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SC-CR-70-6139
December 1970

A METHOD TO DESCRIBE THE FLOW OF
RADIOACTIVE IONS IN GROUND WATER

Prepared by
David B. Grove

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Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

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Aerospace Safety
TID-4500 (54th Ed.)
Category U-36 (150)

SC-CR-70-6139

A METHOD TO DESCRIBE THE FLOW OF RADIOACTIVE IONS
IN GROUND WATER
Final Report
December 1, 1966 through June 30, 1968

Prepared by

David B. Grove
U.S. Geological Survey

December 1970

in collaboration with
Sandia Corporation
Under
Contract No. AL-66-848
(ASB 48-4337)

ABSTRACT

An equation based on instantaneous ion exchange and on a linear adsorption isotherm predicts ionic concentrations in the ground-water system as a function of time and position. This equation accounts for radioactive decay, ion exchange, and longitudinal hydraulic dispersion. Critical constants necessary for solution include ground-water velocity, ion-exchange distribution coefficient, exchange ratio, and dispersion coefficient. The need for simplicity dictates the use of an equilibrium concept rather than a rate process to describe the ion-exchange reaction in the predictive equation.

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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.

A METHOD TO DESCRIBE THE FLOW OF RADIOACTIVE IONS IN GROUND WATER

INTRODUCTION

On December 1, 1966, the Water Resources Division of the U.S. Geological Survey began to evaluate the possibility of ground-water contamination by a SNAP (Systems for Nuclear Auxiliary Power) system. The system is in effect a thermoelectric generator that utilizes a nuclear power source. Some orbiting satellites carry this type of power generator. The work was done in collaboration with the Sandia Corporation, Albuquerque, New Mexico, on behalf of the U.S. Atomic Energy Commission.

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 methods for use in predicting the concentration of ions in the ground-water environment as a function of time and distance. Ion-exchange column data and distribution coefficients generated by Dr. M. C. Schroeder and associates (1963, 1968) of Texas A. and M. Research Foundation have been used to test the suitability of the methods developed by the Geological Survey. In support of this project, the Geological Survey has also completed a study on the geology, soil, and climate at specific points throughout the world (Ruane and others, 1967).

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

Three quarterly reports were prepared in 1967 describing the short-term progress of the study and an annual progress report (Grove, 1970) described the work from December 1, 1966, through November 30, 1967. In the annual report, the author tested a general equation for one-dimensional transport of ions in water-saturated porous media. The equation includes three transport components--mass fluid flow, hydraulic dispersion, and ion exchange. In the same report, the author also discussed the mechanism of ion exchange, the convective fluid transport of the ions, and the effects of dispersion on dilution of the ionic concentration. After evaluation, the best of three conceptual models of the ion-exchange process was adapted to the general equation. Linear-adsorption isotherms, which characterize trace concentrations, were studied exclusively during this period. A digital computer provided a numerical solution to the general flow equation. Relative influences of various components in the equation were evaluated and validity, limitations, and improvements of the equation were discussed.

This final report summarizes selected parts of the Geological Survey's work from December 1, 1966, through June 30, 1968. From December 1, 1967, through June 30, 1968, the program was only partially funded and the amount of time allotted to the project was prorated accordingly. Lengthy derivations, as well as qualitative and quantitative descriptions of the dispersion and ion-exchange processes, are omitted. Analytical equations and their solutions are presented for various situation and boundary conditions.

The mechanics of ion exchange investigated during the last seven months of the study included the theoretical attainment of exchange equilibrium for trace (linear-adsorption isotherm) and nontrace (nonlinear-adsorption isotherm) conditions. Nonequilibrium conditions requiring kinetic considerations were also analyzed for these two conditions. Ion transport by longitudinal hydraulic dispersion and ion exchange with linear-adsorption isotherms were studied for equilibrium and nonequilibrium conditions. The equations describing the various situations were solved for various boundary conditions that include columns and aquifers of finite and infinite length. Because many partial differential equations describing situations of interest do not have explicit analytical solutions, numerical solutions obtained by digital computer are recommended.

One particular series of experiments involved introducing high concentrations of exchangeable ions into a laboratory ion-exchange column. The important difference between these and other laboratory column experiments was the discontinuity in total ionic concentration. This unique situation was investigated by both analytical and numerical methods.

