COMPUTER MODEL OF ONE-DIMENSIONAL

EQUILIBRIUM CONTROLLED SORPTION PROCESSES

By David B. Grove and Kenneth G. Stollenwerk

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ABSTRACT

A numerical solution to the one-dimensional solute-transport equation with equilibrium-controlled sorption and a first-order irreversible-rate reaction is presented. The computer code is written in FORTRAN 77 language, with a variety of options for input and output for user ease. Sorption reactions include Langmuir, Freundlich, and ion-exchange, with or without equal valence. General equations describing transport and reaction processes are solved by finite-difference methods, with non-linearities accounted for by iteration. Complete documentation of the code, with examples, is included.

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INTRODUCTION

The solution of one-dimensional solute transport and reaction equations for flow through porous media has been used to analyze and predict results from laboratory columns and from field experiments. In many cases, equations describing the process are so complex that numerical methods are the most effective means of solution. Even when analytical solutions are available, numerical methods may present the required output in the most reasonable manner; therefore, a general numerical solution to these equations has been developed and is presented herein.

The solute-transport and reactions equation is solved by using a finite-difference method. A variety of input conditions can be simulated, including both pulse and step input, with either flux continuity or constant-concentration boundary conditions. Chemical reactions can be homogeneous, heterogeneous, or both. The homogeneous reaction is a first-order irreversible kinetic expression, such as radioactive decay, with or without the presence of sorption, (a term used for both adsorptive and ion-exchange reactions). The heterogenous reaction represents sorption processes and can be simulated by using the mass-action ion-exchange equation or the Langmuir or Freundlich adsorption equations. All sorption processes are assumed to be equilibrium-controlled during their reaction step.

THEORY

When solute transport is simplified to one dimension, computation becomes easier. The differential equation that describes this transport has only two independent variables: time and distance. The dependent variables in this equation include concentration of the solute in the liquid phase, and, in the case of sorption, concentration of the solute on the solid (the sorbed phase). To solve this equation, additional equations need to be available to define the relationship between dissolved and sorbed phases.

The one-dimensional defining differential equation can be taken from Grove and Rubin (1977) as:

$$\varepsilon \frac{dc}{dt} + \varepsilon V \frac{dc}{dx} - \varepsilon D \frac{d^2c}{dx^2} = CHEM, \qquad (1)$$

where

    ε is the effective porosity;
    c is the concentration of the solute (mass of solute/volume of liquid), ML^{-3};
    t is the time variable, T;
    V is the interstitial fluid velocity, LT^{-1};
    x is the distance variable, L; and
    D is the coefficient of hydrodynamic dispersion, L^2T^{-1};

when CHEM equals $- \rho_b \dfrac{d\bar{c}}{dt}$ for equilibrium-controlled adsorption and exchange reactions, and

$-k(\varepsilon c + \rho_b \bar{c})$ for first order irreversible-rate reactions with equilibrium controlled ion exchange or adsorption, and

where ρ_b is the bulk density of the porous medium, ML^{-3};

$\bar{c}$ is the concentration of the species adsorbed on the solid, MM^{-1}; and

k is the rate constant for the kinetic reaction, T^{-1}.

The initial conditions in the column are given as

$$c(x, t = 0) = c_i(x).$$

The input boundary conditions may be either described by flux continuity

$$D \frac{dc}{dx} = - V(c - C_i) \text{ for } x = 0 \text{ at } t,$$

or a constant concentration

$$c = C_i \text{ for } x = 0 \text{ at } t.$$

The output boundary condition is given as

$$\frac{\partial c}{\partial x} = 0 \text{ for } x = L \text{ at } t$$

where C_i is the input concentration of the solute, ML^{-3};
c_i is the initial concentration of the solute in the column, ML^{-3}; and
L is the length of the column, L.

A discussion of these boundary conditions is given in detail by Dankwerts (1953).

The above solute-transport equation (equation 1) contains physical and chemical terms that will now be discussed in more detail. The most notable are the terms defining the chemical reactions, both equilibrium-controlled and kinetically controlled and the dispersion term. Physical processes that include dispersive and convective fluxes will be discussed first.

Physical processes

The second term on the left-hand side of equation 1 describes the convective flux and the third term on the left-hand side of equation 1

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describes the dispersive flux. The convective flux is described by the product of the velocity and concentration. Velocity can be determined in a number of ways: (1) It can be determined independently knowing the volumetric-flow rate and the column's physical characteristics (length, diameter, and porosity), or (2) it also can be determined by introducing a conservative (non-reacting) solute and matching a solution of equation 1 for various values of velocity and dispersivity, until a best fit between experimental results and theoretical prediction is obtained.

The dispersive flux is computed as the product of a dispersion coefficient D and the concentration gradient. This flux is assumed to consist of two components; mechanical dispersion and molecular diffusion. In the accompanying computer program it is described as:

$$D = \alpha V + D, \tag{2}$$

where α is the characteristic dispersive length, L; and
D is the product of the molecular diffusion coefficient and the tortuosity, LT^{-1}.

For most field situations mechanical dispersivity overshadows molecular diffusion to the extent that the latter can be neglected (see as examples Bear, 1972, p. 358 and Freeze and Cherry, 1979, p. 390). The dispersion coefficient usually is determined by introducing a conservative tracer into the column and matching a solution to equation 1 with experimental results. Small values of the dispersion constant, or approximations of larger values, can be calculated as described in Levenspiel (1972, p. 280).

Chemical processes

One of the most common and frequently modeled type of chemical reaction occurring during the movement of solutes through porous media is sorption of the solute onto the solid surface through a physical attraction or an exchange process. When movement of the solute is slow, compared to the adsorption or exchange reaction rate, it is assumed to be equilibrium-controlled, greatly simplifying analysis. This can be illustrated as follows:

$$\frac{\partial \bar{c}}{\partial t} = \frac{\partial \bar{c}}{\partial c} \cdot \frac{\partial c}{\partial t}, \tag{3}$$

where $\frac{\partial \bar{c}}{\partial c}$ is simply the slope of the sorption isotherm of $\bar{c}$ versus c.

The sorption isotherm is defined as a plot of the sorbed phase versus the dissolved phase. Plots are sometimes in terms of relative concentrations, mass fractions, mole fractions, and so forth. The important thing to keep in mind is that the units need to be consistent, and care needs to be taken when transferring data from sorption-isotherm plots to be used with

transport-equation calculations. These sorption isotherms can have a variety of shapes; see for example, Vermeulen (1973, chap. 16, p. 14). However, they usually are defined in terms of favorable or unfavorable isotherms. A favorable isotherm is convex-upward and an unfavorable isotherm is concave-upward. Examples of each case are shown in figure 1. If the sorption process is taking place throughout the full range of concentration, it is evident that the slope of the isotherm is changing, and it can be expressed as a function of dissolved concentration. Favorable isotherms have an increasing slope with decreasing concentrations; and unfavorable isotherms have a decreasing slope with increasing cooncentrations. This explains the shape of pulses passing through chromatographic columns. Sharp breakthrough fronts are obtained from favorable isotherms; diffuse breakthrough fronts are obtained from unfavorable isotherms. When the slope of the isotherm is constant, a pulse of solute travelling through a column should be unchanged in shape, except for a flattening from the effect of dispersion. Note that the terms favorable and unfavorable refer to the sorption of the solute. Elution from the column has the opposite effect and an isotherm that is favorable for sorption is unfavorable for elution. Examples of pulses within a column and exiting from a column for sorption isotherms that are favorable, linear, and unfavorable are shown in figures 2-7. One should note that dispersion in the columns not only causes the pulse to flatten; but, as shown for the case of the linear isotherm, the pulse only stays symmetric within the column. The dispersion process causes a tail to occur in the breakthrough curve that should not be mistaken for adsorption with a favorable isotherm. When sorption processes do occur, the breakthrough curve usually is displaced several pore volumes, when compared to a non-reacting solute.

Now one merely needs a quantitative relation between $\bar{c}$ and c to evaluate the slope of the isotherm. There are a variety of ways to describe this isotherm or equation, that relate the concentration on the solid in equilibrium with the concentration in solution. Three of the most common expressions used are the Langmuir and the Freundlich adsorption equations, and the mass-action equilibrium relationship for ion exchange. These three equations and a quantitative description of their use in the mass-transport equation will be given in the next section.

A second common chemical process is that of an irreversible first-order rate reaction, such as radioactive decay. In this code, it is assumed that this reaction occurs for both sorbed and dissolved chemical species, it is written:

$$CHEM = -k(\epsilon c + \rho_b \bar{c}).$$ (4)

Radioactive decay is well known to be a first-order irreversible-rate reaction. The rate constant k is, by convention, given the symbol, λ, and through its definition is shown to be:

$$\lambda = \frac{\ln 2}{t_{1/2}}$$ (5)

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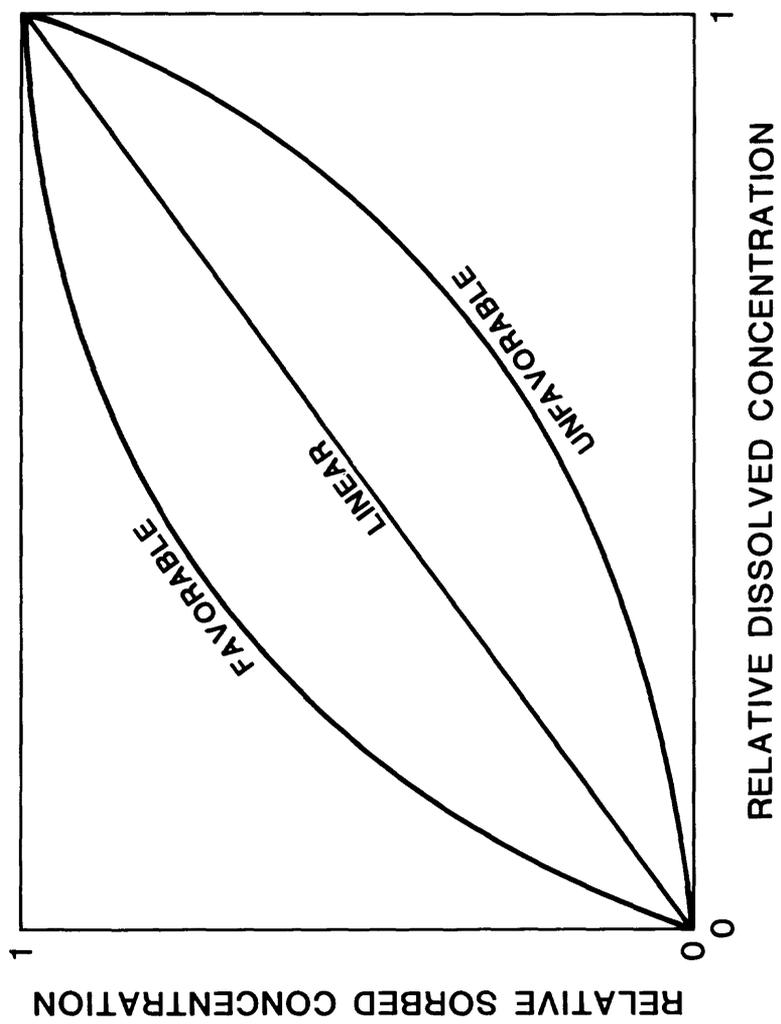
Figure 1. Diagram showing typical isotherms for favorable, linear, and unfavorable sorption.
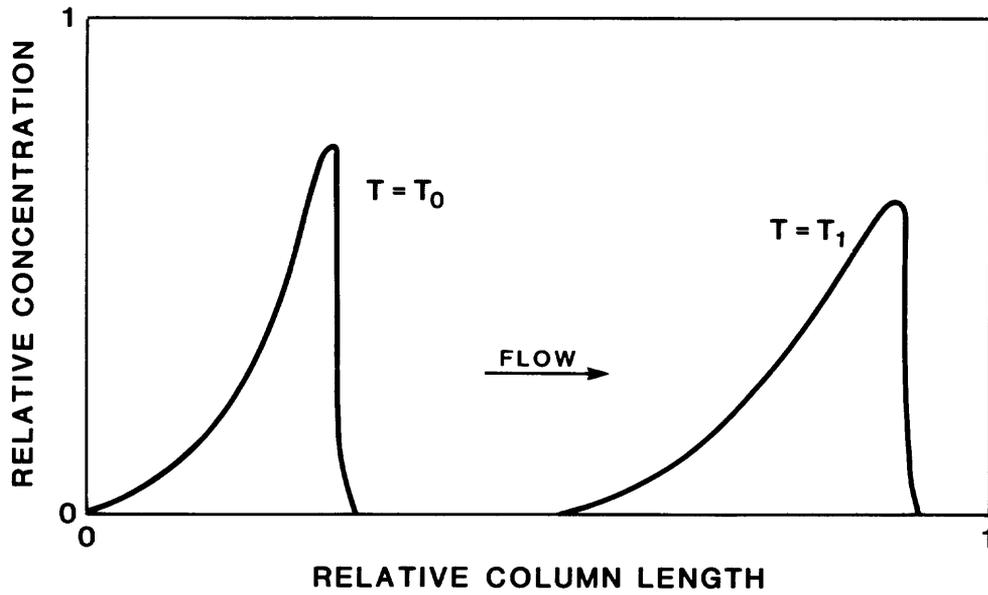
Figure 2. Concentration profile of a pulse, at two different times, within a column that has favorable sorption characteristics.
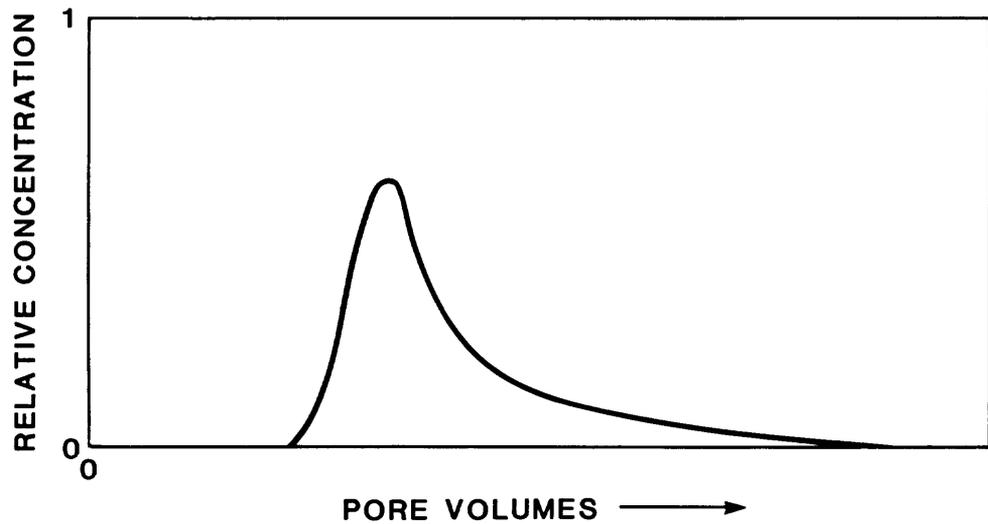
Figure 3. Concentration profile of a pulse exiting from a column with favorable sorption characteristics.

