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THE DEVELOPMENT OF THEORETICAL EQUATIONS
TO DESCRIBE THE FLOW OF A RADIOACTIVE ION
IN GROUND WATER, ANNUAL REPORT,
DECEMBER 1, 1966 TO NOVEMBER 30, 1967

Prepared by
David B. Grove
U. S. Geological Survey

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David B. Grove
U.S. Geological Survey

in collaboration with
Sandia Laboratories
Under
Contract No. AL-66-848

ABSTRACT

This report describes a mathematical modeling study of the flow of trace concentration of ions through a porous media. The theoretical work in this report was performed as an aid in evaluating possible hazard resulting from the earth burial of a SNAP device containing radioactive fuel material.

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SUMMARY

A one dimensional transport equation that includes convective, dispersion, and ion exchange terms is derived and examined for the flow of trace concentrations of ions through porous media. Ion-exchange processes examined included instantaneous equilibrium, the use of theoretical plates, and the assumption of a second-order kinetic-rate reaction. The theoretical plate and kinetic rate ion exchange concept compared well with laboratory column experiments. The instantaneous equilibrium model's ease of use is its most attractive feature. A general partial differential equation utilizing the kinetic concept to describe the ion-exchange reaction was formulated into a finite difference equation by means of the Taylor's series and solved by a digital computer. Variables in the equation indicate that a decrease in fluid velocity or an increase in the kinetic rate constant increases the peak concentration in the ionic pulse. High fluid velocities or low rate constants result in early peaks in the effluent from a laboratory column. Stability problems limit the present usefulness of the derived difference equations to short range distance predictions.

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THE DEVELOPMENT OF THEORETICAL EQUATIONS TO DESCRIBE THE FLOW OF A RADIOACTIVE ION IN GROUND WATER

INTRODUCTION

On December 1, 1966, the Water Resources Division of the U.S. Geological Survey, in cooperation with the U.S. Atomic Energy Commission and in collaboration with the Sandia Corporation, Albuquerque, New Mexico, began a study to evaluate the possibility of ground-water contamination by a SNAP (Systems for Nuclear Auxiliary Power) system. The system is in effect a thermo-electric generator that utilizes a radioactive material as its power source. Some orbiting satellites carry this type of power generator.

The SNAP project seeks to define certain aspects of radioactive contamination of ground water that could result if a SNAP system should accidentally plummet to and become buried in the earth's surface. The Geological Survey's responsibility is to develop or recommend equations for use in predicting, within an allowable degree of accuracy, the concentration of an ion in the ground-water environment as a function of time and distance. The Sandia Corporation contracted Dr. M. C. Schroeder of Texas A&M Research Foundation to obtain ion-exchange column data and distribution coefficients that could be used to test the suitability of the equations developed by the Geological Survey. In addition, to support the Sandia safety program the Geological Survey has finished a study on the geology, soil, and climate at specific points throughout the world (Ruane et al, 1967).

This summary report on SNAP describes the Geological Survey's work from December 1, 1966, through November 30, 1967. Three quarterly reports to Sandia in 1967 described the short-term progress of the study.

The project has developed into a comprehensive study of the dynamic ion-exchange characteristics of saturated porous aquifers. Some of the mechanisms of ion exchange have been discussed as background material, but the work has been mainly quantitative in nature. The study has relied heavily on formal analytical methods and computer solutions of numerical finite-difference equations.

A general equation was derived and tested for the one-dimensional transport of ions in water-saturated porous media which includes three transport components--mass fluid flow, hydraulic dispersion, and ion-exchange. Three conceptual models of the ion-exchange process were evaluated and the one best suited to the overall flow model was adapted to the equation. The general flow equation was solved numerically with the aid of a digital computer. The relative influences of various components in the equation were evaluated. Validity, limitations, and improvements of the equation were evaluated. The course of future studies is discussed.

This report concerns itself with the flow and the exchange of "trace" amounts of ions in aquifers and columns. If the concentration of the ion under study is low in relation to the concentration of the other ions in solution, certain assumptions simplifying the computations necessary for a satisfactory solution can be made. The assumption that the porous media are homogeneous and isotropic are recognized as non-ideal but do not, in the author's opinion, form a serious limitation to the applications of the methods suggested.

The author has attempted a logical approach to the problem's solution. By building up and adding to the preliminary equations he has developed expressions that should adequately describe the ion-exchange process. These equations can be solved by analytical or by numerical means and can be compared with data obtained from laboratory experiments.

The author expresses his gratitude to the many individuals who contributed technically and administratively to the results of this study. Particular thanks to R. E. Smith, Dr. J. Yguerabide, and Dr. R. Sallach of Sandia Corporation; Dr. M. C. Schroeder of Texas A&M Research Foundation; and W. A. Beetem, B. P. Robinson, and S. W. West of the U.S. Geological Survey. Recognition is also accorded to Dr. R. W. Witters, of the U.S. Geological Survey's Computer Division, who wrote the computer programs used in this report.

FLOW THROUGH POROUS MEDIA

The continuity equation is used to define the flow or convective transport of fluids through porous media. Hydraulic dispersion results in a variation of flow patterns and can be an important aspect of ion transport and dilution. These two factors, convective transport and hydraulic dispersion, are discussed in the following two sections. Equations that define the flow of a non-exchanging ion as it is transported through a porous medium will be developed.

Convective transport

The convective transport of an ion, by an incompressible fluid flow through a porous medium, can be described in terms of an elemental cube having the dimensions dx , dy , dz .

If u , v and w are the velocities along the x , y and z axes respectively, c the ion concentration per unit volume, and ϵ the porosity, the input and output per unit time are

$$\text{Input} = u\epsilon dydz + v\epsilon dx dz + w\epsilon dx dy \quad (1)$$

$$\text{Output} = \text{Input} + \frac{\partial}{\partial x}(u\epsilon dx dy dz) + \frac{\partial}{\partial y}(v\epsilon dx dy dz) + \frac{\partial}{\partial z}(w\epsilon dx dy dz). \quad (2)$$

The net change of mass in the cube is

$$\frac{\partial}{\partial t}(c\epsilon dx dy dz) = \text{Input} - \text{Output} = - \left[\frac{\partial}{\partial x}cu + \frac{\partial}{\partial y}cv + \frac{\partial}{\partial z}cw \right] \epsilon dx dy dz \quad (3)$$

therefore

$$\frac{\partial c}{\partial t} = - \frac{\partial}{\partial x}(cu) - \frac{\partial}{\partial y}(cv) - \frac{\partial}{\partial z}(cw) \quad (4)$$

and for unidirectional flow in the x direction, where $u = U$ is an average velocity, the equation reduces to

$$\frac{\partial c}{\partial t} = - U \frac{\partial c}{\partial x} \quad (5)$$

When the initial and boundary conditions

$$\begin{aligned} c(x, 0) &= 0, \quad x \geq 0 \\ c(0, t) &= c_0, \quad t \geq 0 \end{aligned}$$

are imposed, the solution to this equation is

$$\frac{c}{c_0} = f(t - x/U) \quad (6)$$

where

$$f(z) = \begin{cases} 0, & z < 0 \\ 1, & z > 0 \end{cases}$$

If a pulse of tracer material is introduced into the system, during time Δt , the solution is

$$\frac{c}{c_0} = f\left(t - \frac{x}{U}\right) - f\left(t - \frac{x' + U\Delta t}{U}\right) \quad (7)$$

Figure 1 is an idealized plot representing a concentration profile of the effluent from a column that has been continuously charged with a tracer material. Figure 2 represents effluent from an identical column, but the tracer material has been injected as a slug or pulse of finite width. These effluent breakthrough curves represent the respective solutions to equations 6 and 7. Effluent or breakthrough curves such as these are never obtained in actual practice owing to ion exchange, adsorption, dispersion, diffusion, and lack of true homogeneous media. However, in the absence of these natural phenomena they do illustrate how ions might flow through porous media.

