25
8	189	glass beads	0.280	0.632	250	2.1×10^{-5}	-	0.40
9	352	glass till #3	2.433	2.530	330	2.3×10^{-5}	-	0.26
10	189	glass till #3	0.660	0.617	267	3.1×10^{-5}	40	0.26
11	352	glass till #3	5.352	2.530	330	4.2×10^{-5}	80	0.25
12	189	glass till #3	0.528	1.584	230	6.1×10^{-5}	40	0.25
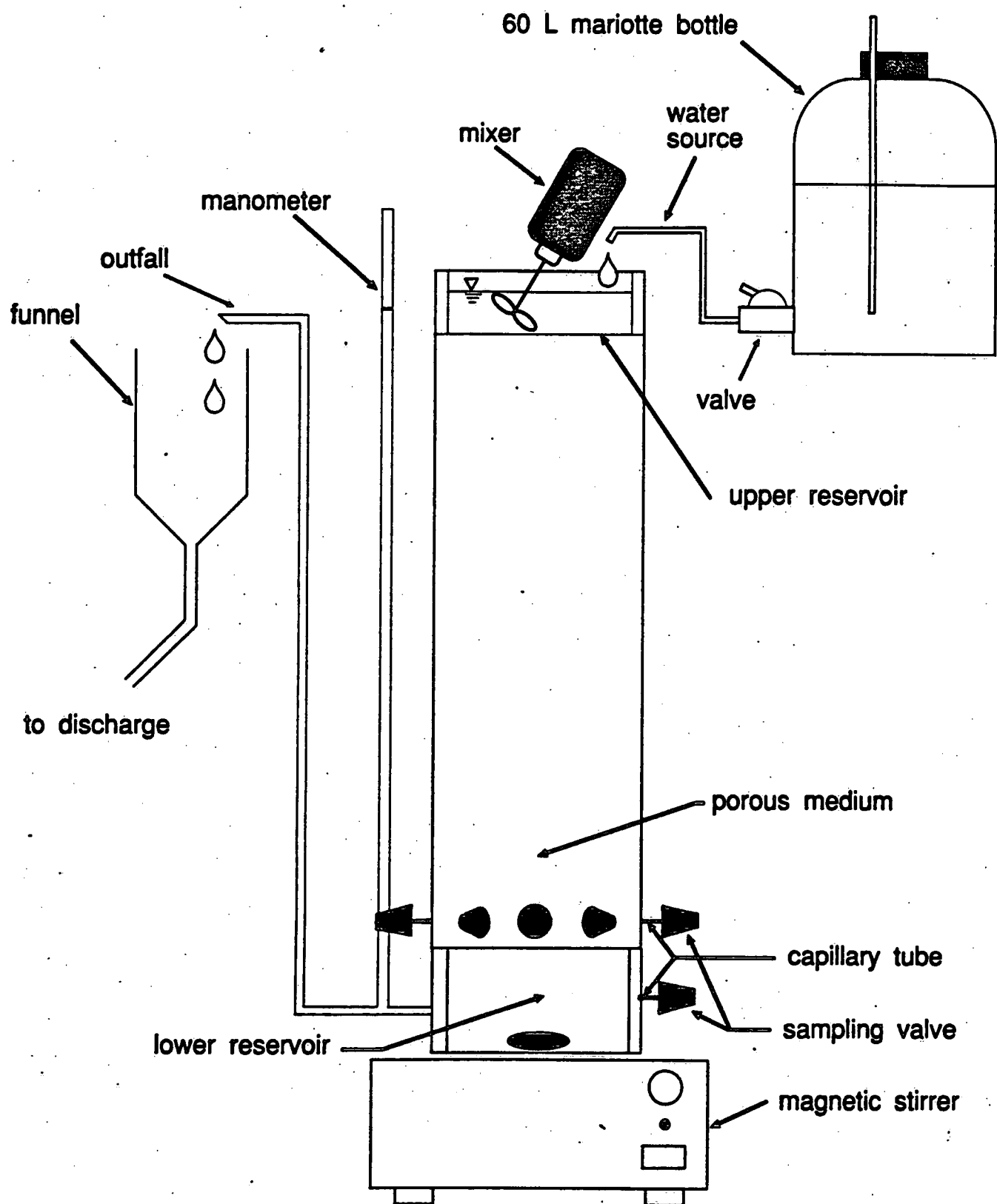
Figure 1. Schematic diagram of the column and associated apparatus.