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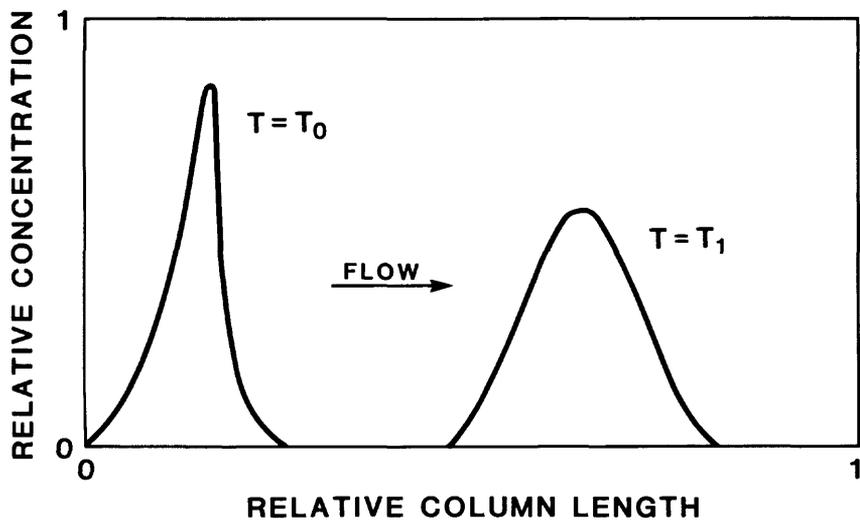
Figure 4. Concentration profile of a pulse, at two different
times, within a column that has a linear-sorption
isotherm.
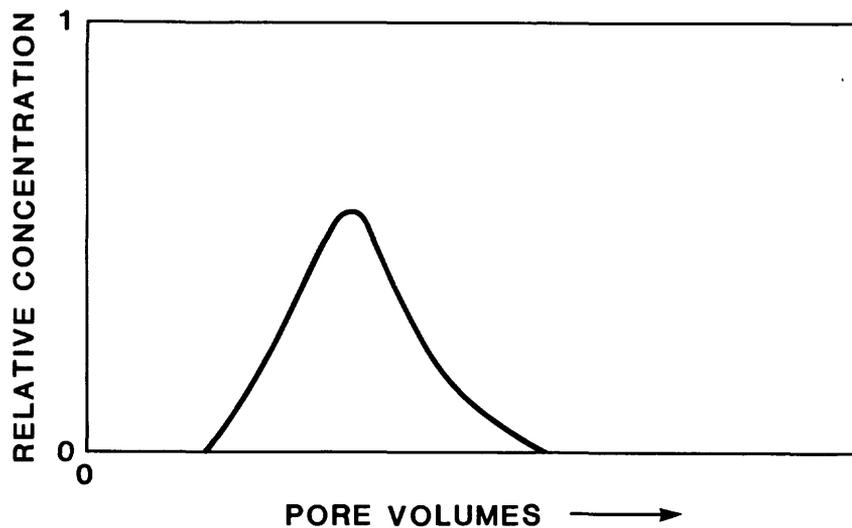
Figure 5. Concentration profile of a pulse exiting from a column
that has a linear-sorption isotherm.

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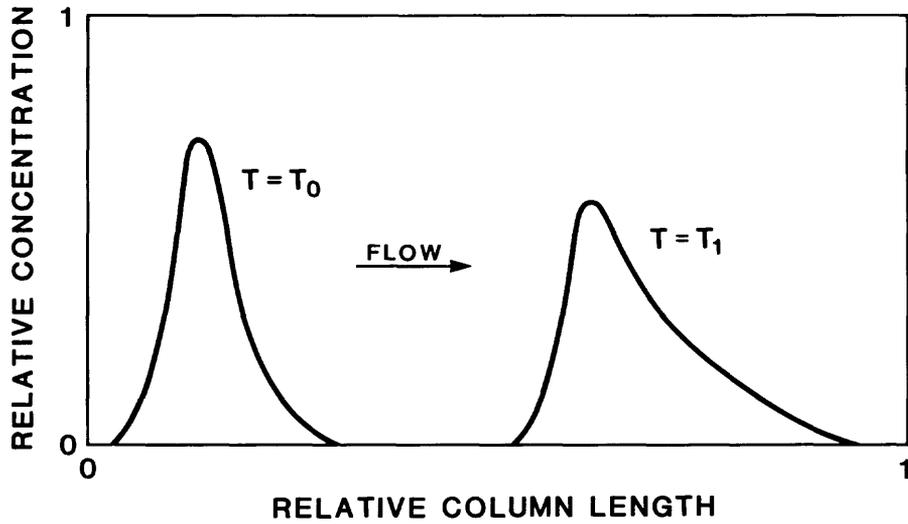
Figure 6. Concentration profile of a pulse, at two different times, within a column that has an unfavorable-sorption isotherm.
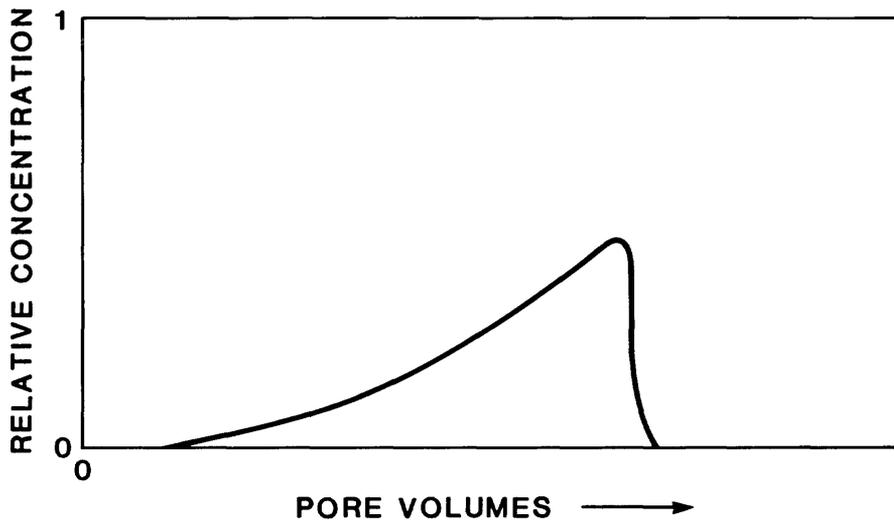
Figure 7. Concentration profile of a pulse exiting from a column that has an unfavorable-sorption isotherm.

where

λ is the rate constant k, T^{-1};
ln 2 is the natural logarithm of 2; and
$t_{1/2}$ is the radioactive half-life of the element, T.

Langmuir adsorption

The equation that describes Langmuir adsorption is given as:

$$\bar{c} = \frac{K_1 Q c}{1 + K_1 c} \qquad (6)$$

where K_1 is the adsorption equilibrium constant, and
     Q is the maximum number of adsorption sites.

The terms K_1 and Q can be evaluated from plots of experimental data of $1/\bar{c}$ versus $1/c$. If Langmuir adsorption applies, this should result in a straight line with slope $1/(K_1 Q)$ and intercept $1/Q$. The slope of the Langmuir isotherm is given as:

$$\frac{d\bar{c}}{dc} = \frac{K_1 Q}{(1 + K_1 c)^2} \cdot \qquad (7)$$

For small concentrations, slope is given by the constant, KQ.

Freundlich isotherm

The equation that describes the Freundlich isotherm is given by:

$$\bar{c} = K_f c^n \qquad (8)$$

where K_f is the Freundlich adsorption equilibrium constant, and
     n is the Freundlich exponent.

The terms K_f and n can be evaluated from plots of experimental data of ln $\bar{c}$ versus ln c. If a Freundlich isotherm applies, this should result in a straight line with a slope of n and an intercept of ln K.

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The slope of the isotherm is given as:

$$\frac{d\bar{c}}{dc} = nK_f c^{n-1}.$$ (9)

When the exponent n is equal to one, the slope is linear (constant), independent of the concentration and equal to K_f.

Mass-action equilibrium

Four types of ion-exchange processes will be considered, depending on the values of m and n for the equation:

$$m\,c_1^n + n\,\bar{c}_2 \underset{\longleftarrow}{\overrightarrow{}} m\,\bar{c}_1 + n\,c_2^m$$ (10)
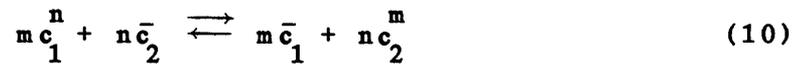
where n is the valence for ion 1, and,
  m is the valence for ion 2.

The ion-exchange selectivity coefficient for equation 10 is defined as:

$$K_m = \frac{\bar{c}_1^m\, c_2^n}{\bar{c}_2^n\, c_1^m},$$ (11)

when the total-solution concentration and ion-exchange capacity are constant, and only two ions are involved, we can write:

$$nc_1 + mc_2 = C_o, \quad \text{and}$$ (12)

$$n\bar{c}_1 + m\bar{c}_2 = Q.$$ (13)

Typical units of concentration for dissolved and sorbed species would be, moles per liter for c_1 and c_2, and millimoles per gram $\bar{c}_1$ and $\bar{c}_2$. Units for the total concentration, C_o, would then be equivalents per liter and units for the cation-exchange capacity, Q, would be millequivalents per gram. Equations 12 and 13 will be substituted into equation 11 in order to eliminate component 2 from the equation. The slope of the ion-exchange isotherm can then be computed.

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Monovalent-monovalent-exchange

In this example both ions have a valence of one $(n = m = 1)$. A typical example might be the exchange of sodium and potassium,

$$Na^+ + KX \; \overset{\rightarrow}{\leftarrow} \; NaX + K^+ \qquad (14)$$

using equations 11, 12, and 13, the equilibrium concentration of adsorbed sodium would be:

$$\bar{c} = \frac{K_m Q c}{c(K_m - 1) + C_o}. \qquad (15)$$

Both concentrations shown are of sodium as the potassium concentrations have been eliminnated through the use of equations 12 and 13. Equation 15 can be used to construct the ion-exchange isotherm for sodium, for this particular system. Dissolved and adsorbed equilibrium concentrations of potassium can be calculated using equations 12 and 13.

The slope of the isotherm is given as:

$$\frac{d\bar{c}}{dc} = \frac{K_m Q C_o}{[c(K_m - 1) + C_o]^2}. \qquad (16)$$

When $K_m = 1$, or for small values of c, the slope becomes:

$$\frac{d\bar{c}}{dc} = \frac{K_m Q}{C_o}. \qquad (17)$$

When the slope of the isotherm, whether exchange or adsorption, is linear, either because of the value of the equation coefficients or because of relatively small concentrations of the solute of interest, it has been termed the distribution coefficient, and sometimes given the value K_d. One should note that, in this case, the distribution coefficient is affected significantly by the total-solution concentration. As the total-solution concentration increases, the distribution coefficient decreases, as a result of computation of the counter ion for the exchange sites. Some authors (Helfferich, 1962, p. 154) define the distribution coefficient as the ratio of the adsorbed to the dissolved ions. This would be equal to the slope of the isotherm only for linear isotherms.

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Divalent-divalent exchange

In this example both ions have a valence of two ($m = n = 2$). A typical example might be the exchange of calcium and strontium.

$$Ca^{++} + SrX \underset{\longleftarrow}{\overrightarrow{}} CaX + Sr^{++} \tag{18}$$
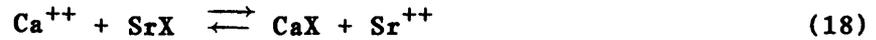
The equilibrium concentration of adsorbed calcium would be:

$$\bar{c} = \frac{K_m Qc}{2c(K_m-1) + C_o}. \tag{19}$$

The slope of the isotherm is given as:

$$\frac{d\bar{c}}{dc} = \frac{K_m QC_o}{[2c(K_m-1) + C_o]^2}. \tag{20}$$

For $K_m = 1$ or for small values of c the limiting value for the slope is the same as for the mono-monovalent exchange, that is equation 17.

Monovalent-divalent exchange

In this example ion 1 has a valence of one and ion 2 has a valence of two ($n = 1$, $m = 2$). An example would be the exchange of sodium and calcium
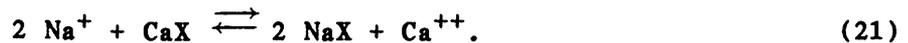
$$2 Na^+ + CaX \underset{\longleftarrow}{\overrightarrow{}} 2 NaX + Ca^{++}. \tag{21}$$

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The equation that could be used to calculate the equilibrium concentration of adsorbed sodium is:

$$\bar{c}^2(C_o - c) + \bar{c}\,(K_m c^2) - K_m Q c^2 = 0,\qquad(22)$$

which can be solved for $\bar{c}$ by the solution procedure for a quadratic equation. The isotherm slope is given by:

$$\frac{d\bar{c}}{dc} = \frac{\bar{c}^2 - \bar{c}2cK_m + 2cK_mQ}{2\bar{c}(C_o - c) + c^2K_m}\qquad(23)$$

where the value for $\bar{c}$ can be obtained from equation 22 in terms of c. For small concentrations of ion 1, such that $\bar{c} \ll Q$, and $\bar{c} \ll C_o$, the isotherm slope reduces to:

$$\frac{d\bar{c}}{dc} = \left(\frac{K_m Q}{C_o}\right)^{1/2}.\qquad(24)$$

Divalent-monovalent exchange

In this example ion 1 has a valence of two and ion 2 has a valence of one (n = 2, m = 1). While this may seem a trivial extension of the previous monovalent-divalent case, a separate solution is included for user ease. An example similar to equation 21 for calcium sodium exchange would be:

$$Ca^{++} + 2\ NaX \ \underset{\longleftarrow}{\overset{\longrightarrow}{}}\ 2\ Na^+ + CaX\qquad(25)$$

The equation that could be used to calculate the equilibrium concentration of adsorbed calcium is:

$$\bar{c}^2(4K_m c) + \bar{c}(-4K_m Qc - (C_o - 2c)^2) + K_m Q^2 c = 0,\qquad(26)$$

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which can be solved for $\bar{c}$ by the solution procedure for a quadratic equation. The slope of the isotherm is given by:

$$\frac{d\bar{c}}{dc} = \frac{4K_m\bar{c}(Q-\bar{c}) - 4\bar{c}(C_o-2c) - K_mQ^2}{- 4K_mc(Q-2\bar{c}) - (C_o-2c)^2} \qquad (27)$$

where the value of $\bar{c}$ can be obtained from equation 27 in terms of c. For small concentrations of ion 1, such that $\bar{c}_1 \ll Q$ and $c_1 \ll C_o$, the isotherm slope reduces to:

$$\frac{d\bar{c}}{dc} = \frac{K_mQ^2}{c_o^2}. \qquad (28)$$

General linear equation

The previously discussed chemical-reaction terms can be incorporated into equation (1) in the following manner: Assume that during its transport, a chemical species is disappearing by some first-order irreversible reaction, and that it is being exchanged reversibly by an equilibrium-controlled process in which the exchange isotherm is linear, and its slope can be represented by the distribution coefficient (described previously). Equation (1) can now be written:

$$\varepsilon \frac{\partial c}{\partial t} \left(1 + \frac{K_d\rho_b}{\varepsilon}\right) = \varepsilon D \frac{\partial^2 c}{\partial x^2} - \varepsilon V \frac{\partial c}{\partial x}$$

$$- \varepsilon kc\left(1 + \frac{K_d\rho_b}{\varepsilon}\right). \qquad (29)$$

A retardation factor R_f, which usually is used in equilibrium-controlled, trace-exchange reactions, can be defined as:

$$R_f = 1 + K_d\rho_b/\varepsilon. \qquad (30)$$

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Equation 29 can then be written as:

$$\frac{\partial c}{\partial t} = \frac{D}{R_f}\frac{\partial^2 c}{\partial x^2} - \frac{V}{R_f}\frac{\partial c}{\partial x} - kc. \tag{31}$$

Thus, the retardation factor is a measure of the attenuation of the solute-species flux with respect to the actual fluid flow.