Dispersion processes

The velocity of a microscopic water particle varies during its flow through porous media. This variation resembles that observed during the laminar flow of a fluid in a tube where a parabolic velocity distribution occurs in the fluid between the wall and the center of the tube. Velocity gradients develop around particles in the same manner. This velocity distribution and the random path taken by the fluid disperses water particles and ions laterally and longitudinally as the tracer solution travels through porous media. These effects have been termed "hydraulic dispersion." Hydraulic dispersion should not be confused with molecular diffusion which is related to relative ion mobilities. The streamlines of flow through a porous medium (fig. 3) illustrate the dispersion process. These velocity variations and random paths tend to cause a concentration gradient in a tracer front unlike the sharp fronts of figures 1 and 2. Typical breakthrough curves from columns with dispersion are shown as figures 4 and 5 for continuous and pulse feed respectively.

Figure 1. Ideal breakthrough curve with continuous feed

Figure 2. Ideal breakthrough curve with pulse feed

Figure 3. The dispersion of water in porous media

Figure 4. Breakthrough curve with dispersion and continuous feed

Figure 5. Breakthrough curve with dispersion and pulse feed

Although hydraulic dispersion differs from molecular diffusion, the analogy to Ficks diffusion equation has been used to express its results quantitatively. Raffi and others (1956) used this analogy to describe the rate of ion transfer due to dispersion, as

$$J = - D \frac{\partial c}{\partial x}, \quad (8)$$

where D is the coefficient of dispersion and J the rate of transfer.

By mass conservation, taking dispersion into account, assuming unidirectional flow, and considering only longitudinal dispersion the transport equation becomes

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - U \frac{\partial c}{\partial x}. \quad (9)$$

The initial and boundary conditions are given by

$$c(0, t) = c_0, \quad t \geq 0$$

$$c(x, 0) = 0, \quad x > 0$$

$$c(\infty, t) = 0, \quad t \geq 0$$

and the approximate solution of the differential equation is

$$\frac{c}{c_0} = \frac{1}{2} \left[1 - \operatorname{erf} \frac{x - Ut}{2 \sqrt{Dt}} \right]. \quad (10)$$

This error function form of the dispersion equation has been obtained by many and is thoroughly discussed by Raffi and others (1956).

The longitudinal dispersion coefficient D is characterized by a dispersion constant D_m and is a linear function of velocity, equal to $D_m U$. D_m can be evaluated from experimental breakthrough curves of nonadsorbing tracer materials (Raffi and others, 1956). If a pulse of tracer material is moving through a porous media, the concentration relationship formed because of dispersion can be expressed as

$$\frac{c}{c_0} = \frac{1}{2} \left[\operatorname{erf} \frac{x - Ut'}{2\sqrt{Dt}} - \operatorname{erf} \frac{x - Ut}{2\sqrt{Dt}} \right] \quad (11)$$

where t' is $(t - \Delta t)$ and Δt is the time necessary for the fluid to flow one pulse width (Lapidus and Amundson, 1952).

ION EXCHANGE

Ion exchange has long been utilized for the purification or isolation of materials not easily separated by other chemical methods. It is useful in the natural purification of contaminated waters and increased interest has developed in this particular field. The release of radionuclides into the ground-water system by underground nuclear explosions and the effect of adsorption on these radionuclides by earth minerals is of prime interest to the Atomic Energy Commission. The Geological Survey, in cooperation with the Atomic Energy Commission, is involved in several studies related to this possibility. Robinson (1962) prepared a comprehensive literature survey of ion-exchange minerals and disposal of radioactive wastes during the initial phases of this study.

The ion-exchange process has been studied by several methods. The two basic methods have been: (1) to assume thermodynamic equilibrium between the exchanging ions or (2) to assume nonequilibrium conditions, which would necessitate consideration of the kinetic effects. Somewhat intermediate between these two methods is the assumption of a number of theoretical plates or reaction units. This method of study assumes that equilibrium is reached on each plate, but the kinetics of the reaction govern the number of plates required. The theoretical plate method of

analyzing the exchange process requires that there be a linear relationship between the concentration of the ion on the exchanger and in solution. This requirement does not hinder the present phase of the Geological Survey studies but such equations do not apply when high concentrations of exchanging ions are present. Molecular diffusion and hydraulic dispersion may also play an important part in the ion-exchange process. These are covered briefly in the section Exchange processes, which follows the next section, Mechanism.

Mechanism

Three theories used to explain the mechanism of ion exchange are: the crystal lattice theory, the double-layer theory, and the Donnan membrane theory.

The crystal lattice theory considers the constituents of the lattice to be present as ions instead of molecules; an ionic solid is therefore considered to be completely dissociated. The ion exchange takes place when the forces binding the ion to the crystal are diminished to such a degree that this ion can exchange for another ion, or react with another ion in solution. The exchange of ions then depends upon the (1) nature of the forces binding the ion to the crystal, (2) concentration of the exchanging ion, (3) charge of the exchanging ion, (4) sizes of the two ions, (5) accessibility of the lattice ions, and (6) solubility effects.

The double-layer theory proposed by Helmholtz (1879) and later modified by Gouy (1910) and Stern (1924) assumes a fixed inner electrical layer on the surface of a colloid with a diffuse and mobile outer layer of charges. The diffuse outer layer extends into the solution. Ion exchange taking place by a change of ion concentration in the external solution upsets the equilibrium. Ions then migrate to or from the diffuse outer layer in a stoichiometric reaction causing the exchange to occur.

The Donnan theory of ionic exchange is a special case of the Donnan membrane theory. The interface between the solid and liquid phase is considered as a membrane. If the principle of electro-neutrality is obeyed, then exchange of ions takes place until the concentration ratios are equal in both phases. The Donnan theory explains the (1) inability of electrolytes to enter the resin phase of resins having a high exchange capacity, (2) effect of valency, (3) effects of solution volume and electrolyte concentration, and (4) effect of the fixed-ion concentration of the resin phase.

These three similar theories satisfy the principle of electro-neutrality. They differ in the position and the origin of the exchange site.

The affinity and the selectivity of resins for ions are primarily dependent on the following factors (Helfferich, 1962): (1) The ion exchange prefers the competing ion of higher valence, (2) this preference increases with dilution of the solution and is strongest with ion exchangers of high internal molality, and (3) the ion exchanger prefers the ion with the smaller solvated equivalent volume. Figure 6 is a reproduction of Jenny's plot (Kunin, 1958) on the relative degree of ion exchange in clay as a function of unsolvated ionic radius. The unsolvated ionic radius is inversely proportional to the solvated radius.