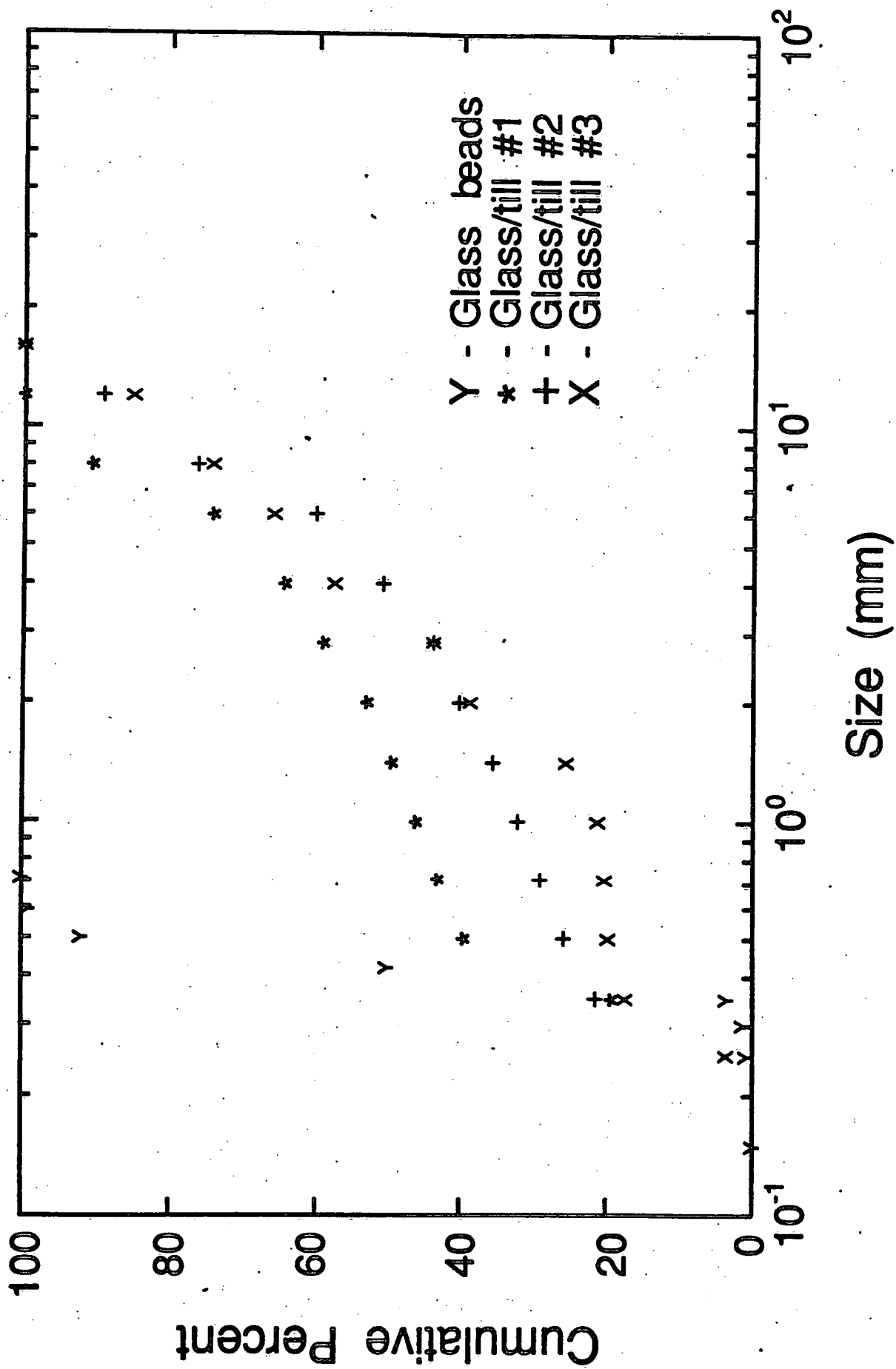
Figure 2. Grain size distributions of the material employed to pack the columns.
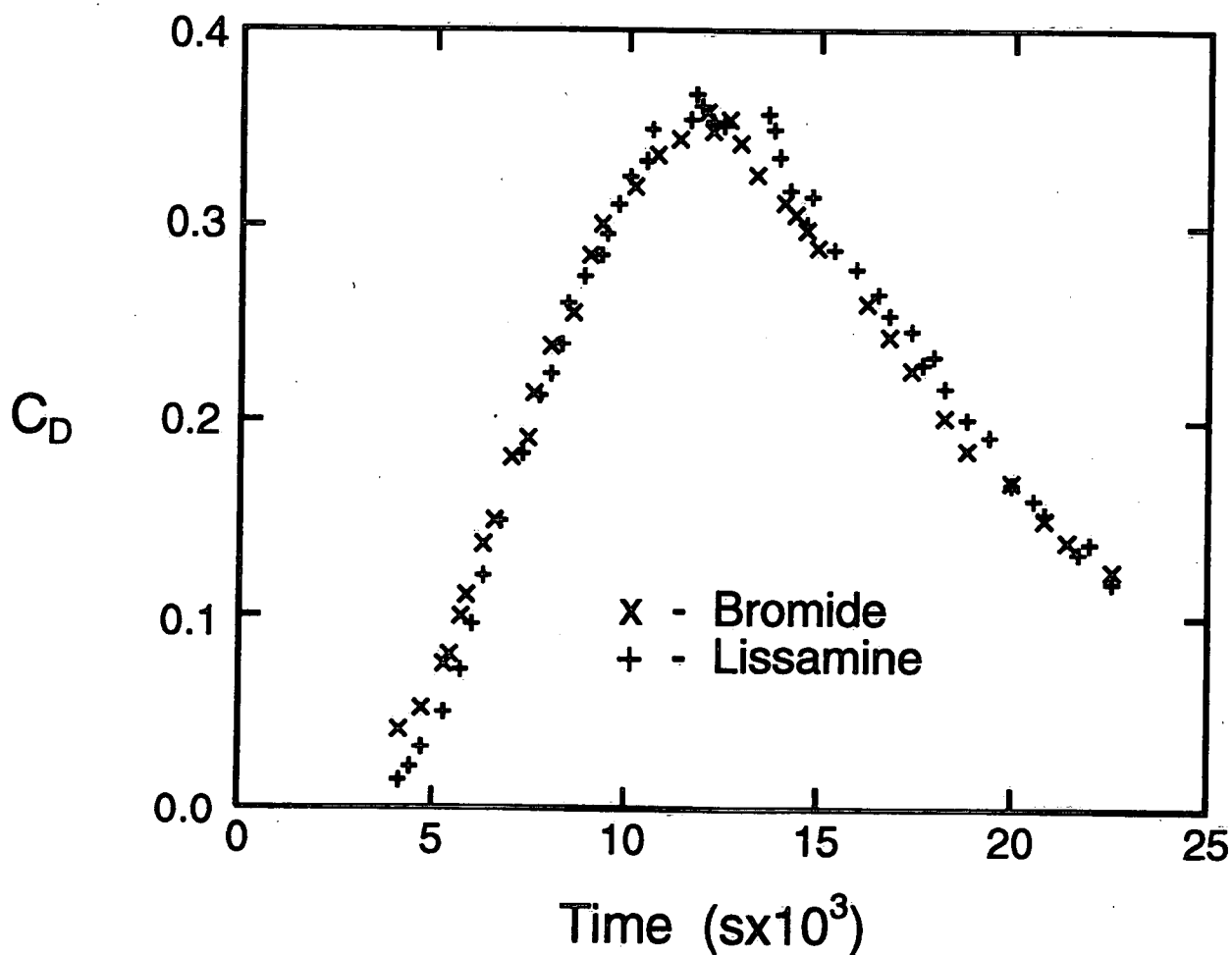
Figure 3. Comparison of the conservative tracer Bromide to the fluoroscent tracer employed for this study. Concentrations measured at the column outfall.
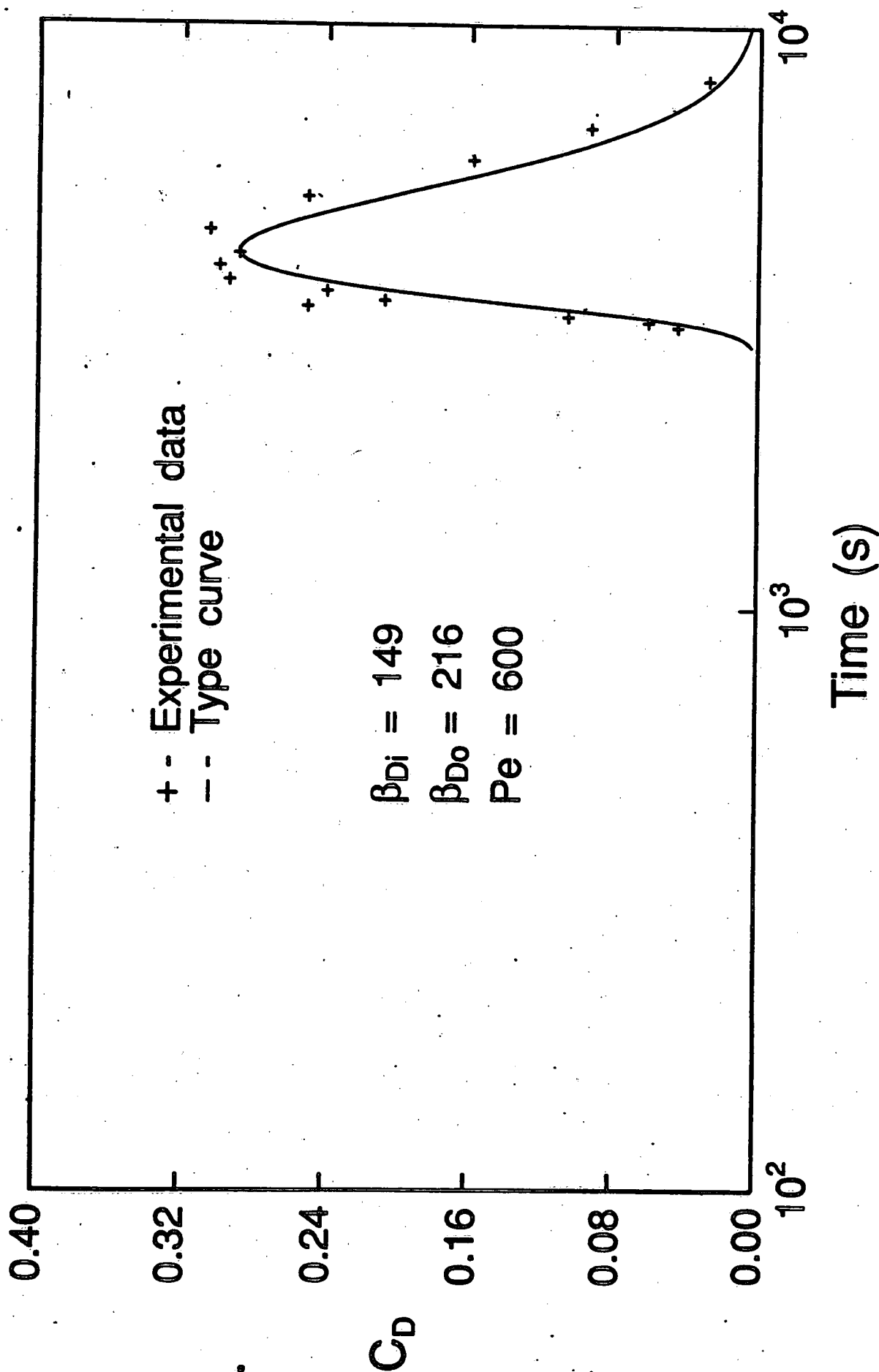
C_D