The following computer code calculates solutions to this linear form of the one-dimensional transport equation as well as the more complex non-linear forms.

NUMERICAL-SOLUTION TECHNIQUES

The one-dimensional differential equation describing solute transport and reaction was solved using standard finite-difference equations. Spatial derivatives were approximated with central differences; the time derivative is approximated by using Crank-Nicholson techniques. When non-linear terms appear in the equation, the equation is solved by using the Douglas predictor-corrector approach (as outlined by von Rosenberg, 1969, p. 59). In all cases, the solution matrix was tridiagonal, allowing a direct Gaussian elimination technique, known as the Thomas algorithm, for solution. Although the solution method is unconditionally stable concerning time, it is always considered good practice, in terms of solution accuracy, that a solute particle travel less than one space increment during one time step. This can be assured if the condition is:

$$\frac{V\Delta t}{\Delta x} < 1. \tag{32}$$

The space- and time-centered numerical method provides no numerical dispersion that could decrease accuracy. However, from such a centering method, the possibility exists of severe numerical oscillation, if the proper ratio of several solution parameters is not observed. In general, such oscillation will not occur if:

$$\frac{D}{2V\Delta x} > 1. \tag{33}$$

When this is not observed, the program aborts, signals the error, and prints out the number of nodes to be used to prevent such an occurrence.

A number of alternative-solution techniques can lessen the impact of the above restrictions; the most notable technique is the use of finite elements, using the Galerkin method (Grove, 1977). The author has found that, for one-dimensional problems, enough nodes can be used with finite-difference methods to overcome any oscillation problems without taxing computer storage and time requirements. The use of integration techniques, such as finite elements, thus, is not necessary for most one-dimensional cases. When continuous derivatives are necessary at node locations and boundaries, some investigators have found it necessary to use finite elements with higher-order (cubic) basis functions.

COMPUTER PROGRAM

General program features

The computer program is written in FORTRAN 77 and is operational on the USGS PRIME minicomputer. As this program is not expected to place much of a demand on most computers for core storage, no great attempt has been made to optimize the size of the program. If storage does present a problem, as it might in the case of a small microcomputer, the user simply has to redimension the arrays to the minimum value necessary for program operation. All arrays are presently dimensioned to 101, which allows the user to use as many as 101 nodes in a problem. The program is modular in concept; it consists of a main program, eight subroutines, and a function program; all variables are passed as arguments. A description of the program follows.

Main routine

The main routine of the program provides the instructions for reading the input data, selects the type of computation and printout requested, and calls the various subroutines that compute the new concentration at the new time step. The input is assumed to be on disk; and is written in free-field format. File input and output names are requested at the console during program execution. This input is separated into three groups. The first group defines the number of nodes, time increment, input boundary conditions, and the kind of output that will be printed. The number of nodes dictates the node spacing. The time increment and velocity defines the distance that a solute will travel in one time step (iteration). The user can fix this parameter or can define a dimensionless group (CDELT) that is the fractional distance between nodes that a solute particle with or without reaction will travel per time step. A new time increment based on this fraction is then computed and used in the program. A value of 0.2 has been determined to be satisfactory for CDELT. Input boundary conditions of constant concentration or constant flux can be specified. Some analytical solutions to the solute transport and reaction equation assume constant-concentration boundary conditions. They also may assume columns of infinite length. When matching computed solutions to analytical solutions of this type, a longer-than-normal column can be used, with output printed out at an interior node. The code automatically corrects for column length, for such printouts as pore volumes are based on a column of the length at the location of the interior node. For matching actual

column experimental data, the flux-boundary condition is applicable. The user has the option to print the concentration at any one selected node in the column as a function of pore volume throughput at that node or at preselected nodes within the column as a function of column distance where the pore volume is a function of total column length. Printout of selected data to a disk unit is available for possible graphing purposes. Both of the above printouts occur at user-selected, incremental, pore-volume-output intervals and computation ceases at a specified number of pore-volume output.

The second group of data inputs the fixed physical characteristics of the column, the porous media and the solute. This includes the duration of input pulse, length of column, interstitial velocity of fluid, molecular-diffusion coefficient, mechanical dispersive-characteristic length, bulk density of porous media and effective porosity.

The third group of input data contains information about the possible chemical reactions. This group includes:

1. The type of adsorption or ion exchange that may occur,
2. The input solute concentration,
3. The use of and value for a linear isotherm (distribution coefficient),
4. The sorptive capacity of the porous media,
5. The total solution concentration (for ion exchange),
6. The first order irreversible-rate constant,
7. Equilibrium coefficients and exponents for Langmuir and Freundlich adsorption isotherms, and equilibrium ion-exchange isotherms.

The mass-balance calculation computes and outputs the following: total input, total output, loss through chemical reaction, quantity in pores, quantity sorbed, and a fractional error for the cumulative run. Although a small fractional error does not guarantee an accurate solution, a large one certainly indicates a problem.

Subroutines

Besides supplying input, output and mass-balance calculations MAIN directs the computations to the various subroutines. Eight subroutines and one function routine are included in the code. The subroutines FREUN, LANG, EXC, EXCM, and EXCD calculate the coefficients specific to each of the sorption processes mentioned earlier.

The subroutine REACT uses the previously calculated coefficients to compute the concentration at the new time step. Options are available to skip nonlinear computations, when only linear reactions are occurring. When non-linearities have to be taken into account, non-linear coefficients are calculated at TIME + DELT/2, using values at the old time step. Computations at the required TIME + DELT then use this precomputed value. Only one iteration is used, and smaller time steps are neded if greater accuracy is required. The set of linear-algebraic equations that results is solved by the subroutine TRIMAT. A function-subroutine QUADX also is used for solution of the quadratic equation that results from the unequal

valence equilibrium reaction, when solution for the concentration in the solid phase is necessary. Selected example problems are illustrated. The program has been written so that output is presented in a format that is no more than 80 columns wide, suitable for most terminal uses.

Evaluation of model results

Evaluation of model results could be done on a firm basis for only a few cases. The use of analytical expressions to test the model is the most common verification procedure, however, these analytical solutions only are available for linear systems. This means that equations that contain certain chemical reactions, such as linear sorption isotherms and first-order reactions can be solved analytically, but the more complicated systems cannot. In cases like the latter, solutions where the isotherms approach linearity, and the mass balances of the solute species can be checked. However, the user needs to be skeptical of the results when theoretical output seems to contradict expected results.

Because the analytical solution used for comparison purposes was developed for a semi-infinite column, and the finite-difference computer solution was developed for a fixed-length column, some means was necessary to compare one with the other. This was accomplished by selecting a point within the column that should not be affected by the concentration leaving the column at that particular time. The pore volume throughout, concentration profile, and so forth, were then based on this interior point. A position halfway up the column normally was used.

Linear reaction terms

The analytical solution to equation 1 with flux boundary conditions and no chemical reactions is presented by Brenner (1962). In this paper, Brenner gives dimensionless concentration as a function of dimensionless time (pore volume) for various values of the Brenner number (VL/4D). Results for Brenner numbers of 2 and 20 illustrating examples with relatively large and relatively small dispersive mixing during transport are shown in figure 8. Theoretical values of Brenner are shown by the solid lines, and results from this computer code are shown by the open circles. An excellent agreement is shown. These first values and the analytical solution were for the flux-boundary condition. The solid circles represent the same runs with constant concentrations. Note that, for this case of significant dispersion, this boundary condition does not give a good result. When moderate values of dispersion are present, the use of a flux-boundary condition is needed. In fact, the use of any other boundary condition only is appropriate when checking the code with analytical solutions using that particular boundary condition. A similar comparison of Brenner numbers of 2 and 20 is shown in figure 9, except that a pulse of one pore volume is input, rather than the step input as illustrated in figure 8. The analytical solution for a pulse is obtained by subtracting one step input from another, after a time corresponding to a pulse input.
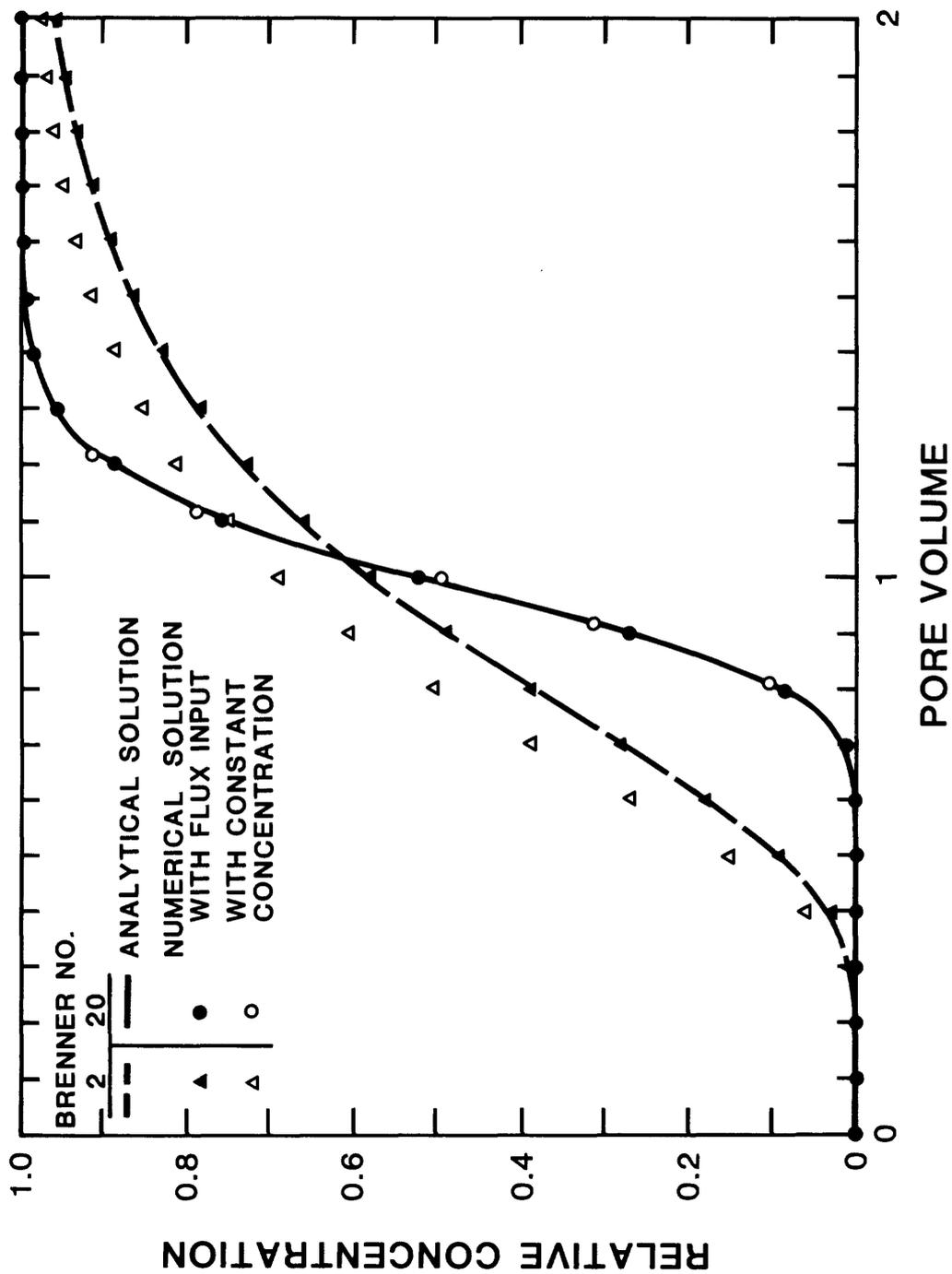
Figure 8. Graph showing comparisons of model and analytical
solutions to the convective-diffusion equation for
Brenner numbers of 2 and 20 for a step input.
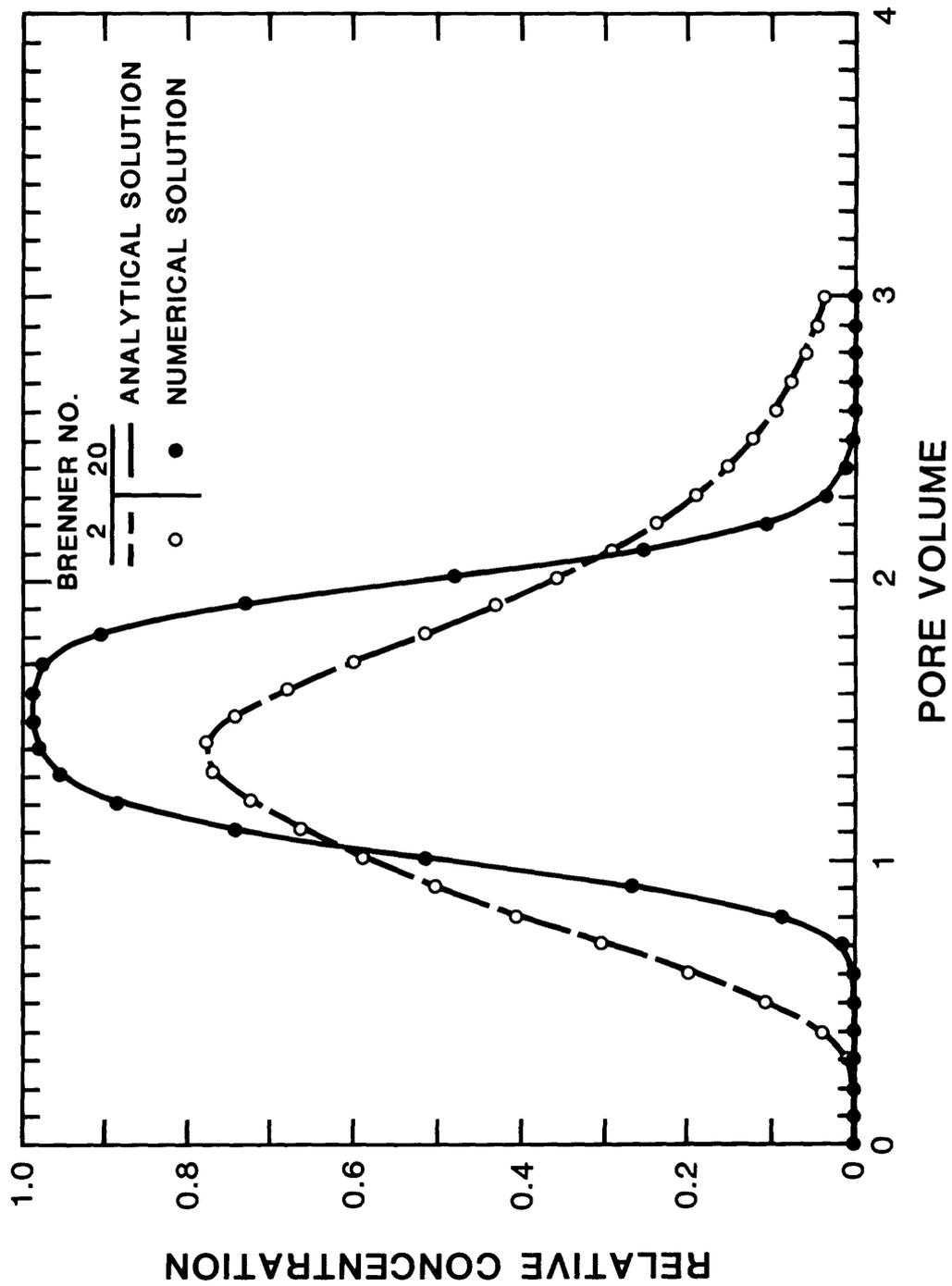
Figure 9. Graph showing comparisons of model and analytical
solutions to the convective-diffusion equation for
Brenner numbers of 2 and 20 for a pulse input.