ACKNOWLEDGMENTS

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.

ION TRANSPORT PROCESSES

Grove (1970) applied the transport equation for exchangeable ionic species in one-dimensional flow. In this equation,

$$\frac{\partial c}{\partial t} = -U \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} - \frac{\partial m}{\partial t}, \quad (1)$$

c is ion concentration in the liquid, t is time, U is the interstitial fluid velocity, D is the longitudinal dispersion coefficient, and m is the amount of ion adsorbed on the solid per unit of time. This equation for certain boundary conditions and qualifying assumptions can be solved. The equation considers only flow in the x -direction, and the hydraulic dispersion coefficient D applies only for flow parallel to this x -axis. Simple transport with no dispersion or exchange involves the first two components of equation 1; and although its solution is not trivial, a qualitative interpretation of the time necessary for a particle with velocity U to flow from point x_1 to point x_2 is trivial. Most of the available analytical solutions to the equation are explained in the following sections.

Dispersion

Hydraulic dispersion in the direction of flow is due to varying velocities of liquid within an aquifer and results in a diffuse tracer front of any labeled tracer in the liquid.

Dispersion solely in the x direction is termed longitudinal dispersion. In the absence of ion exchange, the term $\frac{\partial m}{\partial t}$ is absent and equation 1 can be written as

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

When initial and boundary conditions are given by

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

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

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

an approximate solution to equation 2 is

$$\frac{c}{c_0} = \frac{1}{2} \left[1 - \operatorname{erf} \frac{x-Ut}{2\sqrt{Dt}} \right] \text{ where } \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt. \quad (3)$$

This solution has been obtained by numerous investigators including Rifai, Kaufman, and Todd (1956, p. 56). These investigators also discovered that the dispersion coefficient is directly proportional to velocity and can be described by the equation

$$D = D_m U, \quad (4)$$

where D_m is the dispersion constant.

The dispersion constant for aquifers is usually difficult to obtain. For spherical grains it can be estimated; for some nonspherical grains it can be determined by laboratory column experiments. Some dispersion coefficients obtained by either of the two methods have proved to have a difference with the value obtained in field by as much as two orders of magnitude (C. V. Theis, oral commun., 1968). Spherical grains of uniform diameter d_p have a dispersion constant D_m near $2d_p c$ for laminar flow. Grove (1970) used this relation in that report.

If a pulse of tracer material is moving through a porous medium, the concentration resulting from dispersion can be expressed as

$$\frac{c}{c_0} = \frac{1}{2} \left[\operatorname{erf} \frac{x-Ut'}{2\sqrt{Dt'}} - \operatorname{erf} \frac{x-Ut}{2\sqrt{Dt}} \right], \quad (5)$$

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

The mass-action relation is commonly used to quantify ion exchange. An example of its use for a general exchange reaction is

where A is the exchanging ion and B is the ion initially attached to the resin. Valences of ions A and B are given by α and β , respectively.

If the concentrations are assumed equal to the activities, a pseudo-equilibrium constant, K_c , can be defined as

$$K_c = \frac{q_A^{\beta} c_B^{\alpha}}{q_B^{\alpha} c_A^{\beta}}, \quad (7)$$

where q is the concentration of ion on the solid and c is the concentration of ion in solution.

Mayer and Tompkins (1947) defined the ratio of the amount of ion adsorbed on the solid to that dissolved in solution as K_d , the distribution coefficient. For the general exchange reaction illustrated by equation 6, the distribution coefficient can be written as

$$K_d = q_A / C_A \quad (8)$$

Vermeulen (1958) defined the distribution ratio as

$$D_A = \frac{K_d \rho_b}{\epsilon} = K_d \rho_e \quad (9)$$

where ρ_b is the bulk density, ϵ is the porosity of the resin, and $\rho_e = \rho_b / \epsilon$. The distribution coefficient K_d is a measure of the number of exchange sites on the solid, and denotes the resin's ability to adsorb ions. When the concentration of the exchanging ion C_A is small, the concentration of the ions on the q_b exchanger is nearly equal to the ion-exchange capacity of resin Q ; and the concentration of the major ion in solution C_B is nearly equal to the total fluid concentration C_o . Based on equations 7 and 8 and the previous assumptions, the distribution coefficient is

$$K_d = \frac{QK_c}{C_o} \quad (10)$$

where Q is the ion-exchange capacity and C_o is the total fluid concentration. Equation 10 is a common and useful equation to determine the distribution coefficient or, knowing the distribution coefficient, to determine the equilibrium constant.