0.40 — 0.32 — 0.24 — 0.16 — 0.08 — 0.00

10^2 10^3 10^4

Time (s)

+ - - Experimental data
- - Type curve

$\beta_{Di} = 149$
$\beta_{Do} = 216$
$Pe = 600$

Figure 4a. Experimental results and type-curve fit for a tracer experiment conducted in a 76 mm column packed with glass beads and having a lower reservoir of large volume.
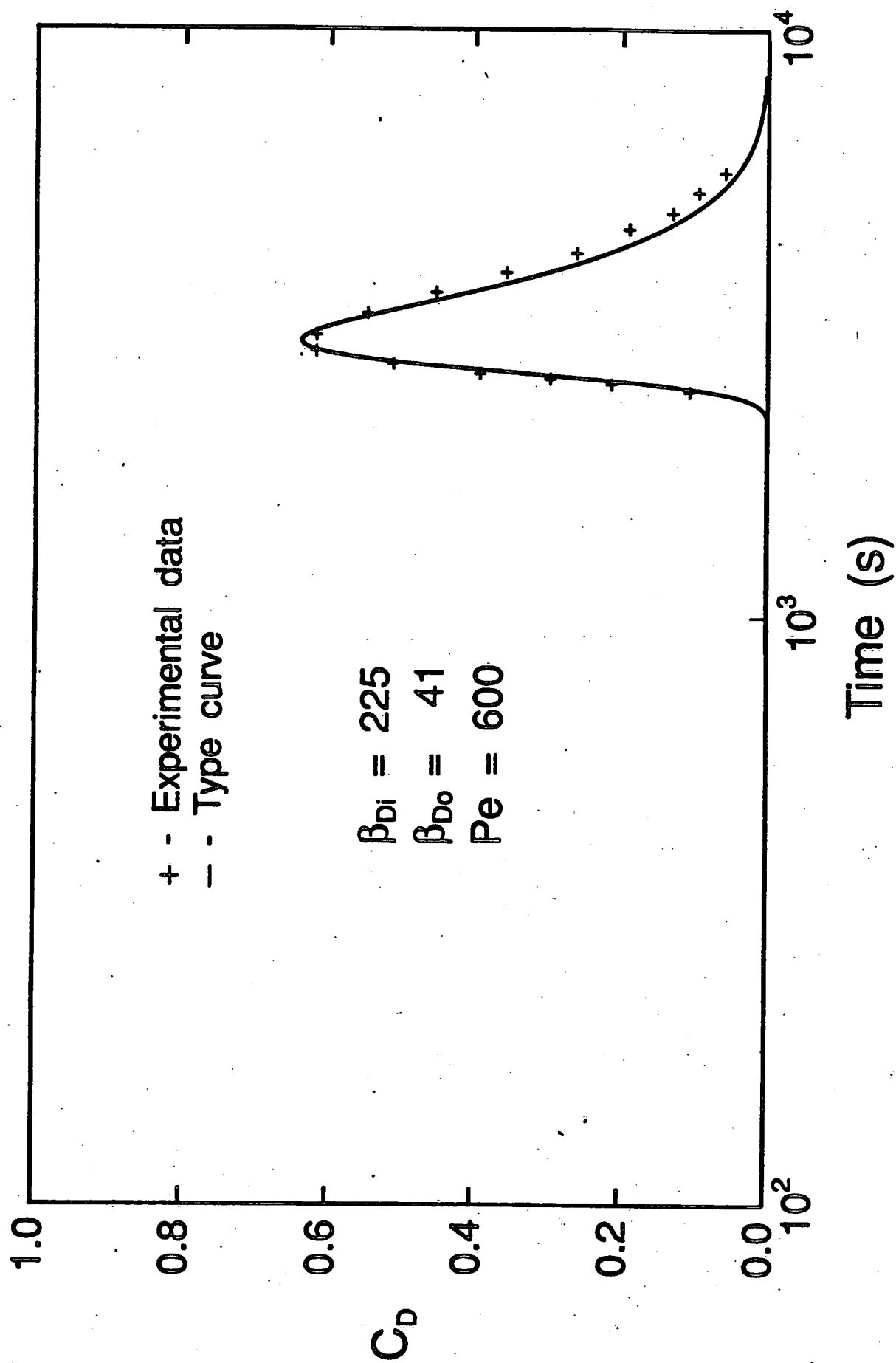