When linear sorption and a first-order irreversible-rate reaction are both present, equation 31 results, and the solution is given by Bear (1972, p. 630) as follows:

$$C(x,t) = 1/2 \ C_o \ \exp(Vx/2D)[\exp(-x\beta)\mathrm{erfc}\ \frac{x - (V'^2+4kD')^{1/2}\ t}{2(D't)^{1/2}}$$

(35)

$$+ \exp(x\beta)\mathrm{erfc}\ \frac{x + (V'^2+4kD')^{1/2}t}{2(D't)^{1/2}}]$$

where $\beta^2 = \dfrac{V^2}{4D^2} + \dfrac{k}{D'}$, $V' = V/R_f$ and $D' = D/R_f$.

Agreement with the analytical solution and the computer solution for values of k of 0 and 0.01, and isotherm slopes of 0 and 0.3, is shown in figure 10 to be excellent in all cases. Physical properties used in these tests are given in table 1. Using these values, an isotherm slope of 0.3 results in a retardation coefficient of 2.29.

Table 1.—Physical properties used in sorptive-model tests

Number of nodes in column (NI)	51
Column length (XL)	8 centimeters
Fluid velocity (V)	0.1 centimeters per second
Molecular diffusion coefficient (D)	0
Characteristic length (ALPHA)	1.0 centimeter
Bulk density (RHOB)	1.587 grams per cubic centimeter
Porosity (POR)	0.37
Duration of fluid pulse (DPUL)	160 seconds
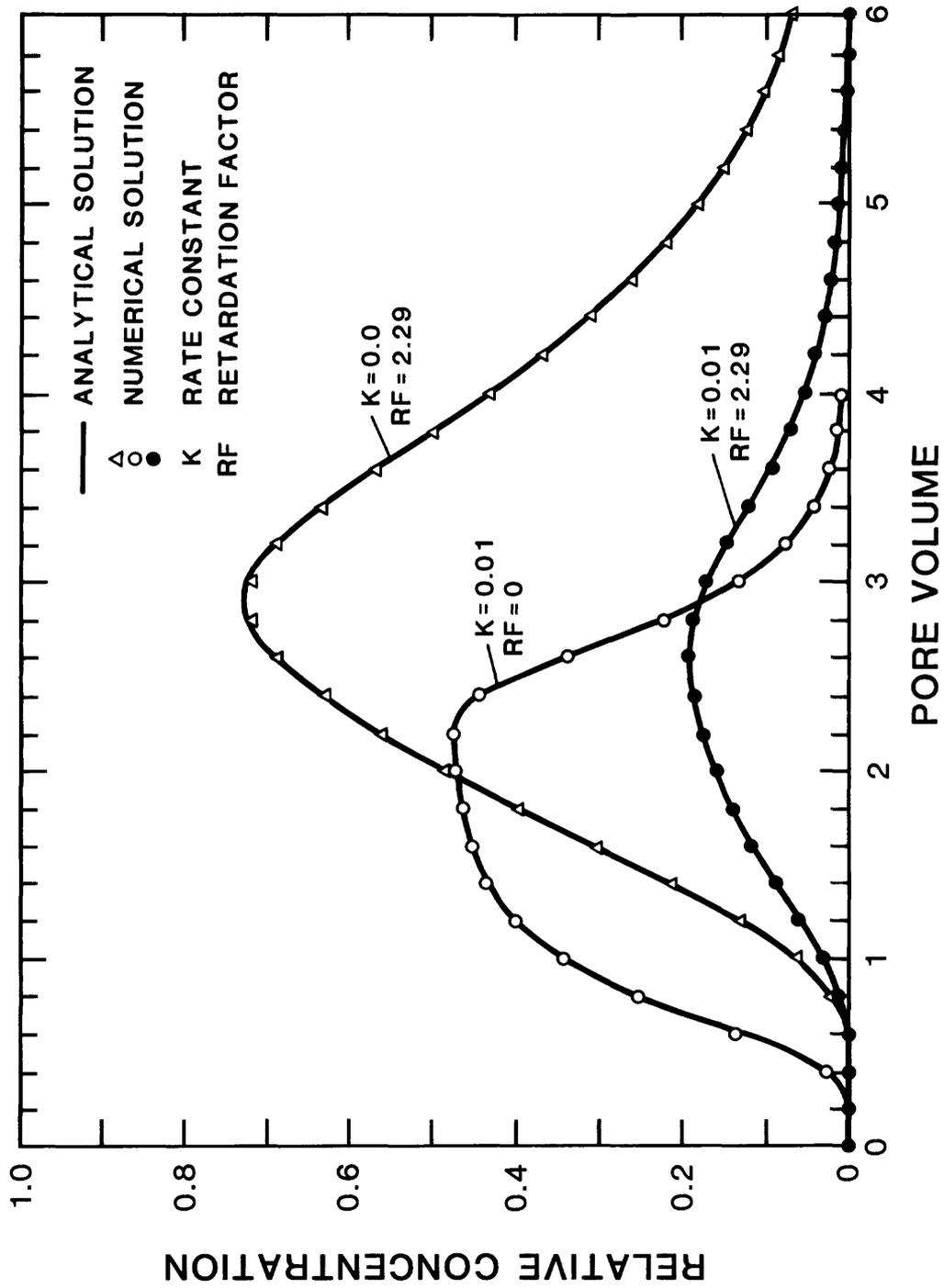
Figure 10. Graph showing a comparison of model and analytical solutions for linear sorption and first-order irreversible-rate reactions.

Non-linear reaction terms

Verification of the code for non-linear sorption isotherms had to be accomplished in a more heristic manner. Two methods of checking were involved. The first was a mass-balance approach(defined previously). The second approach was to allow the slope of the sorptive isotherm to become linear and check the convergence to the analytical solution, for all six available sorptive models. All six sorptive models used a pulse input with the physical properties shown in table 1 as a basis. Chemical properties used for each run are shown in table 2. Three runs were made for each sorptive process. A base curve with the given-constant isotherm slope was used as a standard. This curve represents data previously used, it was accurate by comparison with analytical solutions. The three runs made with each possible sorption equation represent one run, where the coefficients produced a linear isotherm with slope equal to the standard, and two runs with values for coefficients that stressed the computations (large non-linearities) that would provide output that could be checked both from a visual sense and for mass-balance accuracy.

Table 2.--Chemical parameters used for column runs.

Langmuir and Freundlich sorption

Isotherm slope (S)	0.3 milliliters per gram
Total sorption capacity (Q)	0.003 micrograms per gram
Total solution concentration (CTOT)	0.10 milligrams per liter
Range of input concentration (CI)	0.0005-.05 milligrams per liter
Langmuir equilibrium coefficient (EKL) 100	liters per milligram

Freundlich equilibrium coefficient (EKF) 0.3 $\left(\dfrac{\text{micrograms}}{\text{gram}}\right)\left(\dfrac{\text{liters}}{\text{milligram}}\right)^n$

Freundlich slope exponent (XNF)   0.7, 1.0, and 1.3

Ion Exchange

Isotherm slope (S)	0.3 milliliters per gram
Rate constant (K)	0.01 1/second
Range of input concentrations (CI)	0.00005-.05 moles per liter
Total sorption capacity (Q)	0.003 millequivalents per gram
Total solution concentration (CTOT)	0.10 equivalents per liter
Monovalent-monovalent and divalent-divalent-divalent equilibrium coefficient (EK)	1.0 and 10.0
Monovalent-divalent equilibrium coefficient (EK)	3.0 milliliters per gram
Divalent-monovalent equilibrium coefficient (EK)	333.0 grams per milliter

---

A plot of a pulse throughput using a Langmuir isotherm to characterize
the sorptive process is shown in figure 11. Concentrations of 0.05, 0.005
and 0.0005 milligram per liter were input to the column. The greater
concentrations generated sufficient nonlinearities in the equation to show
a significant departure from the linear model. As the concentration input
was decreased to 0.0005 milligram per liter, an excellent match occurred
between this concentration input and input for a linear isotherm; the shape
of the breakthrough curve denotes a favorable isotherm.

A plot of a pulse throughput, using a Freundlich isotherm to
characterize the sorptive process is shown in figure 12. The exponent was
given values of 0.7, 1.0, and 1.3. At a value of 1.0, a match was obtained
with the linear-isotherm analytical solution. The long tail for the
exponent value of 0.7 illustrates the increase in sorptive ability as
concentration decreases.

A plot of a pulse throughput, using the equilibrium exchange isotherm
with mono-monovalent ion exchange is shown in figure 13. As concentrations
decrease from 0.05 to 0.0005 moles per liter, the distribution-coefficient,
or linear-isotherm form of the equation appears. A linear isotherm also is
apparent when the equilibrium-selectivity coefficient is decreased from
10.0 to 1.0. At 1.0, or for small input concentrations of solute, an
excellent match for a similar linear isotherm is evident with the
analytical solution. Similar results were obtained for the di-divalent ion
exchange simulations.

A plot of a pulse throughput for equilibrium mono-divalent ion
exchange is shown in figure 14. The points for a concentration of 0.0005
moles per liter plot on the analytical curve computed by using the values
for a linear isotherm. At input concentrations of 0.005 and 0.05 moles per
liter, the resulting non-linearities result in displaced curves.

A plot similar to figure 14 for di-monovalent exchange is shown in
figure 15. Again, small concentrations of the input solute produce a
linear isotherm that results in an excellent match of the analytical
solution. In this instance it was necessary to reduce the input
concentration to 0.00005 moles per liter to simulate a linear isotherm.