The average velocity of ions traveling through a porous medium can be calculated using the distribution coefficient. The equation

$$U_{\text{ion}} = U_{\text{water}} \frac{1}{(1 + K_d \rho_e)} \quad (11)$$

relates the movement of the ion in relation to the movement of water.

The factor $1/(1 + K_d \rho_e)$ is commonly called the retardation factor.

The retardation factor equals the fraction of ions in solution.

Equation 11 and the assumption of instantaneous equilibrium during the ion-exchange process have been commonly used to predict the movement of radioactive ions away from underground nuclear detonation sites.

Equilibrium reactions

When ion exchange is instantaneous and the concentration of the exchanging ion in solution is small, the adsorption isotherm can be assumed to be linear. Equation 8 can also be written as

$$K_d = \frac{m}{c} \cdot \frac{c}{\rho_b} = \frac{m}{\rho_b c} \quad (12)$$

The rate of ion exchange, $\partial m / \partial t$, on the solid can now be written as a function of the rate of the exchange in the liquid phase as,

$$\frac{\partial m}{\partial t} = K_d \rho_e \frac{\partial c}{\partial t} \quad (13)$$

In the absence of dispersion equation 1 and equation 13 can be combined to give

$$\frac{\partial c}{\partial t} = \frac{U_{\text{water}}}{1 + K_d \rho_e} \frac{\partial c}{\partial x} = U_{\text{ion}} \frac{\partial c}{\partial x} \quad (14)$$

which can be evaluated as mentioned previously.

Under many conditions the adsorption isotherm is not linear. DeVault (1943) made the first thorough evaluation of this condition for equilibrium exchange reactions and developed equations to quantify favorable (an equilibrium constant greater than unity), unfavorable (an equilibrium constant less than unity), and linear adsorption isotherms. For fixed bed, or column adsorption, favorable equilibrium leads to a sharp, leading concentration profile and a diffuse, trailing profile for a "slug" of tracer injected into a column. Unfavorable equilibrium has the reverse effect; a diffuse leading edge is followed by a sharp trailing edge. Linear isotherms produce no change in the concentration profile of the input pulse.

Lightfoot (1957) solved the nonlinear isotherm under equilibrium conditions and with longitudinal diffusion. He cited several important examples showing that the solution is useful for the correlation of data.

The advantages of the equilibrium model of ion exchange are the simplicity of use and the few variables necessary for evaluation. Many polluted waters contain only trace amounts of the contaminant; and when dispersion and diffusion are neglected, the ions will move with their initial concentration profile but at a retarded velocity, in accordance with the equilibrium model. The disadvantages are that equilibrium is probably never attained and that diffuse concentration profiles attributed to dispersion and diffusion may in fact result from incomplete ion exchange owing to a rate-controlling mechanism.

Rate-controlling ion-exchange reactions

As mentioned in the preceding section, the ion-exchange reaction may occur at a finite rate and this rate may govern the shape of a breakthrough curve from a column or the concentration profile of an ionic contaminant in an aquifer. A kinetic rate model based on these precepts is described in this section.

Thomas (1948) was one of the first investigators who treated chromatography as a rate process. Others who later expanded the idea included Heister and Vermeulen (1952), Vermeulen and Heister (1952), Heister, Fields, Phillips, and Radding (1954), and Vermeulen (1958). Thomas used several parameters to predict concentration profiles. These included an equilibrium parameter, r , as an independent variable, the number of reaction units, N_R , and the throughput ratio, Z . The equilibrium parameter or separation factor, r , is inversely proportional to the equilibrium constant and the sharpness of the front of the breakthrough curve increases with decreasing r . Z is a throughput ratio 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 $Z = (V - v_e)/\bar{V}_A$ where V is the volume input to the column and v the column volume. N_R commonly denotes the number of reaction units that describes the controlling situation, and may be a combination of several terms including: fluid-phase external diffusion, fluid-phase pore diffusion, chemical reaction, and solid-phase internal diffusion.