Exchange processes

Ion exchange has been explained quantitatively by relating it to surface adsorption phenomena. Freundlich and Langmuir isotherms and equations have been developed to the point where they can be used to relate certain ion exchange reactions. The most widely used equation is the mass action relationship (Selke, 1956). It can be developed to a very sophisticated degree through the use of fundamental thermo-

Figure 6.--Effect of ionic radius on ion exchange in clay. After Jenny (1932).

dynamics and statistical mechanics. The use of this technique can be illustrated by the strontium-calcium ion-exchange reaction

that results in the equilibrium relationship

$$K = \frac{(\text{SrX}_2) \gamma_{\text{SrX}_2} (\text{Ca}^{++}) \gamma_{\text{Ca}^{++}}}{(\text{CaX}_2) \gamma_{\text{CaX}_2} (\text{Sr}^{++}) \gamma_{\text{Sr}^{++}}} \quad (13)$$

The concentration of ion on the resin is expressed as meq/g of resin and the concentration of the ion in solution as meq/l. The gammas represent activity coefficients; and if they can be assumed equal, they cancel and give the following relationship for an equilibrium constant K_c .

$$K_c = \frac{(\text{SrX}_2) (\text{Ca}^{++})}{(\text{Sr}^{++}) (\text{CaX}_2)} \quad (14)$$

The ratio of the amount of ion on the solid (SrX_2) and in the liquid phase (Sr^{++}) is referred to as the distribution coefficient, or K_d (Mayer and Tompkins, 1947).

This coefficient is usually determined experimentally with the aid of the equation

$$K_d = \frac{f_s}{f_l} \cdot \frac{V}{M} \quad (15)$$

where f_s is the fraction of ions on the solid, f_l the fraction in the liquid, V the volume of the solution in ml, and M the mass of the solid in grams. If the ion is present in trace concentrations the distribution coefficient can be assumed constant and the effect of varying V/M is to

change the amount of ions on the solid or in the liquid (Baker and others, 1966). For example, if the distribution coefficient was 10, the fraction of ion on the solid for various V/M's would be approximately as follows:

V/M	0.1	1	10	100	1,000
Percent adsorbed	99	91	50	9.1	.99

Thus for large ratios of V/M, as occurs between sediments in streams, a low percentage of the ion may actually be on the sediment (although the concentration may be quite high). In soils, whose porosity is seldom more than 50 percent, most of the ions in ground water will certainly be adsorbed on the soil.

When the concentration of a particular ion in solution is a trace quantity, the average rate of flow of ions in the ground-water environment can be expressed as

$$U_{\text{ion}} = U_{\text{water}} \left(\frac{1}{1 + K_d \rho_e} \right) \quad (16)$$

where ρ_e is the exchange ratio, defined as bulk density of the solid divided by porosity. The fraction of the ions in solution is

$$\frac{1}{(1 + K_d \rho_e)}$$

The distribution coefficient can then be determined through the use of column studies as well as static laboratory experiments. Experimentally determined distribution coefficients compare favorably with those determined from column studies (Schroeder and Jennings, 1963).

The distribution coefficient is related to the various competing ions, the equilibrium constant, and the cation-exchange capacity of the soil. The coefficient was previously defined as the ratio of the amount of ions on the solid (in meq/g) to the amount in solution. The K_d for the previously described strontium reaction is

$$K_d = \frac{SrX_2}{Sr^{++}} \quad (17)$$

Equation 14 then reduces to

$$K_c = K_d \frac{Ca^{++}}{CaX_2} \quad (18)$$

The cation exchange capacity of a material, Q , represents the amount of cations that the resin can hold and, for a system containing only strontium and calcium represents the sum of amount of strontium and calcium adsorbed on the surface,

$$Q = SrX_2 + CaX_2 \quad (19)$$

Equations 18 and 19 can be reduced to

$$K_d = \frac{Q}{Sr^{++} + \frac{Ca^{++}}{K_c}} \quad (20)$$

which defines the distribution coefficient for strontium with calcium as a competing cation (Wahlberg and Fishman, 1962). The concentrations of strontium and calcium are those in solution at equilibrium. This equation shows why K_d is independent of strontium at low strontium concentrations. If, however, the amount of strontium increases beyond trace conditions, and the calcium content remains constant, the distribution coefficient decreases. However, the reaction in the column is an exchange reaction; strontium exchanges for the calcium or vice versa. Therefore, as the amount of strontium in solution is adsorbed by the resin, the calcium concentration must be increased an equivalent amount.

The distribution coefficient then depends on the equilibrium constant. If the equilibrium constant is less than 1, a slight increase in the calcium will be magnified and may considerably decrease the distribution coefficient. If the equilibrium constant is greater than 1, an increase in the calcium content will have a less pronounced effect.

The use of the equilibrium constant, K_c , as defined by equation 14, to calculate the distribution coefficient also causes some problems. This equilibrium constant is based on concentrations and not activities and has been said to be dependent on the actual solution concentration (Kunin, 1958). The relationship of K_c to solution concentration must then be determined to insure a proper evaluation of K_d .

Equilibrium concept

The previous section illustrated the use of the equilibrium constant for the mass action approach to a typical ion-exchange reaction. The equilibrium approach to ion exchange assumes that instantaneous equilibrium is realized at all times during the ion-exchange process. Perhaps DeVault (1943) made the most thorough examination of this process. He characterized favorable, unfavorable, and linear adsorption isotherms and developed equations to quantify their meaning. The isotherm is a plot of the equilibrium relationship of the concentration of ion on the solid and the concentration of ion in solution. The concentration of ion on the solid is plotted as the ordinate and the concentration in solution plotted as the abscissa. Favorable equilibrium is assumed when the isotherm is convex upward and unfavorable equilibrium when the curve is concave upward. The linear isotherm is self defined. For fixed-bed or column adsorption, favorable equilibrium leads to a sharp-leading concentration profile and a diffuse-trailing profile for a slug injection into a column. Unfavorable equilibrium has the reverse effect. A diffuse leading edge is contrasted by a sharp trailing edge. Linear isotherms produce no change in the concentration profile of the input pulse. If the concentration of the exchanging ion is very small with

respect to the total solution concentration (at least an order of magnitude less) the isotherm is usually linear. For many water pollution problems, the contaminant is present in trace concentrations; thus allowing the simplifying assumption of a linear isotherm. If dispersion and diffusion can be neglected, the ions will move through the column with their initial concentration profile but at a retarded velocity. The distribution coefficient can then be used to calculate this retarded velocity.

The advantages of the equilibrium concept are numerous. The only variables necessary for use of this method are those used to calculate the distribution coefficient; the equilibrium constant, the cation exchange capacity of the exchanging medium, and the concentration of the ions in solution. These are either known, may be estimated or can be experimentally determined in the laboratory. The equilibrium concept has been widely used for hazard predictions for possible ground-water contamination following nuclear detonations in saturated media.

The disadvantage is that equilibrium may not actually occur. The usual justification is that the results obtained by this method would be conservative in nature, that is the concept would predict higher concentrations than would probably occur. Even though the maximum concentration predicted by this method would be higher than that predicted by any other method, a low kinetic rate constant could allow a front of relatively high concentration to move far out ahead of that predicted by the equilibrium method. The possibility of high ionic concentrations that would not allow the use of a retardation factor would of course negate the simplification possible with this entire approach.

Theoretical plate concept

The theoretical plate concept assumes that the column or soil section is divided into several units or plates. The exchangeable

ion of interest travels down the column, passing through each plate in series, from top to bottom. Chemical equilibrium is assumed to take place on each plate and the effluent concentration at the bottom of the column is dependent on the number of plates and the exchange capacity of the resin or soil on or comprising each plate or unit. The more plates the better the exchange. As the number of plates increases without limit the effluent concentration breakthrough curve becomes identical to the shape derived for the previously discussed equilibrium concept of ion exchange.