31
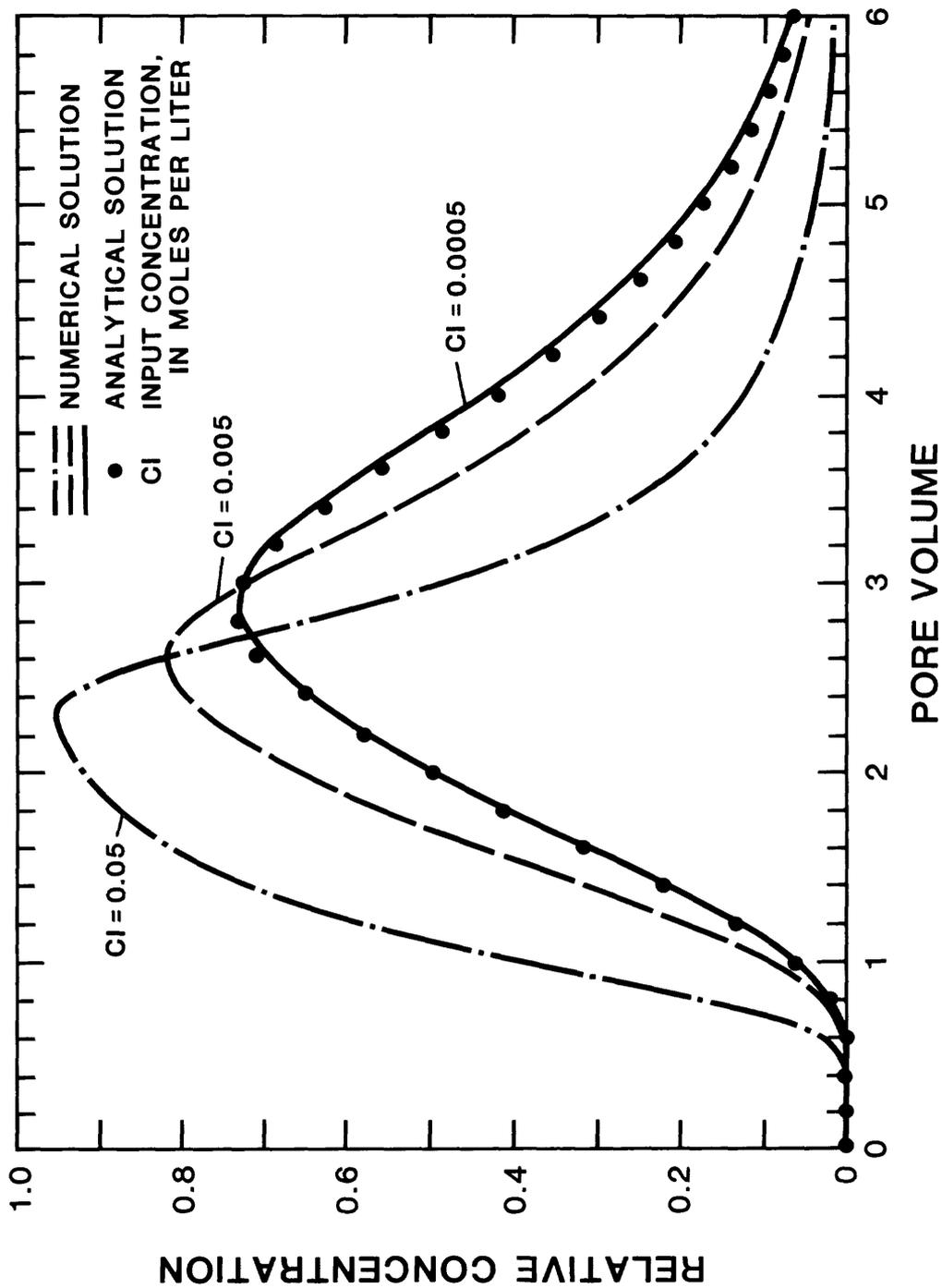
Figure 11. Graph showing a comparison of model and analytical
solution for column throughput with Langmuir sorption
for various values of input concentration.
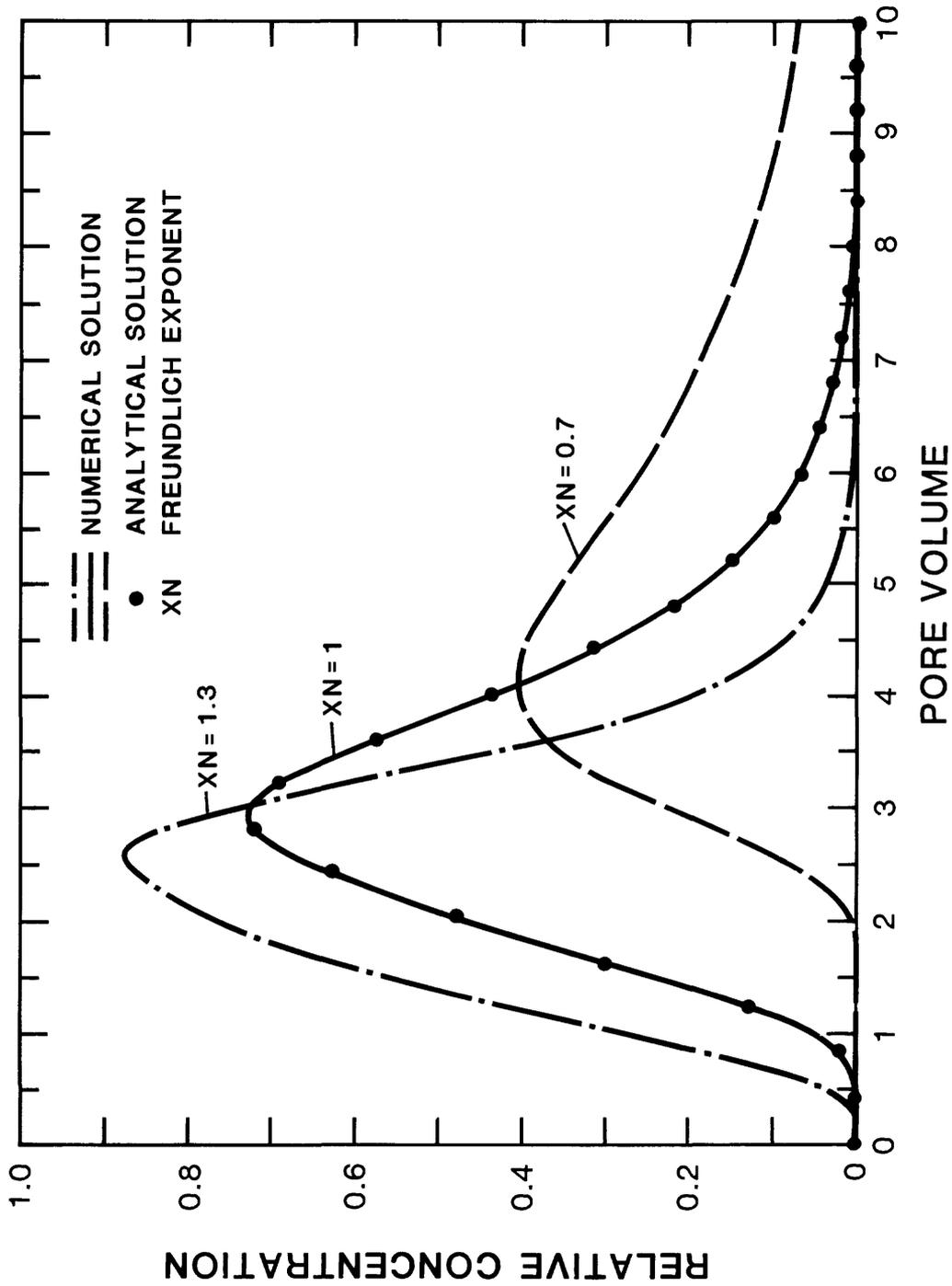
Figure 12. Graph showing a comparison of model and analytical
solutions for column throughput with Freundlich sorption
for various values of the Freundlich exponent.

33
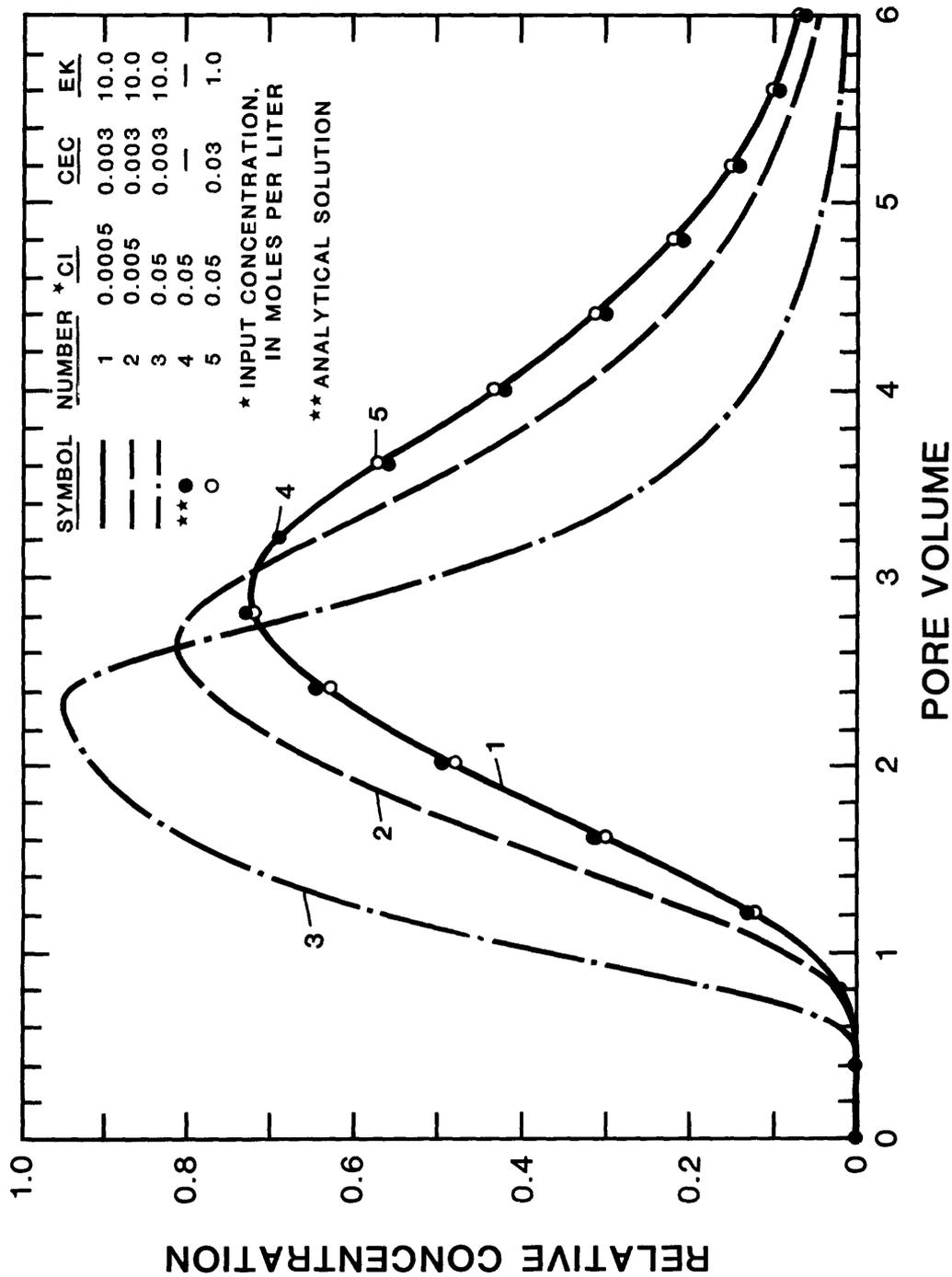
Figure 13. Graph showing a comparison of model and analytical solutions for column throughput with sorption represented by mono-monovalent ion exchange for various values of input concentration.
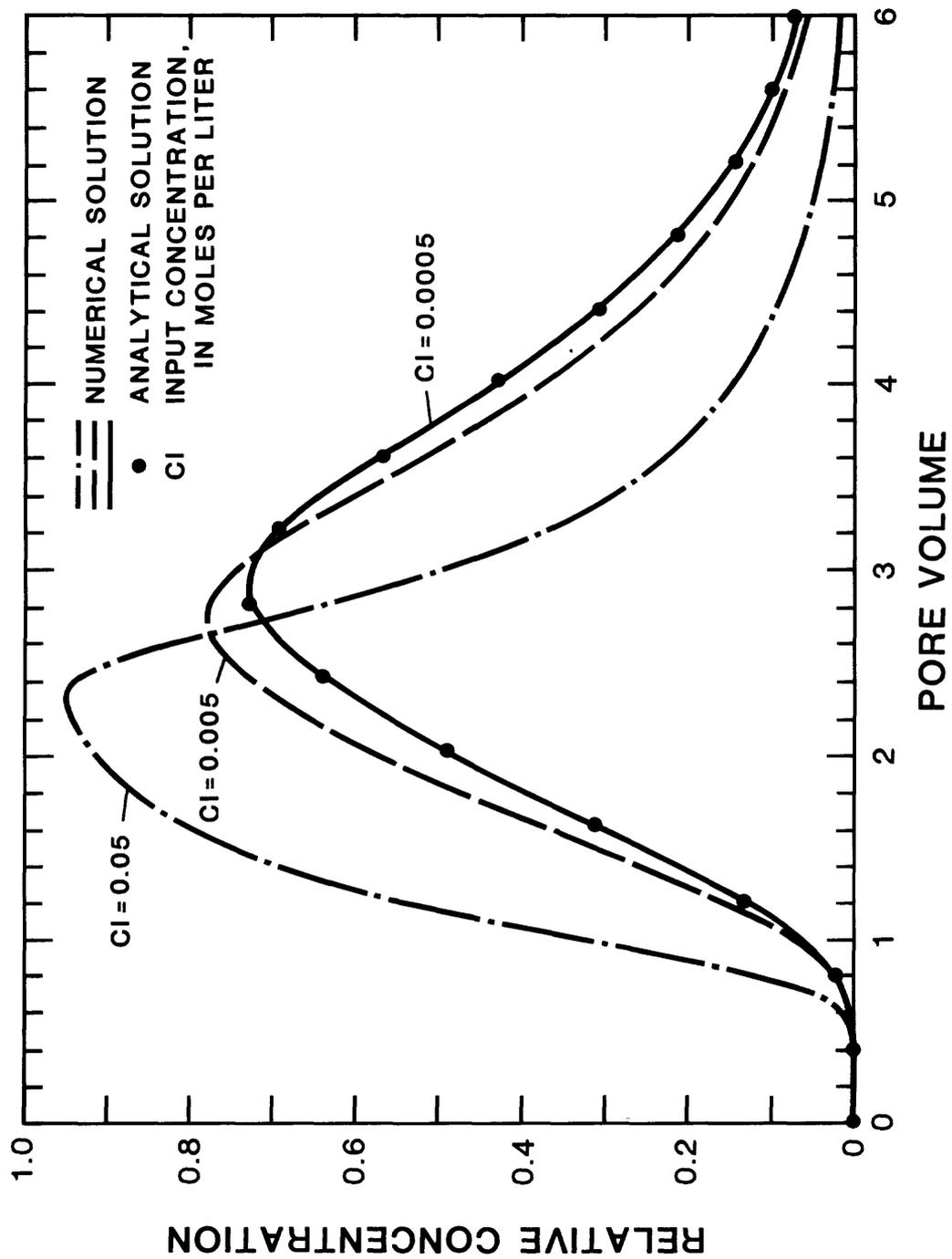
Figure 14.   Graph showing a comparison of model and analytical
solutions for column throughput with sorption
represented by mono-divalent ion exchange for
various values of input concentration.
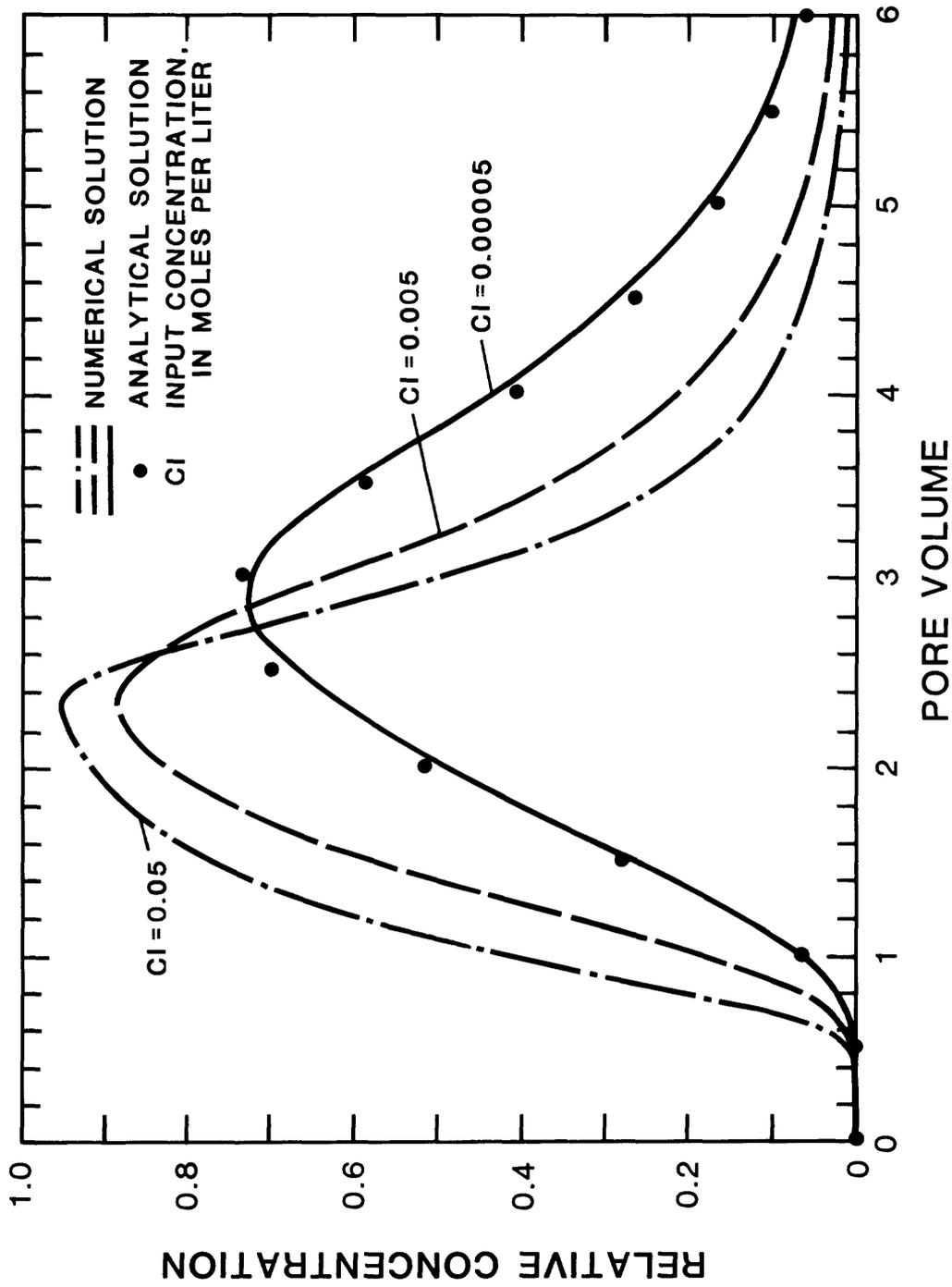
Figure 15. Graph showing a comparison of model and analytical
solutions for column throughput with sorption
represented by di-monovalent ion exchange for
various values of input concentration.

