ONE-DIMENSIONAL MODEL OF THE MOVEMENT
OF TRACE RADIOACTIVE SOLUTE
THROUGH SOIL COLUMNS:
THE PERCOL MODEL

R. C. Routson and R. J. Serne

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Richland, Washington 99352

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by

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Water and Land Resources Department

1972

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SUMMARY

A one-dimensional mathematical model, PERCOL, has been developed to predict the movement of radionuclides through porous media as a function of measureable chemical parameters of the media. Laboratory column studies were conducted to verify the model. System parameters considered include soil type, radionuclide type, waste composition, flow rate, column length, and soil saturation. The agreement between measured radionuclide movement and that predicted by the model is considered good.

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SYMBOLS AND DIMENSIONS

A_T	bottom area of the tank
$a_{i,j}$	area of the basic nodal element
B	boundary coefficient
b	dimensionless parameter from capillary pressure vs. saturation equation
c	arc length, ft
f	porosity of the porous medium, decimal fraction
g	acceleration due to gravity, ft/day^2
h	hydraulic potential
h^0	aquifer bottom surface
h_o	hydraulic potential along an initial condition curve
H_T	liquid head in the tank, ft
i, j	index numbers in the x and z direction
k	iteration index
k_r	relative hydraulic conductivity, ft/day
K	hydraulic conductivity, ft/day
$\bar{K}$	hydraulic conductivity times the radius, r, from the axis of symmetry

$L_1(K, \phi), L_2(K, \phi)$	difference terms in the horizontal and vertical directions as functions of K and ϕ
$M(\theta)$	difference term, a function of moisture content, θ
N	slope of the capillary pressure versus moisture content curve at the half time step
n	time plane index
$\hat{n}$	outward pointing normal vector
P_c	capillary pressure, ft
P_o	coefficient of the capillary pressure versus saturation equation, has dimensions of length
P_1	coefficient of the capillary pressure versus hydraulic conductivity equation, has dimensions of length
q	infiltration flux
$Q_1(K), Q_2(K)$	difference terms in horizontal and vertical directions as functions of K only
R	region of the flow system
$r_{i,j}$	elemental square within region R at index i, j
r	radial distance in axisymmetrical flow system
$\hat{r}$	area/time ratio
s	distance along a streamline (streamtube centerline)
S	saturation, decimal fraction
t	time variable, days
U	coefficient equal to radial distance times $\partial\theta/\partial\phi$
V_T	volume of liquid in tank, ft^3
V_x	velocity in the x direction, ft/day

w_i	width of the streamtube at step i
x, y, z	Cartesian coordinate system, feet
Γ	boundary of $r_{i,j}$ at node i, j
β	coefficient of the capillary pressure versus saturation equation, dimensionless
δ	coefficient of the capillary pressure versus saturation equation, dimensionless
δ_i	steady term in the transmissivity calculation at step i
Δ	increment
Δ_i	transient term in the transmissivity calculation at step i
ε	coefficient of the capillary pressure versus saturation equation, dimensionless
ϕ	hydraulic potential for partially saturated flow, ft of water
θ	moisture content, decimal fraction
σ	storage coefficient
ρ	density of water, lbs/ft^3
τ	coefficient of the capillary pressure versus hydraulic conductivity equation, dimensionless
∇	gradient operator

A ONE-DIMENSIONAL MODEL OF THE MOVEMENT OF TRACE SOLUTES THROUGH SOIL COLUMNS: THE PERCOL MODEL

INTRODUCTION

The one-dimensional model (PERCOL) described in this report represents the initial step in development of a multi-dimensional transport model to predict the potential movement of radionuclides in the hydrogeologic system of the Hanford Reservation. The components of the overall hydrological modeling program are shown in the schematic diagram on page 2.

PERCOL model was developed in order to determine whether independently measureable chemical parameters are adequate for predicting the sorption of radionuclides. Because the average flow rate of solution is simply determinable for laboratory porous media columns, this method was used as an initial verification of the solid-liquid reaction portion of the transport model shown on page 2.

The reaction portion of the PERCOL model has been incorporated directly into the transport model to account for the porous media sorption of radionuclides. In addition, the PERCOL model is a good tool for determining the initial state of a natural porous media system (which is required as input data to the multi-dimensional transport model) and for estimating the results of percolating solutions through porous media systems.