Figure 4b. Experimental results and type-curve fit for a tracer experiment conducted in a 76 mm column packed with glass beads and having a lower reservoir of small volume.
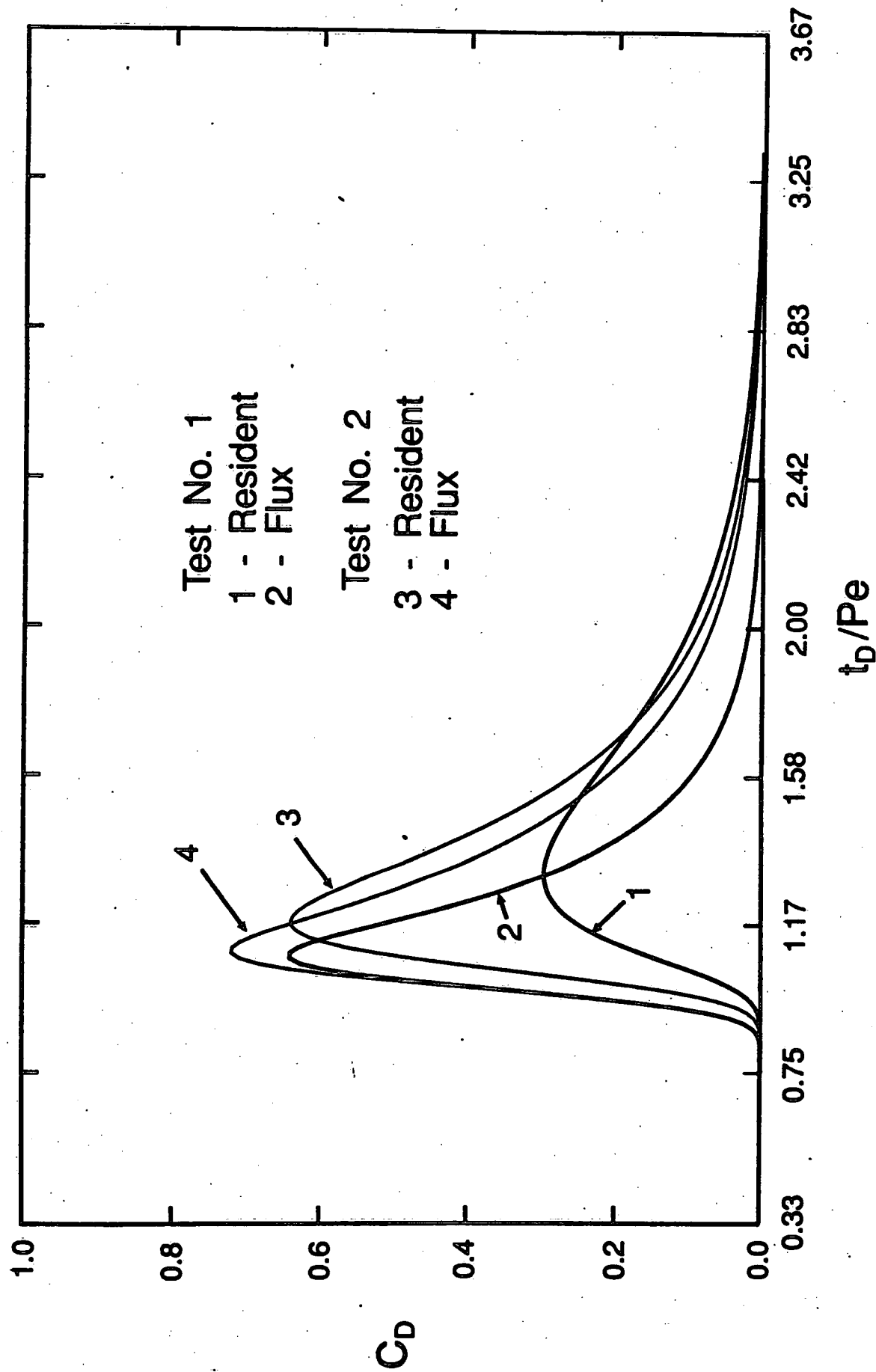
Figure 5. Comparison of resident versus flux concentrations using the experimental conditions as obtained during tests no. 1 and 2.
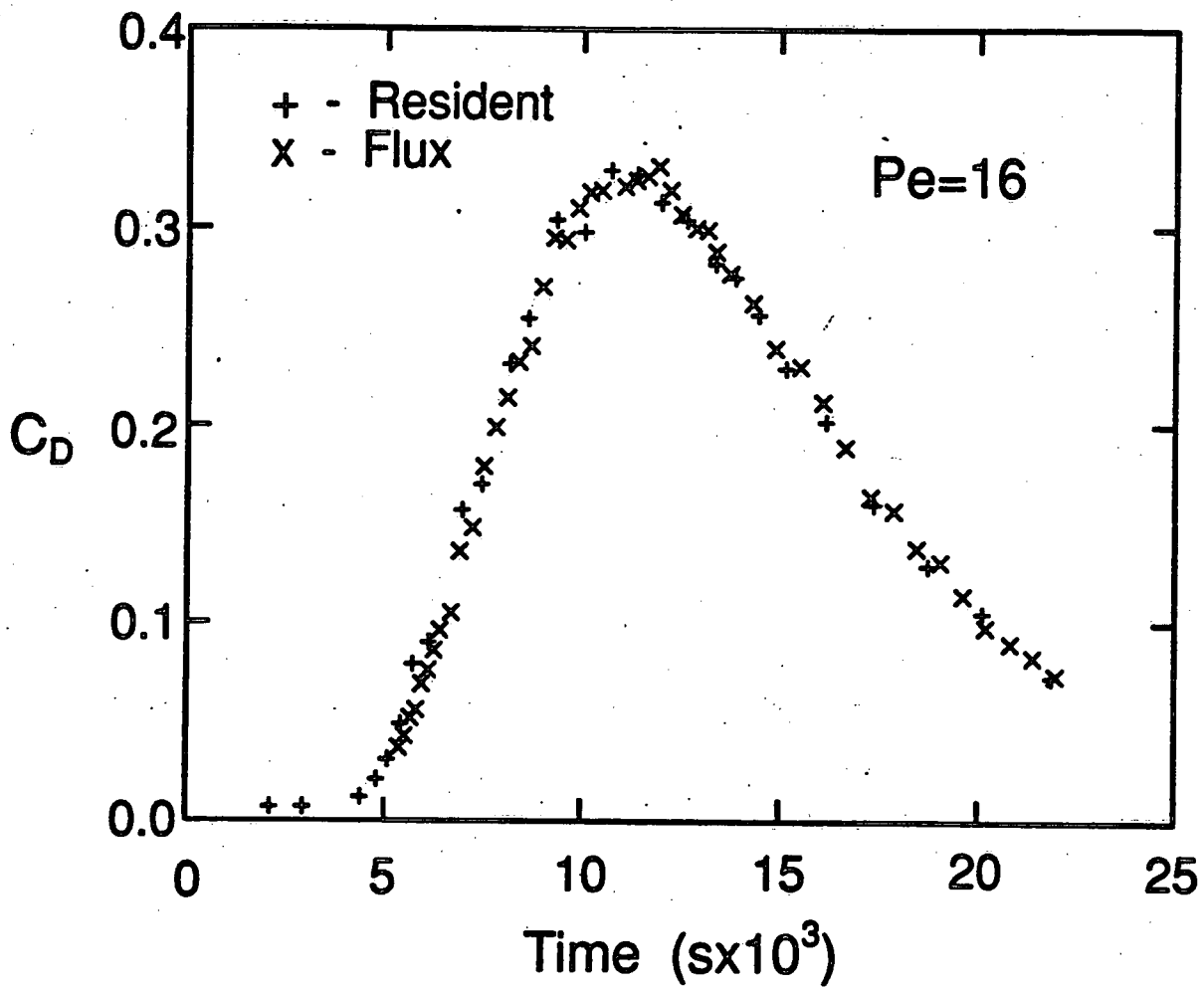