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SUPPLEMENTAL DATA

Attachment I.

Definition of Selected Program Variables

A(I)   Solution-matrix coefficient.

ACC   Solute accumulated in column

ALPHA   Hydraulic-dispersion characteristic length.

B(I)   Solution-matrix coefficient.

C(I)   Solution-matrix coefficient.

CDELT   Fraction of cell distance that ion moves.

CDIM   Dimensionless concentration.

CEC   Cation-exchange capacity.

CI   Initial concentration entering reactor.

COEF(I)   Array that stores (1+RHOB*SLOPE/POR).

CON(I)   Solute concentration at node I.

CTOT   Total-solution concentration.

D(I)   Solution- matrix coefficient (known values).

DELT   Time increment.

DIF   Molecular-diffusion coefficient times torosity.

DIM   Dimensionless concentration (CON/CI).

DIS   Dispersion coefficient.

DPUL   Time of pulse input.

DT   DELT/COEF.

DX   Distance increment.

EK   Ion-exchange equilibrium constant.

EKF   Freundlich-isotherm constant.

EKL   Langmuir-isotherm constant.

FCTF   Variable for Freundlich isotherm.

FCTL   Variable for Langmuir isotherm.

FCTM	Variable for exchange isotherm.
FRAC	Fraction of input-exiting column.
HEAD	Heading to be printed out.
IC	GT 0 for constant concentration boundary condition.
INPUT	Name of data input file.
K	Chemical-reaction rate constant.
N	Number of time steps.
NEXC	Sets type of sorption process (0-6).
NI	Number of nodes in column.
NJ	Node number of printout.
NK	Number of nodes for parameter calculations.
NLIN	1 for linear isotherm.
NNI	Suggested number of nodes to prevent oscillation.
NP1	GT 0 to print last node only.
NP2	Increment of node printout.
NP3	Set equal to 7 for plotting output.
OUTPUT	Name of output file.
PE	Dimensionless-dispersion variable (VAXL/DIS)
PFILE	Name of plot file.
PIPV	Pore-volume increment between printouts.
PON(I)	Intermediate values of concentration at DELT/2.
POR	Effective porosity.
PPV	Incremental pore-volume output.
PSTOP	Number of pore volumes in run.
RCOE(I)	Array that stores (1+RHOB*SLOPE/POR).
RHOB	Soil-bulk density.
RX(I)	Array that stores rate variable (K*CON*RCOE/2).

CBAR(I)   Concentration on the solid phase.

SCC   Solute sorbed in column.

STA   Oscillation coefficient.

TIME   Total time of column run.

TKOUT   Solute output by chemical reaction.

TTIME   Incremental time between printouts.

V   Interstitial-fluid velocity.

XDIM   Dimensionless-column length.

XDIM(I)   Dimensionless distance.

XIN   Solute input to the column.

XK   Dimensionless rate variable (K*XL/V).

XL   Column length.

XMB   Fractional mass balance error.

XNF   Slope of Freundlich isotherm.

XOUT   Solute output from the column.

Data-Input Formats

Line	Data number	Variable	Definition
1	1	HEAD	Description of problem (as many as 70 characters).
2	1	NEXC	Type of sorption; 0 = none, 1 = Freundlich, 2 = Langmuir, 3 = mono-monovalent, 4 = di-divalent 5 = mono-divalent, 6 = Di-monovalent.
2	2	IC	Greater than 0 for constant-concentration boundary condition
2	3	NI	Number of nodes.
2	4	DELT	Time increment.
2	5	PSTOP	Number of pore volumes in simulation
2	6	PIPV	Pore-volume increment between printout.
2	7	NP1	Greater than 0 to print concentration at node number NJ.
2	8	NP2	Increment of node printout.
2	9	NP3	Set equal to 7 to write output to disk for plotting.
2	10	NJ	Node number for data printout.
2	11	CDELT	Fraction of cell distance a solute will move, if greater than 0, computes a new DELT.
2	12	NK	Number of nodes for parameter calculation.

3	1	DPUL	Time of pulse input.
3	2	XL	Column length.
3	3	V	Fluid velocity.
3	4	DIF	Molecular-diffusion constant.
3	5	ALPHA	Hydraulic-dispersion characteristic length.
3	6	RHOB	Soil-bulk density.
3	7	POR	Effective porosity.
4	1	SLOPE	Linear-isotherm slope.
4	2	CI	Input-solute concentration.
4	3	CEC	Total sorption capacity of soil.
4	4	CTOT	Total solution concentration.
4	5	K	First-order rate constant.
4	6	EKF	Freundlich-isotherm constant.
4	7	XNF	Slope of Freundlich isotherm.
4	8	EK	Exchange-equilibrium coefficient.
4	9	EKL	Langmuir isotherm constant.

Input Data for Selected Figures

Record	Line	Free Field Data Input
1		PULSE WITH NO CHEMICAL REACTIONS - FIGURE 9
2		0, 1, 101, .2, 3, .1, 1, 1, 7, 51, .2, 51
3		80, 16, .1, 0, 1, 1.587, .37
4		0, .05, 0, 0, 0, 0, 0, 0, 0

Comments

Output from the column is at node 51 for all parameters such as pore volume, Brenner number, and so forth. This is to allow a comparison with an analytical solution that has the assumption of an infinite column. Pore volume and relative concentration data was printed out for a computer plot.

1. LINEAR SORPTION AND KINETICS - FIGURE 10 -

2. 0, 1, 101, .2, 6, .2, 1, 1, 7, 51, .2, 51

3. 160, 16, .1, 0, 1, 1.587, .37

4. .3, .05, 0, 0, .01, 0, 0, 0, 0

Comments

As in the previous example, a value of 0.2 for CDELT results in the input value of DELT being overridden. A new value of DELT is then computed by the subprogram NEWDT to be 0.73.

1. NON-LINEAR LANGMUIR SORPTION - FIGURE 11

2. 2, 1, 101, .2, 6, .2, 1, 1, 7, 51, 0, 51

3. 160, 16, .1, 0, 1, 1.587, .37

4. 0, .05, .003, 0, 0, 0, 0, 0, 100

Comments

A Langmuir isotherm is assumed with most of the other values the same. The value of DELT of 0.2 was not overridden this time. Values for CEC of 0.003 and EKL of 100. were chosen for comparison with the linear isotherm slopes of 0.3.

1. NON-LINEAR FREUNDLICH SORPTION - FIGURE 12

2. 1, 1, 101, .2, 6, .2, 1, 1, 7, 51, .2, 51

3. 160, 16, .1, 0, 1, 1.587, .37

4. 0, .05, 0, 0, 0, .3, .7, 0, 0

Comments

A Freundlich isotherm is assumed with an exponent of 0.7. As shown in figure 12, a sharp peak with a long tail results.

1. DI-DIVALENT ION EXCHANGE

2. 4, 1, 101, .5, 6, .4, 1, 1, 7, 51, .2, 51

3. 160, 16, .1, 0, 1, 1.587, .37

4. 0, .05, .003, .1, 0, 0, 0, 10, 0

Comments

Di-divalent ion exchange is assumed. Output for this example is shown as attachment IV.

Example of computer output

```
*******************************************************************************
*                                                                             *
*            DI-DIVALENT ION EXCHANGE                                          *
*                                                                             *
*******************************************************************************
```

0   USER DEFINED OPTIONS AND PARAMETERS

0   TIME INCREMENT(DELT)............................... 0.5000
        PORE VOLUME INCREMENT BETWEEN PRINTOUTS(PIPV).... 0.4000
        NUMBER OF NODES(NI)................................101
        TOTAL PORE VOLUME OF RUN(PSTOP)................... 6.0000
        PRINT NODE NJ ONLY(NP1)...........................YES
        NODE FOR PRINTOUT(NJ)............................. 51
        NUMBER OF NODES FOR PARAMETER CALCULATION(NK).... 51
        INCREMENT OF NODE PRINTOUT(NP2).................. 1
        NAME OF PLOT DATA FILE(PFILE)....................RPT14.PLT
        FLUX INPUT BOUNDRY CONDITION(IC).................NO
        FRACTION OF CELL THAT ION MOVES(CDELT)...........0.20
        CODE FOR POSSIBLE SORPTION(NEXC)................EXCHANGE(4)

    PHYSICAL CHARACTERISTICS OF COLUMN,SOIL, AND SOLUTE

        TIME DURATION OF PULSE(DPUL)..................... 0.160E+03
        COLUMN LENGTH(XL)............................... 16.000
        INTERSTITIAL FLUID VELOCITY(V).................. 0.100E+00
        MOLECULAR DIFFUSION COEF(DIF)................... 0.000E+00
        DISPERSION CHARACTERISTIC LENGTH(ALPHA).......... 1.000
        MEDIUM BULK DENSITY(RHOB)........................ 1.587
        MEDIUM POROSITY(POR)............................. 0.370

    CHEMICAL CHARACTERISTICS OF POROUS MEDIUM AND SOLUTE

        SLOPE OF LINEAR ISOTHERM(SLOPE).................. 0.000E+00
        SOLUTE INPUT CONCENTRATION(CI)................... 0.500E-01
        SORPTION OR CATION EXCHANGE CAPACITY(CEC)........ 0.003
        TOTAL SOLUTION CONCENTRATION(CTOT).............. 0.100E+00
        KINETIC RATE CONSTANT(K)........................ 0.000E+00
        FREUNDLICH ISOTHERM CONSTANT(EKF)............... 0.000E+00
        EXPONENT OF FREUNDLICH ISOTHERM(XNF)............. 0.000
        ION EXCHANGE CONSTANT(EK)....................... 0.100E+02
        LANGMUIR SORPTION CONSTANT(EKL)................. 0.000E+00
```

CALCULATED VALUES

DISPERSION COEFFICIENT(DIS)........................ 0.1000
OSCILLATION COEFFICIENT(STA)...................... 0.0800
DISTANCE INCREMENT(DX)............................ 0.1600
PECLET NUMBER(V*XL/DIS)........................... 8.000
KINETIC FACTOR(K*XL/V)............................ 0.000E+00
BRENNER NUMBER(V*XL/(4*DIS))...................... 2.000
MINIMUM RETARDATION FACTOR(RF).................... 1.01
DELT CALCULATED FROM CDELT(DELT).................. 0.324E+00


1


CONCENTRATION AT NODE " 51" IN COLUMN


| N | TIME | PV | CON(NJ) | DIM | FRAC |
|---|------|-----|---------|-----|------|
| 0 | 0.00E+00 | 0.000 | 0.000E+00 | 0.000E+00 | 0.000 |
| 99 | 0.32E+02 | 0.401 | 0.509E-04 | 0.102E-02 | 0.000 |
| 198 | 0.64E+02 | 0.802 | 0.138E-01 | 0.276E+00 | 0.047 |
| 297 | 0.96E+02 | 1.203 | 0.330E-01 | 0.660E+00 | 0.193 |
| 395 | 0.13E+03 | 1.600 | 0.427E-01 | 0.855E+00 | 0.337 |
| 494 | 0.16E+03 | 2.001 | 0.470E-01 | 0.940E+00 | 0.451 |
| 593 | 0.19E+03 | 2.402 | 0.468E-01 | 0.937E+00 | 0.643 |
| 692 | 0.22E+03 | 2.804 | 0.305E-01 | 0.609E+00 | 0.801 |
| 790 | 0.26E+03 | 3.201 | 0.160E-01 | 0.319E+00 | 0.891 |
| 889 | 0.29E+03 | 3.602 | 0.840E-02 | 0.168E+00 | 0.937 |
| 988 | 0.32E+03 | 4.003 | 0.473E-02 | 0.946E-01 | 0.963 |
| 1087 | 0.35E+03 | 4.404 | 0.283E-02 | 0.567E-01 | 0.978 |
| 1185 | 0.38E+03 | 4.801 | 0.178E-02 | 0.356E-01 | 0.987 |
| 1284 | 0.42E+03 | 5.202 | 0.114E-02 | 0.228E-01 | 0.992 |
| 1383 | 0.45E+03 | 5.603 | 0.745E-03 | 0.149E-01 | 0.996 |
| 1481 | 0.48E+03 | 6.000 | 0.492E-03 | 0.985E-02 | 0.998 |


MASS BALANCE CALCULATION

COLUMN INPUT(XIN).................................. 0.799E+00
COLUMN OUTPUT(XOUT)............................... 0.798E+00
OUT BY CHEMICAL REACTION(TKOUT)................... 0.000E+00
COLUMN ACCUMULATION(ACC).......................... 0.125E-02
COLUMN SORBED ACCUMULATION(SCC)................... 0.131E-02
MASS BALANCE ERROR(XMB)........................... 0.168E-02

## FORTRAN 77 program listing