The most important or controlling reactions are the fluid-phase external diffusion and the solid-phase internal diffusion. The reaction rate for external diffusion is described as

$$\frac{dq_A}{dt} = \frac{k_f a_p \epsilon}{\rho_b} (c_A - c_A^*) , \quad (15)$$

where k_f is the fluid phase mass transfer coefficient, a_p is the external area of particles per unit bulk volume, and c_A^* is the equilibrium concentration of ion A in solution. For internal-diffusion controlling, the rate is usually approximated by the linear driving-force relation

$$\frac{dq_A}{dt} = k_p a_p (q_A^* - q_A) , \quad (16)$$

where k_p is the mass transfer coefficient for internal diffusion and q_A^* is the equilibrium concentration of ion A on the solid. The number of reaction units N_R is related to the overall kinetic rate constant k by the relation

$$N_R = kh/U , \quad (17)$$

where h is the length of an ion-exchange column. The rate constant can be obtained by adding the diffusional resistances in the manner

$$\frac{1}{k} = \frac{1}{k_f a_p} + \frac{1}{k_p a_p D_A} . \quad (18)$$

Usually k is obtained experimentally through a batch experiment or a simulated field model set up in the laboratory.

Vermeulen (1958) details methods of when and how to compute the various parameters used by Thomas when concentrations are so great that nonlinear ion-exchange adsorption isotherms result. These methods and formulas also apply to chromatographic separations. The equations simplify for trace concentrations of ions. These simpler equations are commonly used for non-trace concentrations in chromatographic separation studies. Vermeulen (1958) states, "The column behavior for a charge fed under non-trace conditions becomes nearly identical with that predicted by the comparatively simple calculation methods for fully trace conditions."

The equation that describes the breakthrough curve from a chromatographic column is in essence the difference between a concentration curve starting at $Z = 0$ and a second curve representing a nonexistent saturant starting at $Z' = 0$. This equation is

$$\frac{c_A}{c_0} = J(N_R, ZN_R) - J(N_R, Z'N_R) \quad (19)$$

where $J(s, r) = 1 - \int_0^s e^{-t-\xi} I_0(2\sqrt{t\xi}) d\xi$.

I_0 is the modified Bessel function of the first kind and zero order.

Vermeulen (1958) approximated this solution by the equation

$$\frac{c_A}{c_0} = \frac{Z_{sat}\sqrt{N_R}}{2\sqrt{\pi}} e^{-(N_R/4)(Z-1)^2} \quad (20)$$

where Z_{sat} is the difference between Z' and Z and/or equal to $\bar{V}_{sat}/D_A v_e$ where V_{sat} is the volume of the initial ionic pulse added to the column and v the total column volume. The peak of the breakthrough zone occurs when $Z = 1$ and is

$$\frac{c_A}{c_0} = \frac{Z_{sat}\sqrt{N_R}}{2\sqrt{\pi}} \quad (21)$$

Ion exchange with longitudinal dispersion

Equation 1 has been solved for the following conditions:

1. A linear ion-exchange adsorption isotherm.
2. Assumed instantaneous equilibrium of the ion-exchange reaction.
3. Longitudinal dispersion is present.

The rate of ion exchange $\partial m / \partial t$ is equal to $\frac{\partial c}{\partial t} K_d \rho_e$ (see equation 13)

under these conditions and equation 1 reduces to

$$\frac{\partial c}{\partial t} (1 + K_d \rho_e) = -U \frac{\partial c}{\partial x} + D_m U \frac{\partial^2 c}{\partial x^2} \quad (22)$$

The solution to this equation is similar to that of the simple dispersion equation; here the velocity U is replaced by the velocity of the ion $U_{ion} = U_{water} / (1 + K_d \rho_e)$.

For nonequilibrium conditions equations 15 and 16 are assumed typical of the overall reaction rate controlling equation. Ogata's (1964) solution of equation 1 is

$$\frac{c}{c_o} = \frac{2e^\alpha}{\sqrt{\pi}} \int_{\frac{x}{2\sqrt{Dt}}}^{\infty} e^{-\xi^2 - \alpha^2 / 4\xi^2} J(y, \tau) d\xi \quad (23)$$

where

$$y = k\gamma^2 / \xi^2$$

$$\tau = km(t - \gamma^2 / \xi^2)$$

$$\alpha = Ux / 2D$$

$$\gamma = x^2 / 2\sqrt{D}$$

$$m = 1 / K_d \rho_e$$

ξ = dummy variable.