Mayer and Tompkins (1947) developed a method that uses the binominal distribution to relate the concentration profile of the effluent of a liquid chromatographic column to the number of theoretical plates. Their method assumes complete equilibrium on each plate. The number of plates necessary to predict the concentration of the pulse eluted from the column can be calculated if the position and the maximum concentration of the breakthrough curve are known. Glueckauf (1955) later pointed out that the Mayer and Tompkins model is not valid for continuous operation because it assumes discrete steps from plate to plate and is therefore a discontinuous model. He then derived the correct expression for the theoretical-plate exchange concept in terms of relative error functions. Even though this shortcoming exists, many investigators still use the relatively simple Mayer and Tompkins model. Perhaps Said (1956) developed the simplest, yet most precise, use of the theoretical plate concept in chromatography. A discussion of the derivation and use of this technique follows.

An assumed chromatographic column consists of N theoretical plates and contains S grams of adsorbent. The assumed initial conditions on plates 1, 2, 3, ..., n , ..., N are $y_1^0, y_2^0, y_3^0, \dots, y_n^0, \dots, y_N^0$, where y is the concentration of solute (exchanging ion) in the solid phase on the plate. The subscript represents the plate number and the superscript the time. The ratio of the weight of solute per gram of elutant

to weight of solute per gram of adsorbent is always constant. This constant, k , is the same as the reciprocal of the distribution coefficient, $(1/K_d)$, developed by Mayer and Tompkins and described previously. If the weight of elutant that has crossed the plate at any time is denoted by w , then a differential material balance around plate 1, after Said (1956) gives

$$ky_1 dw = - \frac{S}{N} dy_1 \quad (21)$$

let $x = \frac{\text{weight of elutant that has crossed the plate}}{\text{weight of adsorbent on one plate}}$, then $w = \frac{Sx}{N}$.

Applying the initial conditions, when $x = 0$, $y_1 = y_1^0$, the solution to the differential equation becomes

$$y_1 = y_1^0 e^{-kx} \quad (22)$$

The concentration on any plate n is shown (Said, 1956) to be

$$y_n = e^{-u'n} \sum_{r=1}^{n} y_r^0 \frac{u'^{n-r}}{(n-r)!} \quad (23)$$

where u' denoted k_x . This equation expresses the solute concentration on any plate n in the column after an amount of elutant equal to x units (unit is equal to weight of adsorbent on one plate) has passed through the plate.

Mayer and Tompkins assumed that the first plate contained all of the solute. For this condition equation 23 reduces to

$$y_n = y_1^0 e^{-u'} \frac{u'^{n-1}}{(n-1)!} \quad (24)$$

or

$$\frac{y_n}{y_1^0} = e^{-u'} \frac{u'^{n-1}}{(n-1)!} = \phi_{n-1}^{u'} \quad (25)$$

which is a Poisson distribution function.

The maximum concentration of the pulse reaches the bottom plate of the column after u' units of elutant, equal to $N-1$, have crossed the bottom plate and

$$R_N^{u' \max} = \frac{e^{-(N-1)} (N-1)^{(N-1)}}{(N-1)!} \quad (26)$$

where

$$R_N^{u' \max} = \left(\frac{y_n}{y_1^0} \right)_{\max} \quad (27)$$

When the total number of plates, N , is large, this maximum concentration can be approximated by the equation

$$R_N^{u' \max} \cong \frac{1}{\sqrt{2\pi N}} \quad (28)$$

Said also investigated the condition when the solute is evenly distributed in a zone at the top of the column in M theoretical plates. The concentration on any plate n in the column for this condition is

$$R_n = P_{n-M}^{u'} - P_n^{u'} \quad (29)$$

where P denotes the Poisson cumulative distribution function.

The distribution of a zone deposited at the top of the column is given by

$$R_n^0 = P_n^{u'0} \quad (30)$$

when the solute concentration is initially zero at any point in the column.

Given this initial distribution ratio the intensity distribution of any zone after the passage of u units of elutant is

$$R_n = P_n^{u'+u'_0} - P_n^{u'} \quad (31)$$

These formulas are very simple to use and their derivation is implicitly correct. Tables for the Poisson distribution functions are available from standard references (Molina, 1943). However, the formulas must be used with linear adsorption isotherms. Also, an estimate of the total number of plates must be initially available.

The usefulness of the theoretical plate approach will be demonstrated in a later section using data derived from column experiments.

Kinetic concept

Thomas (1948) gave the first complete treatment of chromatography as a problem in kinetics. Heister and Vermeulen (1952), Vermeulen and Heister (1952), Heister and others (1954), and Vermeulen (1958) expanded this major contribution to the explanation of ion exchange until it now rests in a very acceptable form. The development of this method for trace conditions follows.

In the general exchange reaction

assumed trace ion A and gross ion B have the respective valence α and β . The equilibrium constant for the exchange is given by

$$K_c = \frac{\left(\frac{q_A^*}{c_A} \right)^\beta c_B^\alpha}{c_A^\beta \left(\frac{q_B^*}{c_B} \right)^\alpha} \quad (33)$$

For these two equations q^* is the concentration of ion A or B on the solid in equilibrium with the liquid and c is the concentration of ion A or B in solution.

The distribution coefficient defined by Vermeulen is

$$D_A = q_A^* \frac{\rho_b}{c_A \epsilon} \quad (34)$$

and is a ratio of the solute concentration on the solid to that in the liquid phase. It is equivalent to the normally encountered $K_d \rho_e$ term described previously. The bulk density of the solids in the column is represented by ρ_b and the porosity by ϵ . This ratio, ρ_b/ϵ , is commonly defined as ρ_e , the exchange coefficient.

The relationship between the distribution coefficient and the equilibrium constant is

$$D_A \frac{\epsilon}{\rho_b} = \frac{q_A^*}{c_A} = \frac{K_c^{1/\beta} (q_B^*)^{\alpha/\beta}}{c_B^{\alpha/\beta}} \quad (35)$$

When trace conditions exist and if all exchanging ions are of the same valence, equation 35 can be written as

$$D_A \frac{\epsilon}{\rho_b} = K_d = \frac{K_c Q}{C_o} \quad (36)$$

where Q is the exchange capacity of the resin and C_o is the total ionic concentration in solution.

If the solid resin phase is not a gel through which colloid diffusion is possible, the exchange of ions is probably controlled by the following processes:

1. The diffusion of ions A and B through the fluid film surrounding the resins and into resin pores of the solid.

2. The reaction at the surface of the solid when ion A displaces ion B.

The surface reaction is assumed to be instantaneous; therefore, initial diffusion reaction will be controlling. The rate equation for the exchange of ions diffusing through the fluid film and into the pores is

$$\frac{dq_A}{dt} = \frac{k\epsilon}{\rho_b} \left(c_A - \frac{C_o q_A}{K_c Q} \right) \quad (37)$$

where k denotes the applicable rate constant (Vermeulen and Heister, 1952). For the flow of ions through a fixed bed this resulting equation is solved with the appropriate conservation equation and the solution is

$$\frac{c_A}{(c_A)_0} = J(N_R, ZN_R) \quad (38)$$

where $J(s, t) = 1 - \int_0^s e^{-t-\xi} I_0(2\sqrt{t\xi}) d\xi$, I_0 is a modified Bessell function of the first kind and zero order, N_R is the number of reaction units and is related to the rate constant or the number of theoretical plates, and Z is the throughput ratio, a value that reaches unity when the amount of feed passing through the column becomes stoichiometrically equivalent to the exchange capacity of the column. The throughput ratio is defined by the relation $Z = (V - v\epsilon)/D_A v\epsilon$ where V is the volume input to the column, v the volume of the column, ϵ the porosity, and D_A the product of the distribution coefficient K_d and the exchange ratio ρ_e .