Figure 6. Comparison of resident versus flux concentration as measured from the column outfall.
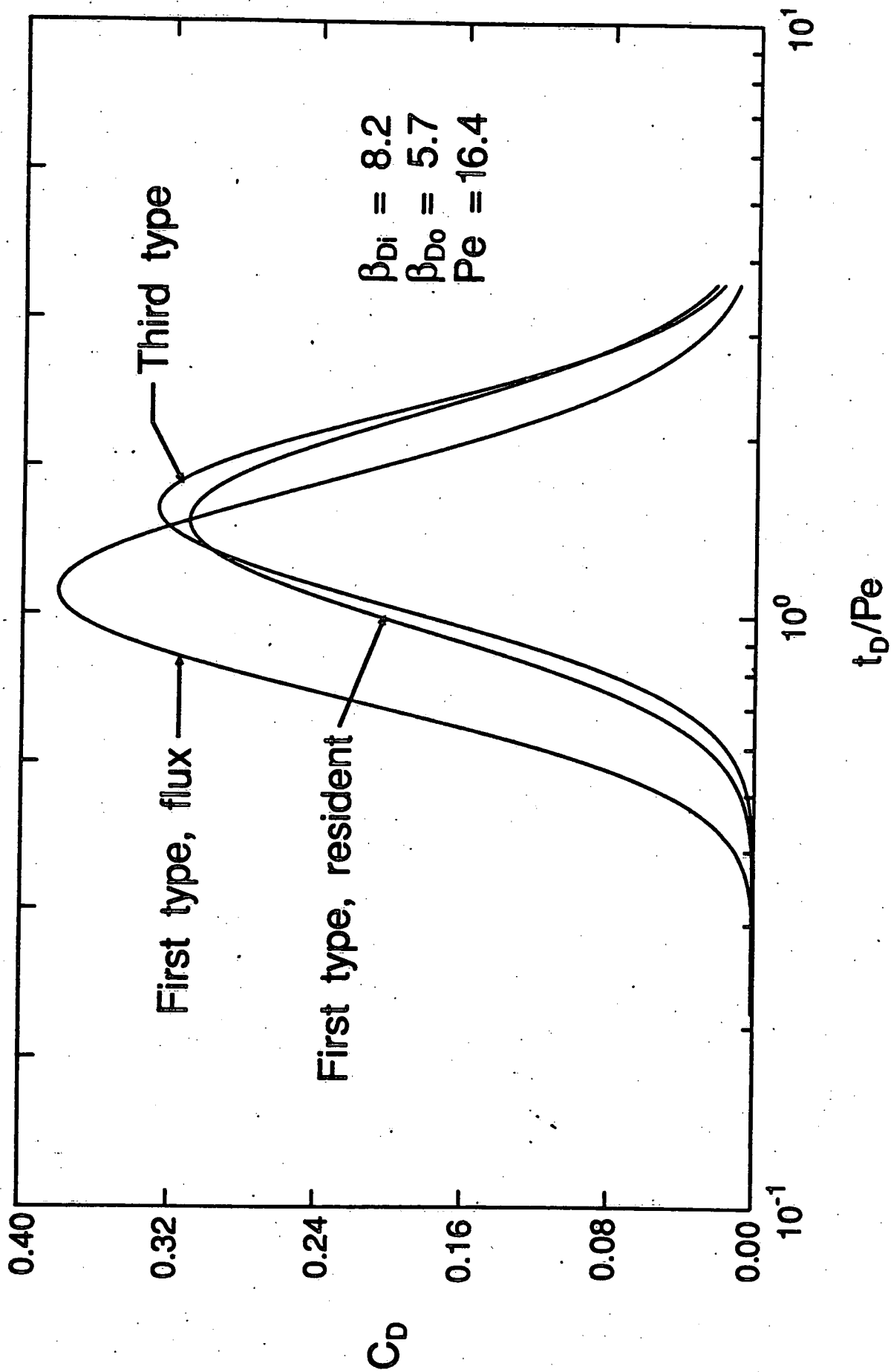
Figure 7. Solutions for resident concentration having first and third type conditions as compared to the solution for flux concentration. Experimental conditions employed are the same as for the previous Figure.