The J function has been previously defined. The solution to equation 23 in a useable form requires the use of a digital computer. Solution of the initial partial differential equation directly by the use of finite difference equations might be easier than solution of equation 23. This approach was used by Knox (1964) and later by Grove (1970). To solve equation 1, they used numerical analysis and an explicit difference scheme. A disadvantage of both solutions is that after long periods of calculation this particular explicit method becomes unstable. As a result, the numerical method works very well when the number of calculations can be held to a minimum, as with ion exchange columns, but when it is applied to aquifers of infinite extent, this method breaks down completely. An interesting sidelight is that most of the previously mentioned solutions for equation 1 had boundary conditions of 0 and ∞ for the length of the column. These solutions were then assumed to apply for a column of any length L also. Bastian and Lapidus (1956) recognized this fact and derived the correct expression for columns of finite length operating under equilibrium conditions. Finite column calculations deviate less than 10 percent from those for an infinite column for situations investigated.

LABORATORY EXPERIMENTS

Schroeder and Jennings (1963) and Schroeder, Crocker, and Blank (1968) provided an abundance of data that can be used to evaluate theoretical or empirical equations developed to explain the system. These data consist of relative concentrations of effluent from an ion-exchange column under carefully controlled conditions.

Trace conditions

The work reported by Schroeder and Jennings (1963) includes mostly column experiments run under trace (linear adsorption isotherm) conditions. Using these data in equation 21, Grove (1970) calculated a value of N_R ; then with that value and equation 18 he compared the experimental and theoretical curves with calculated results usually within 10 percent of experimental. Figure 1 shows the plots of these experimental data and a theoretical curve for the kinetic rate model (Grove, 1970).

Nontrace conditions

Schroeder, Crocker, and Blank (1968) later ran a series of ion-exchange experiments involving non-trace concentrations of ions in the column. The exchanging ion strontium was injected at a high concentration into the top of the column and then was eluted with an ion of less concentration. The literature offered no solution to this type of situation. Various computer solutions to equation 1 for a variable kinetic rate constant, k , and distribution coefficient, K_d , were tried but without complete success.

Figure 1.--Comparison of experimentally and analytically determined breakthrough curves for a cesium-potassium ion-exchange system.

Schroeder, Crocker, and Blank (1968, p. 38) summarized their data in terms of six groups as table 12 of their report. This table is summarized as table 1 of this report. Column lengths of 30 and 60 cm (centimeters) were packed with microcline that passes through a 20-30 mesh screen, and the elutant velocity was maintained at approximately 10 cm per hour. Pulse size, concentration of strontium in the pulse, and concentration of calcium in the eluting solution were varied. The relative concentration of strontium in the effluent from the column and the position(s) of the peak(s) of the breakthrough curve were measured. The first peak denotes the relative concentration that occurred at one pore volume. The second peak's concentration and position with respect to column pore volumes vary.

Table 1.--Summary of conditions and elution curve data for column experiments
(table 12 in Schroeder, Crocker, and Blank, 1968)

Group no.	I	II	III	IV	V	VI
Column length (cm)	30	30	60	30	60	30
Pulse size (ml)	2.5	10	5	10	5	10
Strontium in pulse (molar)	1×10^{-2}	1×10^{-2}	5×10^{-4}	4×10^{-2}	4×10^{-2}	1×10^{-2}
Calcium in eluting solution (molar)	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-5}	1×10^{-5}	1×10^{-5}
First peak (c/c_0)	<0.00035	0.035	not apparent	0.102	0.0039	0.027
Second peak (c/c_0)	0.0012	0.0038	0.0026	not apparent	0.0002	0.0006
Second peak (pore volume)	7.2	5.5	11.8	not apparent	38	29
Experiment number	2, 5 6, 7	1, 4 8, 10	3, 9 11	12, 13 18, 20	14, 15 19, 21	16, 17 22

After a qualitative analysis of the data in table 1, the author reached several conclusions. The concentration of the ion of interest in the peak occurring at one pore volume results from flow through the column without the benefit of peak position retardation owing to ion exchange. The peak concentration is attenuated owing to ion adsorption without the benefit of a desorption reaction. The system, in essence, acts as a sink on this initial pulse. The effectiveness of this sink is proportional to the distribution coefficient, because this coefficient is a measure of the average speed of the ion through the column. As the total concentration of the pulse decreases owing to dispersion, the distribution coefficient increases. At this time the velocity of the ion slows down far below the velocity of the pulse that travels with the fluid. Thus, the concentration of the ion decreases as it flows through the column.