HYDROLOGICAL MODELING PROGRAM COMPONENTS

THEORY OF THE PERCOL MODEL

Substances dissolved in a solution (solutes) move through porous media as a result of both the convective movement of the transporting solution¹ and other natural phenomena within the transporting solution, including hydrodynamic dispersion, diffusion, and solid phase sorption.

Hydrodynamic dispersion results from the movement of the solute through the media with a range of velocities due to variable pore size distribution and tortuous pathways in the media system. Diffusion is the spreading out of solutes due to a concentration gradient. Dispersion and diffusion cause solutes to travel faster than the solution in which they are dissolved, and tend to cause earlier arrival than would be predicted by plug flow. Solid phase sorption is the association of solutes with the solid phase due to electrical interactions, resulting in the essential removal of the portion of the solute from the liquid phase. In contrast to hydrodynamic dispersion and diffusion, sorption retards the movement of solutes in relation to the movement of the solution phase, and can have a much greater effect on the movement of solutes, particularly in trace quantities, than do hydrodynamic dispersion and diffusion. Thus, for any model to adequately predict the movement of sorbable radionuclides, the solid-liquid interactions must be taken into account. *length*

Hanford studies have shown that radionuclides are generally present only in trace concentrations in the solution phase when released to the environment.² A trace solute is defined as one whose presence does not measurably affect the sorption either of other trace solutes or of the macrosolute. In contrast, the solution concentration of the ions present in macro-amounts does affect the sorption of trace components.² Therefore, the first order solid-liquid phase interactions which control the solution concentration of macroions must also be taken into account in the model.

GENERAL MODEL DESCRIPTION

The PERCOL model is a discontinuous equilibrium one-dimensional mass balance model in which the instantaneous fates of macro and trace solutes are accounted for at all times. It has been shown that the sorption of trace solutes by a given porous media is a determinable function of the equilibrium concentration of macroions. Empirical equations, which relate trace solute sorption to equilibrium macroion concentrations, are used to calculate sorption of trace

solutes and the trace solute solution concentration.²

In the model, a porous media column is divided into a finite number of divisions. A column of solution equal to the pore volume of the first division enters the first division where chemical reactions between the solid and liquid phases occur. These reactions, which control the macrosolute concentration, continue until equilibrium is reached. This equilibrium solution is next moved into the second column division and equilibrated, then successively to following divisions until it has moved through the entire column. Thus, the model assumes that the solid-liquid phase reactions can be adequately described by a number of successive equilibrium reactions.

Macroion reactions which are presently considered in the PERCOL model include ion exchange, carbonate, sulfate, and solution ion interaction equilibria for Na, K, Ca, and Mg. These equilibria are successively solved by an iterative computer program. The flexibility of such a technique permits the addition of other ions and other reactions to the program as more exotic systems are required. Only the solution and solid phase equilibrium reactions need to be known or be determinable to extend the model. When reaction rates are found to be slow in relation to the solution's residence time in each model division, kinetics can also be incorporated into the model.

CHEMICAL MODELING

First-order chemical reactions which mathematically describe the sorption of trace solutes (radionuclides) considered in the PERCOL model will be separately discussed under the macrosolute and microsolite categories. Division into these two categories was made for two reasons. First, mathematical simulation of the chemistry of the common macrosolutes in natural Na, K, Ca, and Mg soil systems requires successive interactions to calculate the equilibrium states. In contrast, the sorption of a microsolite can be adequately calculated by an empirical method without iteration; thus, computer time is saved by separating the two systems. Secondly, the sorption of trace solutes is often so complex that theoretical methods have not been developed to account for all different types of sorption which may occur. The method selected for PERCOL model does however empirically integrate the sorption reactions for these trace solutes.

Macro Model Chemistry

The macro chemical model represents a mathematical description of the soil-solution interactions between three phases: a cation exchangeable solid phase, a solution phase, and crystalline salt phases. Interactions which may occur between these three phases are sorption, ion exchange, complexation, dissolution, and precipitation.

Below the zone of root penetration the finely divided mineral surfaces of the soil solid phase are generally negatively charged. The negative charge results largely from the isomorphous replacement of Al^{+3} for Si^{+4} ions and/or Mg^{+2} and Fe^{+2} for Al^{+3} ; and, to a lesser extent, by hydrolysis of hydroxyl groups which are structurally a part of the soil matrix. To maintain electroneutrality, positively charged ions counter the net negative charge of the soil and are susceptible to exchange with other cations in the percolating solution.