two experiments conducted in the 189 mm columns. One experiment was conducted using the packing material of large dispersivity and the other with the material of small dispersivity. Also shown is the poorly-fitting type curve produced by the solution for first-type resident concentration.
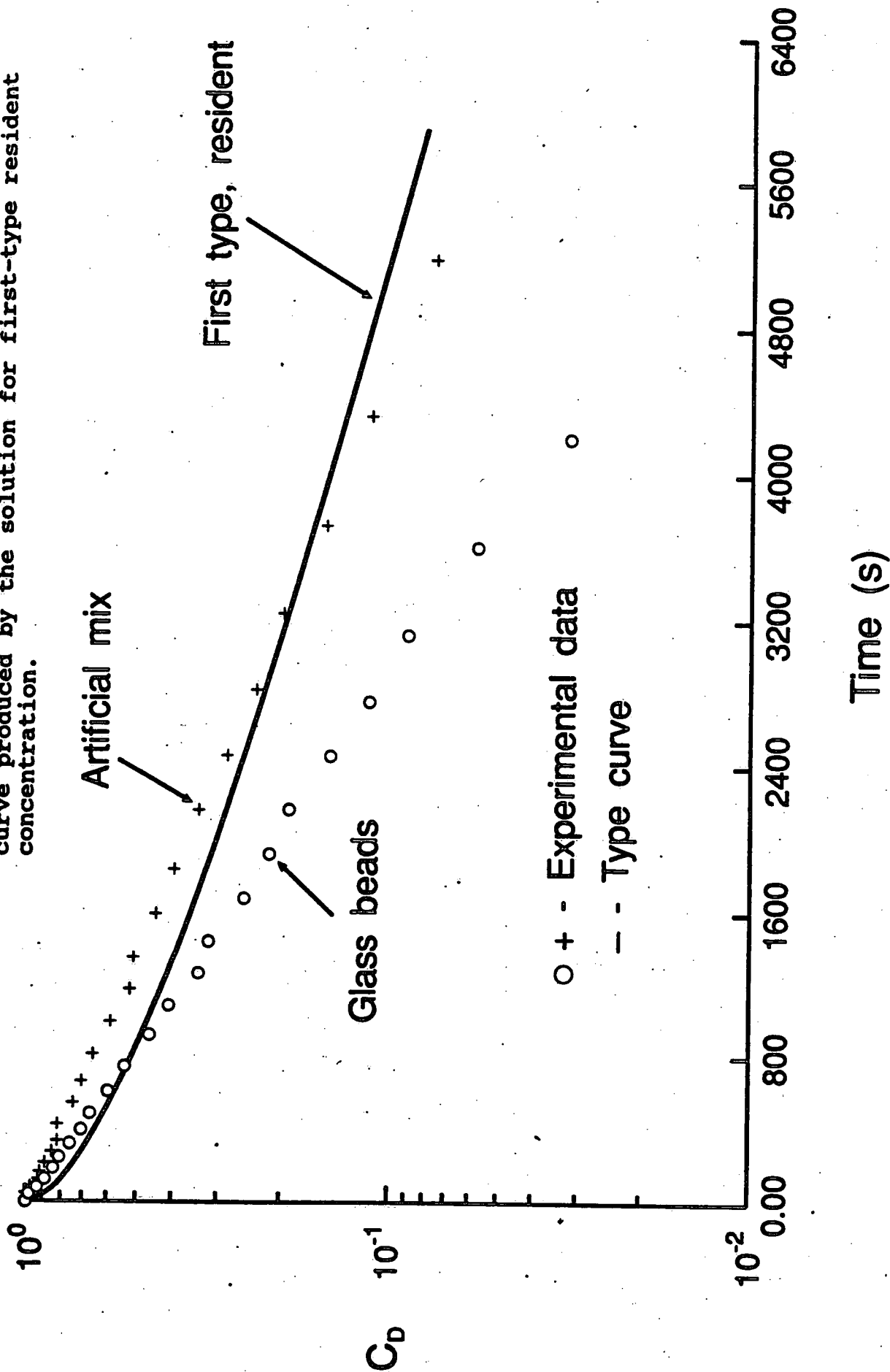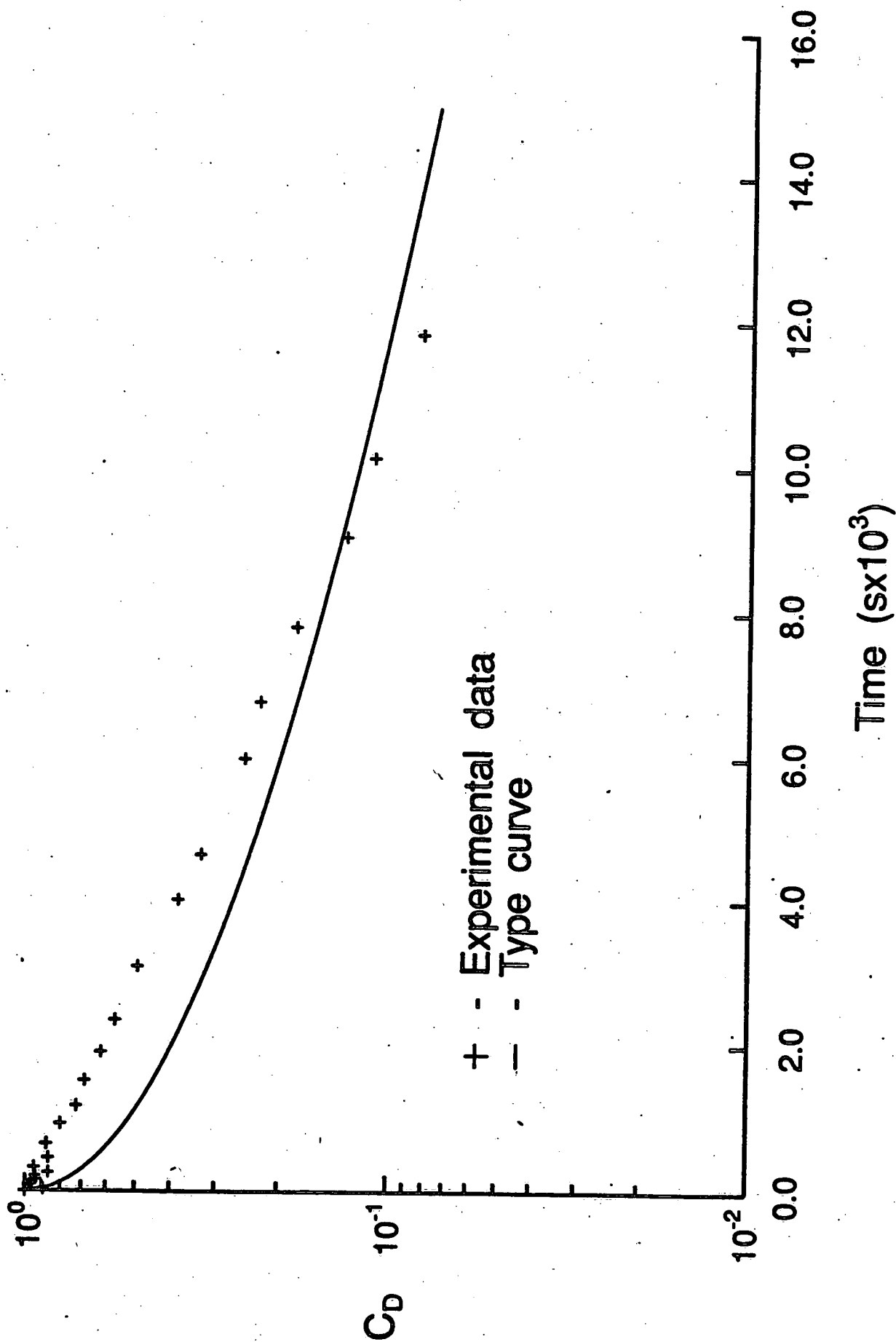
First type, resident