Because the velocity of the pulse is the same as that of the eluting solution, the physical and the chemical characteristics of the eluting solution should have no effect on the concentration profile of the initial pulse. This is aptly demonstrated in table 1 for groups II and VI, where the only variable changed was the concentration of the eluting solution from 1×10^{-4} molar in II to 1×10^{-5} molar in VI. The maximum relative concentrations of the first peak were 0.035 and 0.027 in these two groups, respectively. Analysis of the values for individual runs for each of these groups shows no valid difference between the two means. The concentration of ions in the first peak also seems to be a direct function of the concentration of ions in the pulse. Group IV had a concentration of strontium in the pulse four times that of the pulse concentration in groups II and VI. The relative concentration of the first peak of group IV is three to four times that of groups II and VI.

Column-length and pulse-size effects on strontium concentration is an entirely different matter and has not been adequately explained. For example, group I had a pulse size of 2.5 ml (milliliters) and the first-peak relative concentration was less than 0.00035. This decrease in concentration, from 0.031 (average of II and VI) to less than 0.00035 is difficult to explain by a fourfold decrease in the pulse size, although the size of the pulse obviously has a profound effect on breakthrough concentrations. The effect of column height is also difficult to determine. Groups III and V were run with 60-cm high columns. Attempts to correlate breakthrough curve concentration results for these groups were fruitless.

The position of the second peak is determined primarily by the concentration of the elutant. The ions formulating this second peak were those left behind when the initial pulse moved down through the column. Group III more than any of the other groups represents a column experiment where trace ions were used. There was no first peak at one pore volume for this group of experiments. The position of the only peak resulted at 11.8 pore volumes. This peak approximates that predicted by the static distribution coefficient obtained for group III experiments. The peak should appear at $(1 + K_d \rho_e)$ pore volumes. Schroeder, Crocker, and Blank (1968, p. 36-37) obtained a static distribution coefficient of 2.57 and an exchange ratio of 3.34 for materials used in the group III column experiments. With these results, a value of 9.6 pore volumes is predicted.

Groups IV, V, and VI have an experimentally determined distribution coefficient of 12.2. The theoretical breakthrough curve should then be $1 + (12.2) (3.34) = 41.7$ pore volumes. Group IV represents an anomaly as no second peak was apparent. Evidently the ion-exchange reaction was so slow that all the material eluted through with the first pulse.

Except for group III experiments, the experimental position of the second peak is always earlier than that predicted. This is no doubt due to the method by which the ions are deposited on the column. The ions are not deposited on the top portion of the column in trace concentrations but are deposited in some unknown distribution throughout the column. This condition in essence shortens the column as far as effect is concerned and causes earlier breakthrough curves for the last pulse.

The computer program previously written for column conditions with trace concentrations was modified to take into account the effect of high initial concentrations. A different distribution coefficient and a kinetic rate constant were attributed to the pulse of high concentration as it traveled down the column. This allowed prediction of group II, IV, and VI experiments. Group I was predicted to have a relative concentration less than 1×10^{-4} molar. This concentration may or may not agree with the experimental data because the concentration is below the experimental detection level. The use of the program to predict the results of group V were totally unsuccessful as the concentrations obtained were far too low. A further modification that could recompute the distribution coefficient at any point in the column and not just compute a new K_d and k in the high concentration pulse zone is probably necessary. Figure 2 is a plot of the relative concentration of the ion related to position in the 30-cm column for pore volumes of 0.2, 0.6, and 1.0 eluted through the column. These values were computed using a value of 0.105 for k and 0.051 for $K_d \rho_e$ in the zone of high concentration simulating the conditions of groups II and IV.

Figure 2.--Numerical determinations of concentration profiles in a laboratory ion-exchange column with high input ion concentrations.