When the ions are injected in pulse form and the adsorption isotherm is linear the relative concentration of the ions in the effluent concentration is the difference between the concentration curve for

saturation starting at $Z = 0$ and a second curve representing a non-existent saturant starting at $Z' = 0$. This was demonstrated by Vermeulen and Heister (1952) to be

$$\frac{c}{(c_A)_0} = J(N_R, ZN_R) - J(N_R, Z'N_R). \quad (39)$$

An approximation to this solution, derived by Vermeulen (1958) when the difference between Z' and Z is small is

$$\frac{c}{(c_A)_0} = \frac{Z_{\text{sat}} \sqrt{N_R}}{2 \sqrt{\pi}} e^{-(N_R/4)(Z-1)^2} \quad (40)$$

Z_{sat} is the difference between Z' and Z , and equal to $V_{\text{sat}}/D_{\text{Ave}}$, where V_{sat} is the volume of the initial ionic pulse added to the column.

The peak of the breakthrough curve occurs when $Z = 1$ and is

$$\frac{c}{(c_A)_0} = \frac{Z_{\text{sat}} \sqrt{N_R}}{2 \sqrt{\pi}} \quad (41)$$

The relation between N_R , the number of reaction units, and N , the number of theoretical plates, is approximately

$$N_R = 2N \quad (42)$$

This point will be illustrated more fully in the section General data correlation method.

Knox (1964) in his analysis of the flow of ions through porous media also uses an equation of the form

$$\frac{dm}{dt} = q_1 c - q_2 m \quad (43)$$

where q_1 and q_2 are constants, m the concentration of ion on the solid,

and c the concentration of ion in solution. When equilibrium is attained, the rate of reaction is zero and $q_1 c = q_2 m$. Through the use of the distribution coefficient, where $K_d = m/c\rho_e$, Knox writes $K_d\rho_e c = m$ and assumes during equilibrium conditions, when $dm/dt = 0$, that $q_1 = K_d\rho_e$ and $q_2 = 1$. Equation 43 then can be written as

$$\frac{dm}{dt} = 0 = K_d\rho_e \left(c - \frac{m}{K_d\rho_e} \right). \quad (44)$$

Knox then assumes that this rate equation, derived on an equilibrium basis, will hold for dynamic conditions. Although Knox has had some success using this formula, this author has some doubts to the acceptability of the technique as two independent equations do not seem available to solve for q_1 and q_2 .

The similarity between equation 37 and that used by Knox can be shown as follows. From equation 37 the substitution $q_A = m/\rho_e$, $\rho_e = \rho_b/\epsilon$ and $K_d = K_c Q/C_0$ leads to the equation

$$\frac{dm}{dt} \cdot \frac{1}{\rho_e} = \frac{k}{\rho_e} \left(c - \frac{m}{K_d\rho_e} \right), \quad (45)$$

or the kinetic rate constant used by Vermeulen is equal to $K_d\rho_e$ used by Knox. The kinetic rate constant is related to the number of reaction units and can be calculated by

$$k = N_R \frac{U}{h} \quad (46)$$

where h is the height of the column.

Longitudinal dispersion

The effect of longitudinal dispersion in aquifer systems is difficult to predict. Longitudinal dispersion constants determined in laboratory experiments or through empirical or theoretical equations often have no relationship whatsoever to dispersion constants determined

by actual field experiments. Differences of as much as three orders of magnitude have been reported (C. V. Theis, personal communication). The reason for this anomaly is that the calculations attempt to treat highly nonuniform aquifers as uniform homogeneous systems. Highly uniform systems, such as laboratory columns containing uniform particles are amenable to analytical treatment. The dispersion constant, D_m , is near $2d_p \epsilon$ for laminar flow with spheres of particle diameter d_p (Vermeulen, 1958). The use of this equation to calculate D_m was quite successful to describe column dispersion characteristics reported later in this report.

General data correlation method

Heister and others (1954) developed a general correlation equation to predict ion-exchange reaction rates or reaction units for various commercial ion-exchange resins.

The equation consists of an internal and external-diffusion resistance. Under linear-equilibrium conditions these resistances are added and combined by the equation

$$\frac{1}{k} = \frac{1}{k_f a_p} + \frac{1}{k_p a_p D_A} \quad (47)$$

where k is the kinetic rate constant of the overall reaction, k_f the rate constant for external diffusion, k_p the rate constant for internal diffusion, and a_p the surface area per unit volume of material.

For the exchange of trace quantities the equation is

$$\frac{D_A D_p a_p}{d_p k} = \beta_1 D_A \frac{D_p}{D_A} \left(\frac{D_f}{d_p U} \right)^{\frac{1}{2}} + \beta_2 \quad (48)$$

where β_1 is $\epsilon/6(1-\epsilon)0.38$ and β_2 is $(1-\epsilon)/10$. D_f represents the liquid-phase diffusion coefficient and D_p the coefficient for diffusion into the resin pores. The liquid-phase diffusion coefficient can be calculated from physico-chemical tabulations; but D_p is more difficult to

estimate and usually must be obtained from experiments with the particular exchanging resin. The rate constant for external diffusion, k_f , can be written

$$k_f = 0.38U \left(\frac{U\epsilon}{a_p D_f} \right)^{-\frac{1}{2}} \quad (49)$$

for internal diffusion, k_p , written

$$k_p = \frac{60D_p}{a_p d_p^2} \quad (50)$$

as given by Vermeulen (1958).

Previous studies by M. C. Schroeder and Jennings (1963) for the University of California included numerous column studies for the exchange of trace amounts of ions introduced into the column in pulse form. Using the method developed by Thomas (1948), the author attempted to predict these curves. Since the distribution coefficient was known, and the equilibrium constant could be calculated, the only unknown in the equation was the overall rate constant. As the first approximation, the ion exchange was assumed to be a surface phenomenon. Using equation 49, the kinetic rate constant was calculated. This value was much greater than the value computed from equation 46 after N_R was calculated from equation 41. The assumption that pore diffusion controlled the ion-exchange reaction followed. Unfortunately, the coefficient for diffusion into the pores could not be calculated. Equation 48 was then used to determine this diffusion coefficient after N_R had been calculated from equation 41 and k calculated from equation 46. The pore diffusion coefficient for 45 column experiments involving microcline was calculated by this method. For any one particular set of conditions, this value was reasonably constant but varied when the column characteristics were changed. According to the analytical model, all the variables should be accounted for; but, evidently due to experimental error or model inaccuracies, a consistent set of pore diffusion coefficients was not found. In several of the experiments, the

distribution coefficient was independent of particle size. This compares unfavorably with results obtained when the static K_d 's were determined.

GENERAL EQUATION

Flow, dispersion, and exchange reactions of ion species as they flow through porous media are a combination of the variables previously discussed. Development of a general equation suitable for all conceivable conditions does not seem possible. However, the development of equations for special conditions is possible and will be attempted during the course of this study. The general equation for three-dimensional flow is

$$\frac{\partial c}{\partial t} = -u \frac{\partial c}{\partial x} - v \frac{\partial c}{\partial y} - w \frac{\partial c}{\partial z} + D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} - \frac{\partial m}{\partial t} \quad (51)$$

where $\partial m / \partial t$ is the rate of ion exchange and can be expressed as equation 45. For the case of unidirectional flow, equation 51 reduces to

$$\frac{\partial c}{\partial t} = -U \frac{\partial c}{\partial x} + D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} - \frac{\partial m}{\partial t} \quad (52)$$

If the rate of adsorption $\partial m / \partial t$ is expressed correctly the solution of equation 52 should predict the concentration of an ionic specie at any point in space and at any time. Equation 52 can be further reduced when hydraulic dispersion in the y and z direction is small enough to be neglected. The equation then reduces to the form

$$\frac{\partial c}{\partial t} = -U \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} - \frac{\partial m}{\partial t} \quad (53)$$

This equation is identical with that derived by Knox (1964). Knox compared his theoretical model to column experiments by M. Schroeder at Texas A&M Research Foundation. The correlation between theory and column experiments was usually within 10 percent.