Artificial mix

Glass beads

10^0

10^{-1}

10^{-2}

C_D

O + - Experimental data

- - Type curve

0.00   800   1600   2400   3200   4000   4800   5600   6400

Time (s)

Figure 9. The decline in concentration in the upper reservoir for an experiment conducted in a column of 352 mm diameter packed with glass/till #3. As in the previous Figure, the solution for resident concentration having first-type boundary conditions simulates the results very poorly.

...using the solutions for resident concentrations having first- and third-type boundary conditions. Concentration in the upper reservoir is shown in the upper left of the diagram.

Concentration in the Upper Reservoir

● - Experimental data

1 - Third type, Pe=7.2
2 - Third type, Pe=10.7
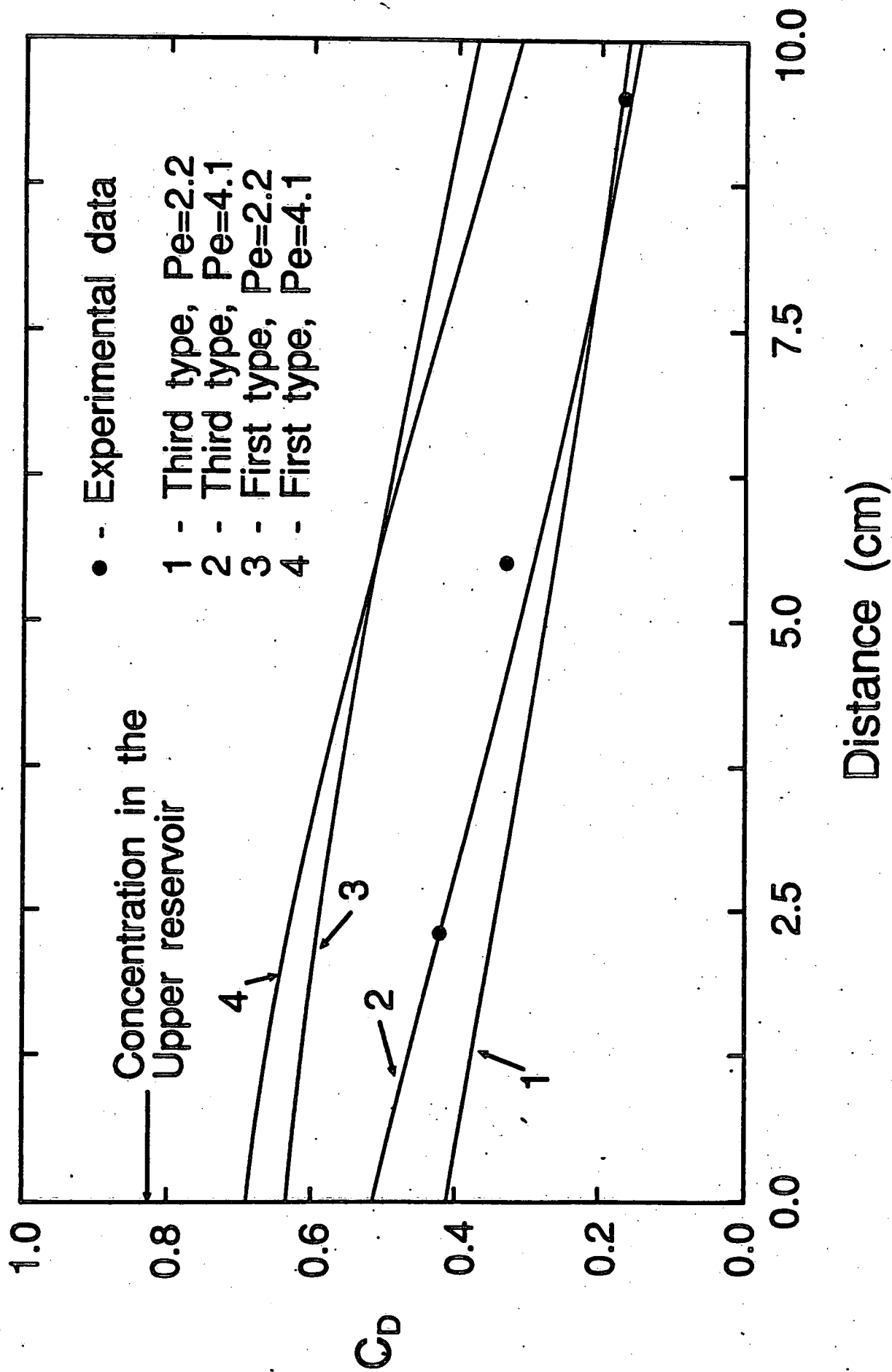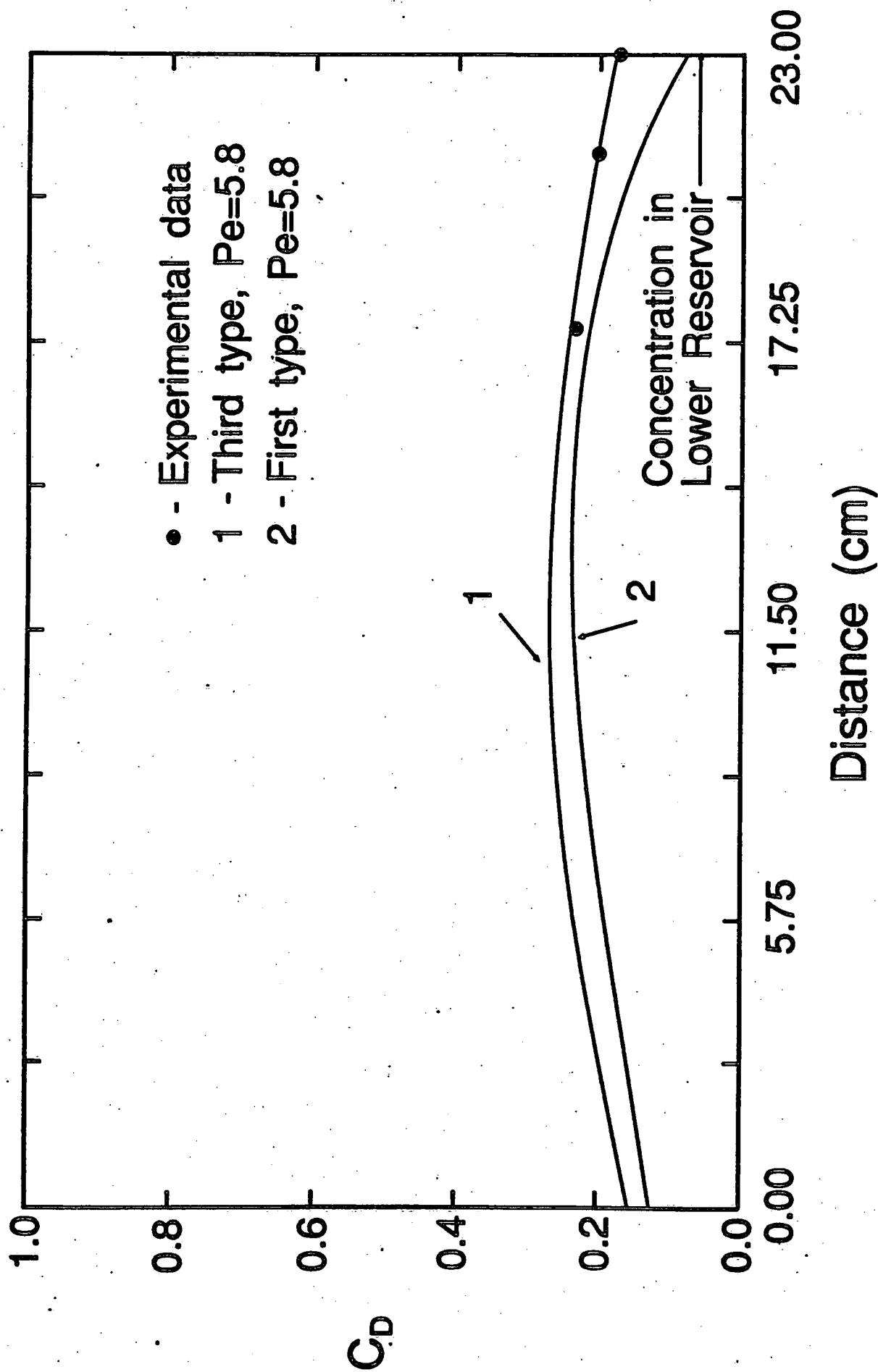3 - First type, Pe=7.2
4 - First type, Pe=10.7