From figure 2 a peak is seen to move through the column with the velocity of the elutant leaving behind a broad, more attenuated band to be eluted later and to appear as the second peak. Also plotted on figure 2 as the dashed line are the maximum concentrations of the pulse simulating the group I experiment. After one pore volume has been eluted, this maximum concentration can be extrapolated to a relative concentration of 5×10^{-6} . Figure 2 illustrates in a qualitative manner what probably happens to the other group experiments. Because it only gives correct results for one type of experiment, the method represented by figure 2 cannot be regarded as a satisfactory model.

RECOMMENDED TRANSPORT MODEL

To predict the movement of any radioactive material through the ground-water system, one must know the hydrologic properties of the area of interest. Ground-water velocity is of prime importance. Earth burial of an object such as the SNAP device in time will probably produce an aquifer void proportional to the size of the impacting device. If this assumption is correct, the same basic method and the equations used to analyze underground nuclear detonations can be applied here.

Various models have been used to explain the transport of radioactive contaminants through a ground-water system. Equation 22 and the previously discussed assumptions necessary to achieve it provide the basis for furnishing a method to make such a prediction, except for radioactive decay. The radioactive decay can be expressed as

$$\frac{c}{c_0} = \exp(-\lambda t) \quad (24)$$

which accounts for radioactive decay where λ is a decay constant.

If the dispersion coefficient D is equal to $D_m U$, division by the constant $1 + K_d \rho_e$ and the use of equation 11, that $U_{ion} = U_{water} / (1 + K_d \rho_e)$ results in

$$\frac{\partial c}{\partial t} = -U_{ion} \frac{\partial c}{\partial x} + D_m U_{ion} \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (25)$$

The solution to this equation combined with equation 24 results in the prediction equation

$$\frac{c}{c_o} = \frac{1}{2} \exp(-\lambda t) \left[\operatorname{erf} \frac{x - U_{ion} t'}{2 \sqrt{D_m U_{ion} t'}} - \operatorname{erf} \frac{x - U_{ion} t}{2 \sqrt{D_m U_{ion} t}} \right] \quad (26)$$

where:

λ = radioactive decay constant = $0.693 / \text{radioactive half life}$

t = time

x = distance

U_{ion} = average velocity of ion = $U_{water} / (1 + K_d \rho_e)$

K_d = distribution coefficient

ρ_e = exchange ratio = ρ_b / ϵ

ρ_b = bulk density of solid

ϵ = porosity

D_m = dispersion constant

$t' = (t - \Delta t)$

Δt = length of slug in terms of time movement.

Although the use of one-dimensional flow departs from real life situations, it is probably conservative because dispersion and ion exchange in lateral and vertical directions would attenuate the concentration profile.

Use of equation 25 first requires the availability of two important parameters--the distribution coefficient and the dispersion constant. The former probably has the most effect, because it controls the velocity of the ion. Figure 3 illustrates presently used distribution coefficients determined for various rock materials from the Nevada Test Site, Nevada. The range is very large, but these values will probably suffice for prediction purposes at other locations as well. Detailed measurements at particular sites are, of course, desired; but unless impact at a known area occurs, it would be impossible to determine an exhaustive list of soil types and distribution coefficients.

Dispersion constants of approximately 0.05 cm were determined for column experiments using 20-30 mesh microcline. Similar laboratory experiments, using aquifer materials expected to occur in situ, would probably be much larger; in fact, C. V. Theis (oral commun., 1968) has reported that dispersion constants have been observed in the field that are two to three orders of magnitude higher than those observed in the laboratory. The value for homogeneous granular aquifers may then be expected to be in the 1- to 1,000-cm range, with a more-probable value near 50 cm. Dispersion constants for flow through fractured rock may be even higher. R. J. Sun, U.S. Geological Survey (written commun., 1966), recommended the use of 30 to 50 feet as a possible dispersion constant in fractured media.

Figure 3.--Ranges of distribution coefficients for various rock types at Nevada Test Site.