If the rate equation takes the form of equation 45, the following equation results

$$\frac{\partial c}{\partial t} = - U \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} - k \left(c - \frac{m}{\rho_e K_d} \right) \quad (54)$$

Equations 38 and 39 are solutions to equation 54 for continuous and pulse flow in the absence of dispersion. The following sections present numerical-methods solutions to the equation.

NUMERICAL SOLUTIONS FOR THE GENERAL EQUATION

As with many partial differential equations, the solution becomes quite complicated unless simplifying assumptions can be made. If the exchangeable ion in question has a linear adsorption isotherm (i.e., present in trace concentrations) and the effect of dispersion is neglected equation 54 can be solved in closed form. Such limiting assumptions defeat the purpose of this study. However, an approximate solution to equation 54 (without assumptions) can be obtained by numerical analysis.

This approach to partial differential equations is similar to the numerical solution of ordinary differential equations. The derivatives in the equation are replaced by finite difference ratios and the equation then becomes a difference equation.

In many solutions the computations necessary to solve the difference equation may be less than those necessary to solve the equation through formal mathematics. This condition may be true because many of the solutions of partial differential equations result in infinite series that must be evaluated numerically. Equation 54 may be in this category. Ogata (1964) has solved the equation but the result is still in very complicated integral form that must again be evaluated numerically.

Finite difference equation

The equation to be solved is usually expanded into a series expression such as the Taylor's series (Mickley, et al, 1957). This series is

$$y = f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(x_0)}{n!} (x-x_0)^n \quad (55)$$

For equation 53, since $c = f(x,t)$, the $f(x,t)$ can be expanded about t for a fixed value of x

$$c(x,t+\Delta t) = c(x,t) + \frac{\partial c}{\partial t} \Delta t + \frac{\partial^2 c}{\partial t^2} \frac{\Delta t^2}{2} + \frac{\partial^3 c}{\partial t^3} \frac{\Delta t^3}{6} + \dots \quad (56)$$

If Δt is chosen sufficiently small, the terms Δt^2 and higher can be neglected and the following equation can be obtained

$$\frac{\partial c}{\partial t} = \frac{c(x,t+\Delta t) - c(x,t)}{\Delta t} = \frac{c_{x,t+1} - c_{x,t}}{\Delta t} \quad (57)$$

Then for a fixed value t , the expansions of $c(x,t)$ are

$$c(x+\Delta x,t) = c(x,t) + \frac{\partial c}{\partial x} \Delta x + \frac{\partial^2 c}{\partial x^2} \frac{\Delta x^2}{2} + \frac{\partial^3 c}{\partial x^3} \frac{\Delta x^3}{6} \quad (58)$$

and

$$c(x-\Delta x,t) = c(x,t) - \frac{\partial c}{\partial x} \Delta x + \frac{\partial^2 c}{\partial x^2} \frac{\Delta x^2}{2} - \frac{\partial^3 c}{\partial x^3} \frac{\Delta x^3}{6} \quad (59)$$

Summing 58 and 59 gives

$$\frac{\partial^2 c}{\partial x^2} = \frac{c(x+\Delta x,t) - 2c(x,t) + c(x-\Delta x,t)}{\Delta x^2} \quad (60)$$

The solution of derivative $\partial c / \partial x$ is similar to that of $\partial c / \partial t$

$$\frac{\partial c}{\partial x} = \frac{c(x+\Delta x, t) - c(x, t)}{\Delta x} - \frac{\partial^2 c}{\partial x^2} \frac{\Delta x}{2} = \frac{c(x+\Delta x, t) - c(x-\Delta x, t)}{2\Delta x} \quad (61)$$

By the same procedures, the rate of ion exchange $\partial m / \partial t$ is

$$- \frac{\partial m}{\partial t} = \frac{m(x, t-\Delta t) - m(x, t)}{\Delta t} \quad (62)$$

from which can be extracted the equation

$$m_{x,t} = m_{x,t-1} + \Delta t \left(\frac{\partial m}{\partial t} \right)_{x,t-1} \quad (63)$$

Equation 53 can now be written as a complete finite difference equation where the concentration c is replaced by the relative concentration $\eta = c/c_o$:

$$\begin{aligned} \eta_{x,t+1} = \eta_{x,t} - \frac{U\Delta t}{2\Delta x} (\eta_{x+1,t} - \eta_{x,t}) + \frac{D_m U \Delta t}{\Delta x^2} (\eta_{x+1,t} - 2\eta_{x,t} + \eta_{x-1,t}) \\ - \frac{1}{c_o} \left(\frac{\partial m}{\partial t} \right)_{x,t} \Delta t \end{aligned} \quad (64)$$

where

$$\frac{1}{c_o} \left(\frac{\partial m}{\partial t} \right)_{x,t} = k \left[\eta_{x,t} - \frac{m}{c_o} \frac{1}{K_d \rho_e} \right]$$

and

$$m_{x,t} = m_{x,t-1} + \Delta t \left(\frac{\partial m}{\partial t} \right)_{x,t-1}$$

Knox (1964) used a difference equation similar to equation 64 for his numerical solution of the same differential equation.

Stability and convergence requirements

One particular problem in the use of finite difference equations is the determination of the accuracy of the result. If the numerical method satisfies the two criteria, "stability" and "convergence", the accuracy can be determined by the number of increments used. Increased accuracy is achieved by increased labor or cost. The usual procedure is to employ two different size increments. If the difference between solutions is tolerable, the solution obtained using the smaller size increment is used.

The convergence criterion requires the numerical solution to approach the exact solution as the number of increments increases without bounds. If this criterion is not fulfilled, the numerical method is unsatisfactory.

The stability criterion requires that the error inherent to the numerical solution does not grow in size as the computation proceeds. This criterion is usually defined by a minimum number of increments and a specific relationship between them as set forth in the equation. Although convergence and stability requirements of linear partial differential equations with constant coefficients can be examined, non-linear equations such as those used in this study do not lend themselves to this type of examination. One must therefore proceed with caution during the analysis.

In applying the von-Neumann approach to computational stability, Knox (1964) learned that for equation 64 the following inequalities must be satisfied.

$$\frac{2U\Delta t}{\Delta x} \leq 1 \quad (65)$$

and

$$\frac{8D_n U \Delta t}{\Delta x^2} \leq 1 \quad (66)$$

These stability criteria were also used as stability requirements for this study.

ANALYTICAL SOLUTIONS TO THE GENERAL EQUATION

The sections that follow present calculations utilizing both the kinetic concept and the theoretical-plate concept and compares them to actual laboratory experiments.

Laboratory column experiment comparisons

To check the validity of his computer program, Knox (1964) used Schroeder's (1963) experiment no. 62, a cesium-potassium exchange reaction on 20-30 mesh microcline, to compare the theoretically calculated breakthrough curve with the experimentally determined curve. The feasibility of using the Heister-Vermeulen or Thomas kinetic model and Said's Poisson theoretical plate treatment to predict the concentration profile of the breakthrough curve was investigated in this same manner.