C_D

Distance (cm)

Figure 11.The results of an experiment conducted in a column of 552 mm diameter using glass/till #3 as compared to the model fits. Only the results from the portion of the column which was excavated are shown. Note the concentration in the upper reservoir as shown in the upper left of the diagram.
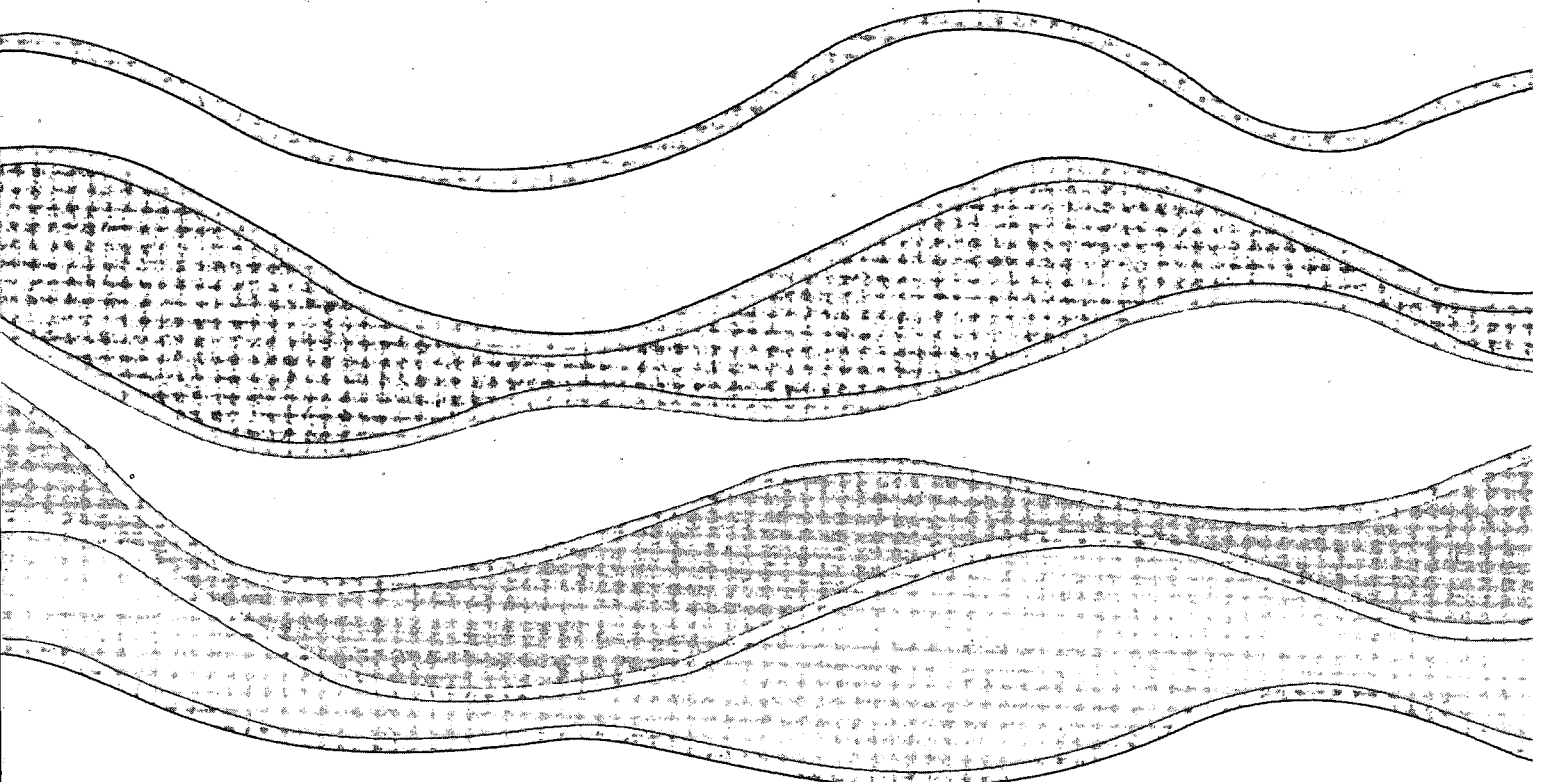
Legend:

• - Experimental data

1 - Third type, Pe=2.2
2 - Third type, Pe=4.1
3 - First type, Pe=2.2
4 - First type, Pe=4.1

Concentration in the Upper reservoir

C_D

Distance (cm)

boundary as compared to solutions having having first-
and third-type boundary conditions. The concentration in
the lower reservoir is shown in the lower right of the
diagram.

- - Experimental data
1 - Third type, Pe=5.8
2 - First type, Pe=5.8

Concentration in
Lower Reservoir

Distance (cm)

C_D

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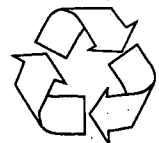P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

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