HYPOTHETICAL CONTAMINATION PREDICTION PROBLEM

Assume a device containing strontium-90 as a fuel material plunged into the earth in south-central Nevada and, because of initial impact, became buried below the water table. The problem is to define the limits of the aquifer contamination produced by the leaching of the water-soluble material (strontium-90) in the device. The radioactive material is bound up as a fairly insoluble source and for some initial time increment Δt the ground water will elute the strontium from its matrix into the ground-water system. Assume that the volume being leached is V equal to $(4/3)\pi r^3$ where r is less than 1 foot and the total volume is approximately 4 cubic feet. Assume the following condition for a hypothetical example. The water velocity is 300 feet per year. As the water flows through the 2-foot diameter void, it dissolves the ion from the matrix at constant concentration c_0 . Enough soluble material is present to provide solute to the ground-water system for 1 year. Assume further that the earth material is alluvial soil and the distribution coefficient can be determined from figure 3. A dispersion constant of 2 feet is probably a reasonable value for homogeneous material. If the radioactive material is strontium, figure 3 gives a reasonable K_d value of 200 and the exchange ratio ρ_e is about 2.5 for most earth materials. The half life for strontium-90 is about 28 years and the decay constant λ can be calculated to be 0.0248. To summarize, the values necessary to draw a concentration profile of the contamination are:

$$\lambda = 0.693/t^{1/2} = 0.693/28 = 0.0248$$

$$U_{\text{water}} = 300 \text{ feet per year}$$

$$K_d = 200$$

$$\rho_e = 2.5$$

$$U_{\text{ion}} = U_{\text{water}} / (1 + K_d \rho_e) = 300 / [1 + (2.5)(200)] = 0.6 \text{ foot per year}$$

$$D_m = 2 \text{ feet}$$

$$\Delta t = 1 \text{ year}$$

$$t = \text{any time after 1 year.}$$

Figure 4 is a plot of the maximum relative concentration profile in the liquid phase of the input pulse, as a function of distance and time.

Figure 4 shows that the initial concentration of strontium-90 is attenuated by about 4 orders of magnitude by the time it travels 100 feet. The main attenuation is due to radioactive decay. For long pulses, the effect of dispersion is not so pronounced as would be expected with shorter pulses. The problem could also be analyzed as one in which an infinite amount of source material (say, strontium-90) was available. This would be the most conservative possibility in question and concentration profiles could be calculated by replacing t' by t in equation 25 and by removing the last error function term.

5

Figure 4.--Concentration profile of a hypothetical contaminated aquifer.

SUMMARY

The equilibrium concept of ion exchange coupled with longitudinal hydraulic dispersion and radioactive decay is the model used to predict ion movement in ground-water systems. The complexity of analyzing a high-concentration pulse precluded the development of a reasonable analytical model. A numerical technique was used to model high-concentration pulses but this technique was not as precise as desired. The main problems are accounting for changes in pulse size and column height. Experience by other investigators in the field of ion movement in ground-water systems show that non-trace concentration pulses quickly deteriorate to trace conditions, lending credibility to the use of the recommended equations. If the radioactive materials of a SNAP (Systems for Nuclear Auxiliary Power) were nearly insoluble, the leaching action produced by the chemical and physical properties of the water and the kinetic action caused by the movement would produce a very dilute concentration of the ion.

Determination of average ion velocity requires knowledge of ground-water velocity, distribution coefficient, and exchange ratio. Knowledge of the area of impact enables one to estimate these parameters as well as the dispersion coefficient.

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NOMENCLATURE

A_p = surface area of particle per unit volume of material

c = concentration of solute in the fluid phase

d_p = particle diameter

D_m = dispersion coefficient

D_a = distribution coefficient defined by Vermeulen equals $K_d \rho_e$

D = coefficient of dispersion

$\text{erf}(x)$ = error function

I_0 = modified Bessel function of the first kind

$J(N_R - ZN_R)$ = mathematical function in the solution of an ion-exchange equation

K = equilibrium constant

K_c = pseudoequilibrium constant, based on concentrations

K_d = distribution coefficient

k = 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

N_R = number of reaction units

q = concentration of ion on the solid

Q = cation-exchange capacity

r = equilibrium parameter or separation factor; also radius of impact zone

NOMENCLATURE--Continued

t = time

U = average interstitial velocity of the fluid

V = volume of solution

V_{sat} = volume of initial ionic pulse added to the column

Z = throughput ratio

Z_{sat} = difference between Z and Z'

x = distance along horizontal axis

Greek letters

α, β = valence of ions A and B

ϵ = porosity

ρ_e = exchange ratio

λ = decay constant

Subscripts

o = initial or entrance condition

Superscripts

$*$ = equilibrium condition

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