```
************************************************************
C***********************************************************
C***********************************************************
C     THIS PROGRAM CALCULATES THE CONCENTRATION PROFILE EXITING FROM
C     OR WITHIN A SOIL COLUMN AS A FUNCTION OF TIME.
C     THE PROGRAM UTILIZES A CRANK-NICOLSON FINITE DIFFERENCE
C     APPROXIMATION TO THE DEFINING DIFFERENTIAL EQUATION AND THE
C     DOUGLAS PREDICTOR-CORRECTOR METHOD TO ACCOUNT FOR THE
C     POSSIBLE NON-LINEAR SORPTION TERM.
C     EQUILIBRIUM CONTROLLED SORPTION IS ACCOUNTED FOR BY
C     EITHER THE MASS ACTION LAW, THE LANGMIUR, OR FREUNDLICH ISOTHERM
C     A FIRST ORDER IRREVERSIBLE RATE REACTION IS INCLUDED.
C            PROGRAM WRITTEN BY D. GROVE,U.S.GEOLOGICAL SURVEY
C            WATER RESOURCES DIVISION, DENVER COLORADO, NATIONAL
C            RESEARCH PROGRAM ON 6/83.
C***********************************************************
C***********************************************************
C            ALPHA = HYDRAULIC DISPERSION CHARACTERISTIC LENGTH
C            CDELT = FRACTION CELL DISTANCE A SOLUTE WILL MOVE IN DELT
C            CEC = CATION EXCHANGE CAPACITY
C            CI = INITIAL CONCENTRATION ENTERING REACTOR
C            CTOT = TOTAL SOLUTION CONCENTRATION
C            DELT = TIME INCREMENT
C            DIF = MOLECULAR DIFFUSION COEFFICIENT
C            DPUL = TIME OF PULSE INPUT
C            EK = ION EXCHANGE EQUILIBRIUM CONSTANT
C            EKF = FREUNDLICH ISOTHERM CONSTANT
C            EKL = LANGMIUR ISOTHERM CONSTANT
C            IC = GT 0 FOR CONSTANT CONCENTRATION BOUNDRY CONDITION
C            K = CHEMICAL REACTION RATE CONSTANT
C            NEXC = 0 FOR NO ADSORPTION
C                 = 1 FOR FREUNDLICH ISOTHERM
C                 = 2 FOR LANGMUIR ISOTHERM
C                 = 3 FOR MONO-MONO EXCHANGE
C                 = 4 FOR DI-DIVALENT EXCHANGE
C                 = 5 FOR MASS ACTION EXCHANGE WITH 2M+=2MX
C                 = 6 FOR MASS ACTION EXCHANGE WITH M++=MX2
C            NI = NUMBER OF NODES IN COLUMN
C            NK = NUMBER OF NODES FOR PARAMETER CALCULATION
C            NJ = NODE NUMBER OF DATA PRINTOUT
C            NP1 = GT 0 TO PRINT NODE NJ ONLY
C            NP2 = INCREMENT OF NODE PRINTOUT
C            NP3 = 7 FOR DISK OUTPUT FOR PLOT ROUTINES
C            PIPV = PORE VOLUME INCREMENT BETWEEN PRINTOUTS
C            POR = EFFECTIVE POROSITY
C            PSTOP = NUMBER OF PORE VOLUMES AT NJ IN REACTOR RUN
C            RHOB = SOIL BULK DENSITY
C            SLOPE = LINEAR SLOPE OF SORPTION ISOTHERM
C            V = INTERSTITIAL FLUID VELOCITY
C            XL = COLUMN LENGTH AT NI
C            XNF = SLOPE OF FREUNDLICH ISOTHERM
C***********************************************************
C***********************************************************
```

```
      DIMENSION A(201),B(201),C(201),D(201),CON(201),CE(201),X(201),
     &PON(201),RX(201),S(201),COEF(201),RCOE(201)
      REAL K
      CHARACTER HEAD*80,INPUT*10,OUTPUT*10,PFILE*12,F1*10,
     1WNP1*3,WNP3*3,WIC*3,WNEXC*12
C
C**********INITIALIZE VARIABLES**********
C
      TKOUT=0.0
      WNP1='NO'
      PFILE='NO PLOT FILE'
      WIC='NO'
      F1='(A)'
      ACC=0.0
      RF=1.0
      N6=0
      N =0
      FRAC=0.0
      TIME=0.0
      NLIN =0
      XIN = 0.0
      XOUT=0.0
      PPV=0.0
      PV=0.0
C
C**********READ INPUT DATA********************
C
      WRITE (*,F1)'TYPE IN NAME OF INPUT FILE'
      READ (*,F1) INPUT
      WRITE (*,F1)'TYPE IN NAME OF OUTPUT FILE'
      READ (*,F1) OUTPUT
      OPEN(5,FILE=INPUT)
      OPEN(6,FILE=OUTPUT)
      READ (5,F1) HEAD
      READ(5,*)NEXC,IC,NI,DELT,PSTOP,PIPV,NP1,NP2,NP3,NJ,CDELT,NK
      READ(5,*)DPUL,XL,V,DIF,ALPHA,RHOB,POR
      READ(5,*)SLOPE,CI,CEC,CTOT,K,EKF,XNF,EK,EKL
      IF(NP1.GT.0) WNP1='YES'
      IF(IC.EQ.0) WIC='YES'
      IF(ABS(SLOPE).GT..1E-20)NLIN=1
      IF(NP3.NE.7) GO TO 50
      WRITE (*,F1)'TYPE IN NAME OF PLOT FILE'
      READ(*,F1) PFILE
      OPEN(7,FILE=PFILE)
   50 CONTINUE
C
      NGO=NEXC+1
      GO TO(11,12,13,14,15,16,17),NGO
   11 WNEXC='NONE'
      GO TO 25
   12 WNEXC='FREUNDLICH'
      GO TO 25
   13 WNEXC='LANGMUIR'
      GO TO 25
```

```
   14 WNEXC='EXCHANGE(3)'
      GO TO 25
   15 WNEXC='EXCHANGE(4)'
      GO TO 25
   16 WNEXC='EXCHANGE(5)'
      GO TO 25
   17 WNEXC='EXCHANGE(6)'
   25 CONTINUE
C**********WRITE INPUT DATA**********
C
      WRITE(6,509)
      WRITE(6,510) HEAD
      WRITE(6,511)
      WRITE(6,520)
      WRITE(6,540)DELT,PIPV,NI,PSTOP,WNP1,NJ,NK,NP2,PFILE,WIC,CDELT,
     &WNEXC
      WRITE(6,530)DPUL,XL,V,DIF,ALPHA,RHOB,POR
      WRITE(6,535)SLOPE,CI,CEC,CTOT,K,EKF,XNF,EK,EKL
C
C**********CALCULATE VARIABLES COMMON TO ALL ROUTINES**********
C
      DO 100 I=1,NI
      CON(I)=0.0
      RCOE(I)=1.0
      COEF(I)=1.0
      RX(I)=0.0
  100 CONTINUE
      IF(NLIN.NE.1) GO TO 120
      RF=1.+SLOPE*RHOB/POR
      DO 110 I=1,NI
      RCOE(I)=RF
      COEF(I)=RF
  110 CONTINUE
  120 CONTINUE
      IF(CTOT.LT..1E-20)CTOT=.1E10
      FCTF=RHOB*EKF*XNF/POR
      FCTL= RHOB*EKL*CEC/POR
      FCTM = RHOB*CEC*EK/(POR*CTOT)
      C3=RHOB/POR
      CTOTH=CTOT/2.
      HDELT=DELT/2.
      CMINF=.001*CI
      II=NI-1
      IF(NJ.EQ.0) NJ=NI
      IF(NK.EQ.0)NK=NI
      III=NJ-1
      PVC=FLOAT(NI-1)/FLOAT(NK-1)
      DX= XL/FLOAT(II)
      DIS=DIF+ALPHA*V
      PE = V*XL/(DIS*PVC)
      BN=PE/4.
      XK = K*XL/(V*PVC)
      XCI=CI
      DO 130 I=1,NI
```

```
  130 X(I)=DX*(FLOAT(I)-1.)
      IF(CDELT.LT..1E-20) GO TO 140
      CALL  NEWDT(NLIN,CDELT,DX,V,NGO,FCTF,FCTL,FCTM,XNF,CI,EKL,CTOT,EK,
     &CEC,RHOB,POR,RF,DELT)
  140 CONTINUE
      D2=DIS/(DX*DX)
      D4= V/(4.*DX) + DIS/(2.*DX*DX)
      D6 = -V/(4.*DX) + DIS/(2.*DX*DX)
      D7 = DIS/(DX*DX)
      I=1
      A(I)=0.0
      C(I)= -DIS/(DX*DX)
      IF(IC.GT.0) C(1)=0.0
      DO 150 I=2,II
      A(I)= -V/(4.*DX) - DIS/(2.*DX*DX)
      C(I)= V/(4.*DX) - DIS/(2.*DX*DX)
  150 CONTINUE
      I=NI
      A(I) = -DIS/(DX*DX)
      C(I)=0.0
C
C*****THE VARIABLE STA MUST BE EQUAL TO OR LESS THAN ONE TO PREVENT
C*****UNDAMPED OSCILLATION FROM OCCURING DURING SOLUTION.
C
      STA = V*DX/(2.*DIS)
      IF(STA.LT.1.0) GO TO 160
      WRITE(6,560) STA
      NNI= XL*V/(2.*DIS)+2.
      WRITE(6,470) NNI
      STOP
  160 CONTINUE
C
C**********WRITE CALCULATED DATA**********
C
      WRITE(6,536) DIS,STA,DX,PE,XK,BN,RF,DELT
  170 CONTINUE
      IF(PV.LT.(PPV-.0001)) GO TO 220
      PPV = PPV + PIPV
      IF(NP1.LT.1) GO TO 200
      IF(N6.GT.0) GO TO 180
      WRITE(6,460) NJ
      N6=1
  180 CONTINUE
      IF(XIN.LT.0.1E-20)GO TO 190
      FRAC=XOUT/XIN
  190 CONTINUE
      CDIM=CON(NJ)/XCI
      WRITE(6,450) N,TIME,PV,CON(NJ),CDIM,FRAC
      IF(NP3.EQ.7)WRITE(NP3,440)PV,CDIM
      GO TO 220
  200 CONTINUE
      WRITE(6,580) TIME,N,PV
      DO 210 I=1,NJ,NP2
      CDIM=CON(I)/XCI
```

```
            XDIM=X(I)/XL
            WRITE(6,570) I,X(I),XDIM,CON(I),CDIM
            IF(NP3.EQ.7)WRITE(7,440) XDIM,CDIM
      210 CONTINUE
      220   CONTINUE
            IF(PV.GT.PSTOP) GO TO 420
            IF(NLIN.EQ.1) GO TO 280
            GO TO(280,230,240,250,255,260,270),NGO
C
C**********CALCULATE THE ISOTHERM COEFFICENTS**********
C
      230 CALL FREUN(CON,CMINF,RCOE,FCTF,XNF,COEF,NI)
            GO TO 280
      240 CALL LANG(NI,RCOE,FCTL,EKL,CON,COEF)
            GO TO 280
      250 CALL EXC(NI,RCOE,FCTM,CTOT,CON,EK,COEF)
            GO TO 280
      255 CALL EXC(NI,RCOE,FCTM,CTOTH,CON,EK,COEF)
            GO TO 280
      260 CALL EXCM(NI,CON,CMINF,CTOT,EK,CEC,RCOE,COEF,C3)
            GO TO 280
      270 CALL EXCD(NI,EK,CEC,CTOT,CON,CMINF,C3,RCOE,COEF)
      280 CONTINUE
            IF(K.LT..1E-20) GO TO 300
            DO 290 I=1,NI
            RX(I)=K/2.*RCOE(I)
      290 CONTINUE
      300 CONTINUE
            IF(NEXC.EQ.0.OR.NLIN.EQ.1) GO TO 380
C
C**********CALCULATE CONCENTRATION AT TIME DELT/2**********
C
            CALL REACT(HDELT,COEF,DIS,DX,V,RX,CON,D1,D2,IC,CI,II,NI,D4,D5,D6,
          &D7,A,B,C,D,PON)
C
C**********CALCULATE ISOTHERM COEFFICIENTS AT TIME+DELT/2****
C
            GO TO(360,310,320,330,335,340,350),NGO
      310 CALL FREUN(PON,CMINF,RCOE,FCTF,XNF,COEF,NI)
            GO TO 360
      320 CALL LANG(NI,RCOE,FCTL,EKL,PON,COEF)
            GO TO 360
      330 CALL EXC(NI,RCOE,FCTM,CTOT,PON,EK,COEF)
            GO TO 360
      335 CALL EXC(NI,RCOE,FCTM,CTOTH,PON,EK,COEF)
            GO TO 360
      340 CALL EXCM(NI,PON,CMINF,CTOT,EK,CEC,RCOE,COEF,C3)
            GO TO 360
      350 CALL EXCD(NI,EK,CEC,CTOT,PON,CMINF,C3,RCOE,COEF)
      360 CONTINUE
            IF(K.LT..1E-20) GO TO 380
            DO 370 I=1,NI
            RX(I)=K/2.*RCOE(I)
      370 CONTINUE
```

```
  380 CONTINUE
C
C**********CALCULATE CONCENTRATION AT TIME + DT**********
C
      CALL REACT(DELT,COEF,DIS,DX,V,RX,CON,D1,D2,IC,CI,II,NI,D4,D5,D6,
     &D7,A,B,C,D,CON)
  390 CONTINUE
      TIME = TIME + DELT
      IF(DPUL.LT..1E-20) GO TO 400
       IF(TIME.GT.DPUL)CI=0.0
  400 CONTINUE
      IF(K.LT..1E-20) GO TO 407
      XKOUT=CON(1)*RCOE(1)/2.
      DO 405 I=2,III
  405 XKOUT=XKOUT+CON(I)*RCOE(I)
      XKOUT=XKOUT+CON(NJ)*RCOE(NJ)/2.
      XKOUT=XKOUT*K*DELT*DX
      TKOUT=TKOUT+XKOUT
  407 CONTINUE
      PV=PVC*V*TIME/XL
      XIN=CI*V*DELT+XIN
      XOUT=XOUT+CON(NJ)*V*DELT
      N=N+1
      GO TO 170
  410 CONTINUE
  420 CONTINUE
C
C**********CALCULATE MASS BALANCE**********
C
      SCC=CON(1)*(RCOE(1)-1.)/2.
      DO 430 I=2,III
      SCC=SCC+CON(I)*(RCOE(I)-1.)
  430 ACC=ACC+CON(I)
      ACC=ACC*DX+(CON(1)+CON(NI))*DX/2.
      SCC=(SCC+CON(NJ)*(RCOE(NJ)-1.)/2.)*DX
      XMB=(ACC+SCC+XOUT+TKOUT-XIN)/XIN
      WRITE(6,600) XIN,XOUT,TKOUT,ACC,SCC,XMB
C
C**********FORMAT STATEMENTS**********
C
  440 FORMAT(F11.3,E12.3)
  450 FORMAT(1H ,1X,I5,E11.2,F11.3,2E12.3,F8.3,E12.3)
  460 FORMAT(1H1,///,5X,'CONCENTRATION AT NODE "',I3,'" IN COLUMN',///
     &,5X,'N '5X,'TIME',9X,'PV',6X,'CON(NJ)',7X,'DIM',
     &7X,'FRAC'//)
  470 FORMAT(1H0, 'OSCILLATION CAN BE ELIMINATED BY INCREASING THE',/
     &'NUMBER OF NODES (NI) TO ',I5)
  509 FORMAT(1H ,'*****************************************************',
     &'************************'/1X,'*',T78,'*')
  510 FORMAT(1H ,'*',3X,A,T78,'*')
  511 FORMAT(1H ,'*',T78,'*'/1X,'**********************************',
     &'**********************************'//)
  520 FORMAT(1H0,'    USER DEFINED OPTIONS AND PARAMETERS',//)
  540 FORMAT(1H0,
```