The following information was presented by Schroeder and Jennings (1963) concerning experiment no. 62.

<u>Physical properties</u>		<u>Chemical properties</u>	
Material	Microcline	Pulse solution	10 ml
Mesh	20-30	Ion	Cesium
Column height	30 cm.	Conc.	1×10^{-6} molar
Column volume	615 cc	Eluting solution	
Wt. of grains	893.5 g	Ion	Potassium
Grain vol.	349.0 cc	Conc.	2×10^{-2} molar

<u>Physical properties</u>		<u>Chemical properties</u>	
Bulk density	1.45 g/cc	Breakthrough curve	
Porosity	43.3%	Peak	3.75 pore vol.
Col. pore volume	266.0 ml	Centroid	5.00 pore vol.
Water velocity	10.2 cm/hr	Peak conc./pulse conc.	0.00912

Figure 7 compares breakthrough curves that were calculated using equations 29 and 40. The number of reaction units N_R was calculated by using the maximum relative concentration of the breakthrough curve in equation 41. This value, 11.8, was used for the Thomas kinetic plot, and according to equation 42 six theoretical plates were assumed for Said's Poisson distribution function plot. The distribution coefficient was calculated from the position of the experimental curve's centroid.

The asymmetric shape of the experimentally determined breakthrough curve indicates the possibility of a nonlinear adsorption isotherm (Vermeulen and Heister, 1952). The breakthrough curve predicted by the kinetic model and the Poisson distribution function appears earlier than actually occurs and terminates before column elution is complete. In the experiment, the molar concentration of cesium, the exchanging ion, was 10^{-6} and that of potassium, the eluting ion, was 2×10^{-2} . The concentration difference of more than four orders of magnitude indicates that trace conditions exist and that the adsorption isotherm should certainly be linear. Schroeder and Jennings (1963) noted that distribution coefficients determined by the desorption of ions from the resin were larger than those calculated by adsorption. The kinetics of adsorption and desorption are probably different. If one assumes a higher kinetic rate constant for adsorption and desorption, the predicted curves would correlate much better with the experimental data. However, this assumption seems to violate the usual rule that the rate constant varies directly with the distribution function. These unanswered questions illustrate the complexity of ion exchange in natural soils.

Figure 7--A comparison of experimentally and analytically determined breakthrough curves for a cesium-potassium ion-exchange system. (Experiment No. 62, Schroeder and Jennings, 1963)

Equations 29 and 40 probably predict a satisfactory effluent history of an ion exchange column. Both equations were derived on the assumption of a large number of plates or transfer units. Since this limitation was neglected in their use, the results may not be as accurate as desired.

Aquifer contamination predictions

The concentration of ions in an aquifer at a certain distance down-gradient and at a certain time can be calculated using equation 40. The height of a reaction unit, H_R , equals the length of the column divided by the number of transfer units. Thus, various column lengths correspond to downgradient distances and the throughput ratio Z corresponds to time. With these assumptions, equation 40 can be rearranged and written as

$$\eta = \frac{L}{2K_d\rho_e} \sqrt{\frac{1}{\pi x H_R}} \exp - \left[\frac{x}{4H_R} \left(\frac{Ut-x}{xK_d\rho_e} - 1 \right)^2 \right] \quad (67)$$

where L is the height or length of the input pulse or distance in the aquifer, H_R the height of a reaction unit, x the distance downgradient from injection point, U the velocity of the fluid, and t the time from initial injection. The relative concentration of ions in the fluid at a point 30 cm downgradient as a function of time using constants consistent with those used to plot figure 7 gave identical results.

COMPARISONS OF NUMERICAL SOLUTIONS TO LABORATORY RESULTS

An IBM 360 model 65 digital computer was used to solve the derived difference equations. Equation 64, derived by the use of Taylor's series, was used in all computations; however, comparative runs using the finite-difference equation developed by Knox (1964) also could have been used. Programs have been written for laboratory column experiments and for actual field conditions that could involve a variety of aquifers. During the numerical prediction process, the growth of parasitic waves during the convective transport process was discovered. This limits

the present computer programs to predictions over relatively short distances such as in column experiments. This unfortunate circumstance emphasizes the need for major changes in the computer programs or in the theoretical models used.

Breakthrough patterns from a laboratory ion-exchange column were determined for a variety of conditions. Two basic systems were investigated: a cesium-potassium system on microcline and a strontium-calcium system on microcline. The cesium-potassium system studied was used as a comparison for values generated by Knox (1964). The strontium-calcium system was also evaluated because it represents the ions that will be used in later tests for conditions whose concentrations cannot be expressed as trace quantities.

Figure 8 compares a numerically determined breakthrough curve with an experimentally determined curve for the previously discussed cesium-potassium ion-exchange system. As did the breakthrough curve calculated from the analytical equations; the numerically calculated curve arrived earlier than the experimental curve and did not have the long trailing edge observed experimentally. Kinetic rate constants used in the calculations were obtained from equation 46 and the number of reaction units necessary to this equation obtained from equation 41. Distribution coefficients used in these calculations were determined from the location of the centroid of the breakthrough curve. A kinetic rate constant of 4.00 and a $K_d\rho_e$ value of 4.00 were used for the calculations involving figure 8. A comparison of figure 7 and figure 8 indicates the similarity between the numerical prediction and the analytic results using the kinetic equation and the Poisson distribution.

Figure 9 shows the effluent breakthrough curve for a strontium-calcium system (Schroeder and Jennings, 1963, experiment no. 33). A $K_d\rho_e$ value of 19.5 and a kinetic rate constant of 5.25 were obtained from the experimental breakthrough curve. The numerical breakthrough

Figure 8.--A comparison of numerically and experimentally determined breakthrough curves for a cesium-potassium ion-exchange system. (Experiment No. 62, Schroeder and Jennings, 1963)

Figure 9 --A comparison of numerically and experimentally determined break-through curves for a strontium-calcium ion-exchange system.
(Experiment No. 33, Schroeder and Jennings, 1963)

curve again agrees reasonably well with the experimental data. An early breakthrough and a sharp trailing edge also applies to this theoretical curve.

The following information was presented by Schroeder and Jennings (1963) concerning experiment no. 73.

<u>Physical properties</u>		<u>Chemical properties</u>	
Material	Microcline	Pulse solution	10 ml
Mesh	20-30	Ion	Strontium
Column height	60	Conc.	2.3×10^{-6} molar
Column volume	1,239 cc	Eluting solution	
Wt. of grains	1,797.4 g	Ion	Calcium
Grain vol.	702.1 cc	Conc.	4.7×10^{-5} molar
Bulk density	1.45 g/cc	Breakthrough curve	
Porosity	43.3 %	Peak	20.5 pore vol.
Col. pore volume	536.9 ml	Centroid	22.5 pore vol.
Water velocity	10.3 cm/hr	Peak conc./pulse conc.	0.00147

Since input variables can be easily varied, runs were made with the dispersion coefficient equal to zero and with various fluid velocities and kinetic rate constants.

The effect of the dispersion constant on the solution of the equations is of paramount importance. In fact, numerical solutions cannot be made unless the dispersion term is present. The equations become unstable, generate parasitic waves and totally disintegrate. The equations as used with the dispersion coefficient still only apply to short-range predictions as extended computations tend to develop this same instability. Knox (1961) discussed this instability to some degree but was unsuccessful in completely eliminating it.