```
     &5X,'TIME INCREMENT(DELT).............................',F7.4/
     &6X,'PORE VOLUME INCREMENT BETWEEN PRINTOUTS(PIPV)....',F9.4/
     &6X,'NUMBER OF NODES(NI)..............................',I3/
     &6X,'TOTAL PORE VOLUME OF RUN(PSTOP)..................',F9.4/
     &6X,'PRINT NODE NJ ONLY(NP1)..........................',A/
     &6X,'NODE FOR PRINTOUT(NJ)............................',I3/
     &6X,'NUMBER OF NODES FOR PARAMETER CALCULATION(NK)....',I3/
     &6X,'INCREMENT OF NODE PRINTOUT(NP2)..................',I3/
     &6X,'NAME OF PLOT DATA FILE(PFILE)....................',A/
     &6X,'FLUX INPUT BOUNDRY CONDITION(IC).................',A/
     &6X,'FRACTION OF CELL THAT ION MOVES(CDELT)...........',F4.2/
     &6X,'CODE FOR POSSIBLE SORPTION(NEXC).................',A)
 530 FORMAT(1H ,///,5X,'PHYSICAL CHARACTERISTICS OF COLUMN,SOIL,'
     &' AND SOLUTE',//,
     &6X,'TIME DURATION OF PULSE(DPUL).....................',E10.3/
     &6X,'COLUMN LENGTH(XL)................................',F8.3/
     &6X,'INTERSTITIAL FLUID VELOCITY(V)...................',E10.3/
     &6X,'MOLECULAR DIFFUSION COEF(DIF)....................',E10.3/
     &6X,'DISPERSION CHARACTERISTIC LENGTH(ALPHA)..........',F9.3/
     &6X,'MEDIUM BULK DENSITY(RHOB)........................',F8.3/
     &6X,'MEDIUM POROSITY(POR).............................',F8.3)
 535 FORMAT(1H ,///,5X,'CHEMICAL CHARACTERISTICS OF POROUS',
     &' MEDIUM AND SOLUTE',//,
     &6X,'SLOPE OF LINEAR ISOTHERM(SLOPE)..................',E10.3/
     &6X,'SOLUTE INPUT CONCENTRATION(CI)...................',E10.3/
     &6X,'SORPTION OR CATION EXCHANGE CAPACITY(CEC)........',F9.3/
     &6X,'TOTAL SOLUTION CONCENTRATION(CTOT)...............',E10.3/
     &6X,'KINETIC RATE CONSTANT(K).........................',E10.3/
     &6X,'FREUNDLICH ISOTHERM CONSTANT(EKF)................',E10.3/
     &6X,'EXPONENT OF FREUNDLICH ISOTHERM(XNF).............',F8.3/
     &6X,'ION EXCHANGE CONSTANT(EK)........................',E10.3/
     &6X,'LANGMUIR SORPTION CONSTANT(EKL)..................',E10.3)
 560 FORMAT(1H ,'PROGRAM CANCLED BECAUSE STA =',E14.7,',IS',
     &' GREATER THAN THE MINIMUM VALUE OF ONE')
 536 FORMAT(1H ,///,5X,'CALCULATED VALUES',//
     &6X,'DISPERSION COEFFICIENT(DIS)......................',F9.4/
     &6X,'OSCILLATION COEFFICIENT(STA).....................',F7.4/
     &6X,'DISTANCE INCREMENT(DX)...........................',F7.4/
     &6X,'PECLET NUMBER(V*XL/DIS)..........................',F8.3/
     &6X,'KINETIC FACTOR(K*XL/V)...........................',E10.3/
     &6X,'BRENNER NUMBER(V*XL/(4*DIS)).....................',F8.3/
     &6X,'MINIMUM RETARDATION FACTOR(RF)...................',F7.2/
     &6X,'DELT CALCULATED FROM CDELT(DELT).................',E10.3///)
 570 FORMAT(1H ,5X,1I4,5(3X,E10.3))
 580  FORMAT(1H1, //6X,'CONCENTRATION WITHIN THE COLUMN',//,6X,
     &6HTIME =,E9.3,/6X,22HNUMBER OF ITERATIONS =,I7/6X, 24HNUMBER OF PO
     &RE VOLUMES =,F9.4,//6X,4HNODE,5X, 8HDISTANCE,3X,'DIM DISTANCE',
     & 4X,'CONC',7X,'DIM CONC')
 600 FORMAT(1H ,///5X,'MASS BALANCE CALCULATION',//
     &6X,'COLUMN INPUT(XIN)................................',E10.3/
     &6X,'COLUMN OUTPUT(XOUT)..............................',E10.3/
     &6X,'OUT BY CHEMICAL REACTION(TKOUT)..................',E10.3/
     &6X,'COLUMN ACCUMULATION(ACC).........................',E10.3/
     &6X,'COLUMN SORBED ACCUMULATION(SCC)..................',E10.3/
     &6X,'MASS BALANCE ERROR(XMB)..........................',E10.3)
```

```
  590 FORMAT(E14.7)
      STOP
      END
C
C
C*********THIS ROUTINE IS THE THOMAS ALGOTHRIUM USED******
C**********TO SOLVE THE TRI-DIAGONAL MATRIX********
C
      SUBROUTINE TRIMAT(A,B,C,D,H,II,NI)
      DIMENSION A(NI),B(NI),C(NI),D(NI),H(NI),BETA(201),GAMMA(201)
      I=1
      BETA(1)=B(1)
      GAMMA(1)=D(1)/B(1)
      DO 100 I=2,NI
      BETA(I)=B(I)-A(I)*C(I-1)/BETA(I-1)
      GAMMA(I)= (D(I)-A(I)*GAMMA(I-1))/BETA(I)
  100 CONTINUE
      H(NI)= GAMMA(NI)
      DO 110 J=1,II
      I=II+1-J
      H(I)=GAMMA(I)-C(I)*H(I+1)/BETA(I)
  110 CONTINUE
      RETURN
      END
C
C
C*********THIS SUBROUTINE SOLVES THE QUADRATIC EQUATION****
C
      FUNCTION QUADX(A,B,C,D)
      QUADX=(-B+D*SQRT(B*B-4.*A*C))/(2.*A)
      RETURN
      END
C
C
C*********THIS SUBROUTINE CALCULATES THE NEW DELT NECESSARY****
C**********TO MOVE A SORBING SOLUTE CDELT FRACTION OF A CELL DISTANCE**
C
      SUBROUTINE NEWDT(NLIN,CDELT,DX,V,NGO,FCTF,FCTL,FCTM,XNF,CI,EKL,
     &CTOT,EK,CEC,RHOB,POR,RF,DELT)
C
      C55=CDELT*DX/V
      IF(NLIN.EQ.1) GO TO 160
      GO TO(100,110,120,130,135,140,150),NGO
  100 DELT=C55
      GO TO 170
  110 RF=1.+FCTF*CI**(XNF-1.)
      DELT=C55*RF
      GO TO 170
  120 RF=1.+FCTL/(1.+EKL*CI)**2
      DELT=C55*RF
      GO TO 170
  130 RF=1.+FCTM/(CI/CTOT*(EK-1.)+1.)**2
      DELT=C55*RF
      GO TO 170
```

```
135 RF=1.+FCTM/(2.*CI/CTOT*(EK-1.)+1.)**2
    DELT = C55*RF
    GO TO 170
140 C3=RHOB/POR
    C2=CI*CI
    AA=CTOT-CI
    BB=C2*EK
    CC=-EK*CEC*C2
    CBAR=QUADX(AA,BB,CC,1.)
    DCBAR=(CBAR*CBAR-CBAR*2.*CI*EK+2.*CI*EK*CEC)
   &/((CTOT-CI)*2.*CBAR+C2*EK)
    RF=1.+C3*DCBAR
    DELT=C55*RF
    GO TO 170
150  C4=EK*CEC
    C3=RHOB/POR
    C5=C4*CEC
    C6=CTOT*CTOT
    C2=CI*CI
    AA=EK*CI*4.
    BB=-4.*C4*CI-C6+4.*CI*CTOT-4.*C2
    CC=C5*CI
    CBAR=QUADX(AA,BB,CC,-1.)
    DCBAR=(-4.*CBAR*CBAR*EK-CBAR*(-4.*C4+4.*CTOT-8.*CI)
   &-C5)/(4.*EK*CI*(2.*CBAR-CEC)-C6+4.*CI*CTOT-C2*4.)
    RF=1.+C3*DCBAR
    DELT=C55*RF
    GO TO 170
160 DELT=C55*RF
170 CONTINUE
    RETURN
    END
C
C
C**********THIS SUBROUTINE COMPUTES THE COEFFICIENTS*******
C**********FOR THE LANGMUIR SORPTION*******************
C
    SUBROUTINE LANG(NI,RCOE,FCTL,EKL,CON,COEF)
    DIMENSION RCOE(NI),CON(NI),COEF(NI)
    DO 100 I=1,NI
    RCOE(I)=1.+FCTL/(1.+EKL*CON(I))
100 COEF(I)=1.+FCTL/((1.+EKL*CON(I))**2)
    RETURN
    END
C
C
C**********THIS SUBROUTINE COMPUTES THE COEFFICIENTS********
C**********FOR EQUAL VALENCE ION EXCHANGE**************
C
    SUBROUTINE EXC(NI,RCOE,FCTM,CTOT,CON,EK,COEF)
    DIMENSION RCOE(NI),CON(NI),COEF(NI)
    DO 100 I=1,NI
    RCOE(I)=1.+FCTM*CTOT/((CTOT-CON(I))+EK*CON(I))
100 COEF(I) = 1.+FCTM/((CON(I)/CTOT*(EK-1.)+1.)**2)
    RETURN
    END
```

56

```
C
C
C*********THIS SUBROUTINE COMPUTES THE COEFFICIENTS******
C**********FOR MONO-VALENT DIVALENT*********************
C
      SUBROUTINE EXCM(NI,CON,CMINF,CTOT,EK,CEC,RCOE,COEF,C3)
      DIMENSION RCOE(NI),CON(NI),COEF(NI)
      DO 110 I=1,NI
      IF(CON(I).LT.CMINF) GO TO 100
      C2=CON(I)*CON(I)
      AA=CTOT-CON(I)
      BB=C2*EK
      CC=-EK*CEC*C2
      CBAR=QUADX(AA,BB,CC,1.)
      RCOE(I)=1.+C3*CBAR/CON(I)
      DCBAR=(CBAR*CBAR-CBAR*2.*CON(I)*EK+2.*CON(I)*EK*CEC)
     &/((CTOT-CON(I))*2.*CBAR+C2*EK)
      COEF(I)=1.+C3*DCBAR
      GO TO 110
  100 RCOE(I)=1.+C3*SQRT(EK*CEC/CTOT)
      COEF(I)=RCOE(I)
  110 CONTINUE
      RETURN
      END
C
C
C**********THIS SUBROUTINE COMPUTES THE COEFFICIENTS*****
C**********FOR DIVALENT-MONOVALENT*****************
C
      SUBROUTINE EXCD(NI,EK,CEC,CTOT,CON,CMINF,C3,RCOE,COEF)
      DIMENSION RCOE(NI),CON(NI),COEF(NI)
      C4=EK*CEC
      C5=C4*CEC
      C6=CTOT*CTOT
      DO 110 I=1,NI
      IF(CON(I).LT.CMINF) GO TO 100
      C2=CON(I)*CON(I)
      AA=4.*EK*CON(I)
      BB=-4.*C4*CON(I)-C6+4.*CON(I)*CTOT-C2*4.
      CC=C5*CON(I)
      CBAR=QUADX(AA,BB,CC,-1.)
      RCOE(I)=1.+C3*CBAR/CON(I)
      A=(-4.*CBAR*CBAR*EK-CBAR*(-4.*C4+4.*CTOT-8.*CON(I))-C5)
      B=(4.*EK*CON(I)*(2.*CBAR-CEC)-C6+4.*CON(I)*CTOT-4.*C2)
      DCBAR=A/B
      COEF(I)=1.+C3*DCBAR
      GO TO 110
  100 RCOE(I)=1.+C3*EK*CEC*CEC/(CTOT*CTOT)
      COEF(I)=RCOE(I)
  110 CONTINUE
      RETURN
      END
C
C
```

```
C********* THIS SUBROUTINE COMPUTES THE COEFFICIENTS***********
C********* FOR FREUNDLICH SORPTION***************************
C
      SUBROUTINE FREUN(CON,CMINF,RCOE,FCTF,XNF,COEF,NI)
      DIMENSION RCOE(NI),CON(NI),COEF(NI)
      XXNF=XNF-1
      DO 110 I=1,NI
      IF(CON(I).LT.CMINF) GO TO 100
      RCOE(I)=1.+FCTF/XNF*CON(I)**XXNF
      COEF(I)= 1.+FCTF*CON(I)**XXNF
      GO TO 110
  100 RCOE(I)=1.+FCTF/XNF
      COEF(I)=1.+FCTF*CMINF**XXNF
  110 CONTINUE
      RETURN
      END
C
C
C**********THIS SUBROUTINE COMPUTES THE CONCENTRATION AT******
C**********THE NEW TIME STEP********************************
C
      SUBROUTINE REACT(DELT,COEF,DIS,DX,V,RX,CON,D1,D2,IC,CI,
     &II,NI,D4,D5,D6,D7,A,B,C,D,PON)
      DIMENSION COEF(NI),RX(NI),CON(NI),A(NI),B(NI),C(NI),
     &D(NI),PON(NI)
      I=1
      DT = DELT/COEF(I)
      B(I)= 1./DT + DIS/(DX*DX) +V*V/(2.*DIS) + V/DX+RX(I)
      D1=    1./DT  - DIS/(DX*DX) -V*V/(2.*DIS) -V/DX-RX(I)
      D(I)=CON(I)*D1+CON(I+1)*D2+V*V*CI/DIS+2.*V*CI/DX
      IF(IC.GT.0) B(1)=1.
      IF(IC.GT.0) D(1)=CI
      DO 100 I=2,II
      DT = DELT/COEF(I)
      B(I) =  1./DT + DIS/(DX*DX) + RX(I)
      D5 =    1./DT - DIS/(DX*DX) - RX(I)
  100 D(I)=CON(I-1)*D4 + CON(I)*D5 + CON(I+1)*D6
      I=NI
      DT = DELT/COEF(I)
      B(I) = 1./DT + DIS/(   DX*DX) + RX(I)
      D8 =    1./DT - DIS/(DX*DX)-RX(I)
      D(I)= CON(I-1)*D7 + CON(I)*D8
      CALL TRIMAT(A,B,C,D,PON,II,NI)
      RETURN
      END
**********************************************************************************
```