One run tested the effect of $K_d\rho_e$ and the kinetic rate constant on the shape and position of the breakthrough curve. A $K_d\rho_e$ value of 2.75 and rate constant of 1.91 (1/hr) were assumed. The maximum concentration of the breakthrough curve occurred at 2.9 pore volumes. The theoretical peak should have occurred at $1 + K_d\rho_e$ pore volumes or 3.75 pore volumes.

A run with a water velocity of 1 cm/hr resulted in a high concentration peak in the effluent breakthrough curve at approximately the same pore volume as the run at a velocity of 10.2 cm/hr. The slower rate enabled a closer approach to equilibrium during the ion exchange reaction. The run with a water velocity of 50 cm/hr resulted in the early breakthrough curve appearing at one pore volume, probably a result of inefficient residence time for the fluid in the column to complete a satisfactory ion-exchange reaction.

The effect of changing the kinetic rate constant was the reverse of the change in velocities. A higher rate constant resulted in a sharp breakthrough peak similar to that of the low velocity. A low kinetic rate constant gave results similar to that obtained with high fluid velocities; a breakthrough curve of high peak concentration appearing at one pore volume.

Table 1 summarizes the computer-generated data from all the column runs discussed in this report. The reader interested in detailed description of columns, materials, and solutions, which are referred to as the experimental data should refer to Schroeder and Jennings's 1963 annual report.

Table 1.--Summary of computer input/output data for column experiments

Purpose of run	$K_d \rho_e$	Rate constant (1/hr)	Fluid velocity (cm/hr)	Maximum $\times 10^{-3}$	Pore volume at max
I. Compare with results generated by Schroeder for cesium-potassium system (experiment no. 62).	4.00	4.00	10.2	9.3	4.4
II. Used Knox's finite difference equation to compare with run I.	4.00	4.00	10.2	9.5	4.4
III. Test effect of $K_d \rho_e$ and rate constant for run I.	2.75	1.91	10.2	10.0	2.9
IV. Compare results with data generated by Schroeder for strontium-calcium system.	19.7	5.25	10.2	1.65	19.5
V. Test effect of velocity for run I.	4.00	4.00	1.0	24.8	4.6
VI. Test effect of velocity for run I.	4.00	4.00	50.0	28.6	1.0
VII. Test effect of rate constant for run I.	4.00	1.00	10.2	17.7	1.0
VIII. Test effect of rate constant for run I.	4.00	8.00	10.2	12.9	4.6

CONCLUSIONS

The general partial differential equation derived for flow, dispersion, and exchange of ions through porous media can be represented by a simplified analytical expression or a finite-difference equation derived by the use of Taylor's series. Data generated from finite-difference equations and data generated from analytical models that included a Poisson distribution equation and a kinetic equation compare favorably with experimental data obtained in the laboratory. These equations can be used to evaluate the effect of the velocity, the kinetic rate constant, and the distribution coefficient on the shape of the breakthrough curve. A decrease in velocity or an increase in the kinetic rate constant increases the sharpness of the breakthrough curve, and a change in the distribution coefficient changes the location of the breakthrough curve with respect to the volume of effluent. High velocities and low kinetic rate constants give early breakthrough curves appearing at 1 pore volume. This is attributed to insufficient residence time to allow ion exchange to occur.

An analytical model was modified to allow calculation of the ionic concentration in an aquifer at any prescribed time or distance. The computer program written to solve the numerical model that involves finite difference equations gives virtually the same results as those obtained through the analytical equations for short distance predictions. The numerical model, however, breaks down and becomes unstable when longer distance predictions are attempted.

A computer program that solves a finite-difference equation derived from the basic partial differential equation or the use of analytical expressions give comparable results for both effluent concentrations from an ion exchange column and solution concentrations in an aquifer. The advantages of using a computer to solve the equations are ease of operation, speed, adaptability of output and input data, ability to

program changes in the characteristics of a column or aquifer as the fluid is flowing, or to solve equations without the simplifying assumptions necessary for a closed form analytical solution.

Equations used in this report apply to ion exchange reactions with linear adsorption isotherms only. Attempts are currently being made to adapt these equations that will allow analysis for ion exchange reactions that have non-linear isotherms. Analytical methods seem inapplicable to this problem because the gross concentrations of ions in solution tends to vary throughout the laboratory column or aquifer. Presently used numerical techniques should lead to more sophisticated techniques capable of predicting ionic concentrations for non-trace conditions.

RECOMMENDATIONS FOR FURTHER STUDY

This report by no means completes all the work necessary to the prediction of movement and exchange of trace amounts of ions in porous media. Establishment of kinetic rate constant values and the effect of variables such as velocity and equilibrium constants on these rate constants is a typical problem worthy of study. An empirical method to predict such constants would be of immeasurable help for contamination conditions envisioned by this study as the wide variety of earth materials could not possibly lend themselves to complete laboratory examination. Multidimensional models that would incorporate lateral dispersion, the effect of molecular diffusion at low flow rates and decay of radioactive ions should also be considered for further study.

NOMENCLATURE

a_p	= surface area of particle per unit volume of material
c	= concentration of solute in the fluid phase
C_o	= total ionic concentration in solution
D_p	= solid phase diffusion coefficient
D_f	= liquid phase diffusion coefficient
d_p	= particle diameter
D_m	= dispersion coefficient
D_A	= distribution coefficient defined by Vermeulen equals $K_d c_e$
D	= coefficient of dispersion
$\text{erf}(x)$	= error function
f	= fraction of solute or solvent
h	= height of a column
H_R	= height of a reaction unit
I_o	= modified Bessel function of the first kind and zero order
J	= rate of mass transfer
$J(N_R, ZN_R)$	= mathematical solution for ion exchange equation
K	= equilibrium constant
K_c	= pseudo-equilibrium constant, based on concentrations
K_d	= distribution coefficient
L	= length of input pulse
k	= constant for column analysis using theoretical plates, equal to $1/K_d$; also kinetic rate constant
k_f	= kinetic rate constant for external diffusion
k_p	= kinetic rate constant for internal diffusion
m	= concentration of ion on the solid per unit volume
M	= mass of solid
N_R	= number of reaction units
N	= number of theoretical plates in a column
n	= plate number
P_n^u	= Poisson cumulative distribution function
q	= concentration of ion on the solid

q_1, q_2 = constants in Knox's equation
 Q = exchange capacity of the resin
 R_n = ratio of concentration on plate n to initial concentration
 S = mass of adsorbent on plates
 ρ = dummy variable
 t = time; also dummy variable
 U = average interstitial velocity
 u = interstitial fluid velocity along the x axis
 u' = product of k_x for theoretical plate analysis
 V = volume of solution
 V_{sat} = volume of initial ionic pulse added to the column
 v = interstitial fluid velocity, along the y axis; also volume of the column
 w = interstitial fluid velocity, along the z axis
 x = ratio of weight of elutant that crossed plate to weight of adsorbent on plate; distance along horizontal axis
 y = concentration of solute in the liquid and solid phase; also distance along vertical axis
 Z = throughput ratio
 ∞ = infinity
 Z' = throughput ratio represent a non-existent saturant
 Z_{sat} = difference between Z and Z'
 z = distance normal to plane formed by x, y axis

Greek letters

α, γ = valence of ions A and B
 γ = activity coefficient
 Δ = incremental change
 ϵ = porosity
 η = relative concentrations, c/c_0
 ρ_e = exchange ratio, $\rho_b \epsilon$
 ρ_b = bulk density of solids in the column
 u_n = Poisson distribution function
 w = weight of elutant that has crossed a plate
 ξ = dummy variable

Subscripts

l   = liquid phase
o   = initial or entrance condition
s   = solid phase

Superscripts

*   = equilibrium condition

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