Mathematical descriptions of the cation exchange reactions between soil and solution used in the PERCOL model are a combination of theoretical exchange equations and empirical results. It is assumed that multicomponent exchange reactions can be approximated as a system of binary reactions.

The mass action equation for a heterogeneous reaction such as

at constant temperature and pressure formulated for this model is

$$K = \frac{[B^{+n}]^b [A_a^{+m}X]}{[A^{+m}]^a [B_b^{+n}X]} \quad (2)$$

where

a, b = number of moles of constituent present,

n, m = ionic charge of constituent,

X = total solid phase soil matrix,

$[]$ = activities of constituents,

A, B = constituent ions in solution or on the soil.

Since no experimental means for measuring solid phase soil activities presently exist, an empirical approach has been utilized.³ Data from batch system experiments for each binary reaction were analyzed and found to approximate a linear relationship when plotted as a log-log function. The log of the solute activity ratio,

$$\frac{[B^{+n}]^b}{[A^{+m}]^a}$$

was plotted on the ordinate. The log of the ratio of the concentration in the soil solid phase

$$\frac{(B_b^{+n_X})}{(A_a^{+m_X})}$$

was plotted on the abscissa. The slope of the line yields a solid phase activity correction and the antilog of the intercept yields the empirical selectivity constant. The general empirical exchange expression obtained by this method is

$$K^* = \frac{[B^{+n}]^b}{[A^{+m}]^a} \left\{ \frac{(A_a^{+m_X})}{(B_b^{+n_X})} \right\}^p \quad (3)$$

where

() = concentrations of constituents

[] = activity of constituents

K* = selectivity constant

p = empirical activity correction

The activities of the solution phase are defined as

$$[A] = \gamma_A (A)$$

where

γ_A = activity coefficient of ion A

The activity coefficient is calculated from Davies' extension of the Debye-Huckel theory at 25°C.⁴

$$-\log \gamma_i = .509 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} \right) - .2I \quad (4)$$

where

z_i = valence of ion i

I = ionic strength of solution.

The ionic strength of the solution is calculated from the expression⁴

$$I = 1/2 \sum C_i z_i^2 \quad (5)$$

where

C_i = molal concentration of ion i

and the summation is taken over all the cations and anions in solution.

Dissolution-precipitation reactions in the soil-solution are represented by their heterogeneous equilibria

Slightly soluble salt and complex ion formation reactions are based on the solubility product rule in terms of activities,

$$K_{sp} = [A^{+y}]^x [B^{-x}]^y \quad (7)$$

Presently, the chemical model includes three binary cation exchange reactions between the solution and soil. These are sodium-potassium, sodium-calcium, and calcium-magnesium. The exchange reactions in symbolic form are:

The empirical equations for calculating the equilibrium concentrations are respectively:

$$K^*_{Na-K} = \frac{(Na^+)}{(K^+)} \left\{ \frac{(KX)}{(NaX)} \right\}^{P_1} \quad (8)$$

$$K^*_{Ca-Na} = \frac{\gamma_{Ca} (Ca^{+2})}{\gamma_{Na}^2 (Na^+)^2} \left\{ \frac{(Na_2X)}{(CaX)} \right\}^{P_2} \quad \text{and} \quad (9)$$

$$K^*_{Ca-Mg} = \frac{(Ca^{+2})}{(Mg^{+2})} \left\{ \frac{(MgX)}{(CaX)} \right\}^{P_3} \quad (10)$$

Note that the activity coefficients of like valenced ions in the same ionic strength solution are equal and thus cancel out as in equations 8 and 10.

Two slightly soluble salts and one complex ion formation are also included in the present macro model. These are gypsum ($CaSO_4 \cdot 2H_2O$), limestone ($CaCO_3$), and undissociated calcium sulfate ($CaSO_4$) aq.

The equilibrium concentrations for the gypsum reaction,

are determined using the solubility product rule and assuming the activity of water to be one. The mass action equation becomes

$$K_{Sp} \geq [Ca^{+2}][SO_4^{-2}] = \gamma_{Ca} (Ca^{+2}) \gamma_{SO_4} (SO_4^{-2}) \quad (11)$$

The reaction of the aqueous complex calcium sulfate,

is modeled using the dissociation constant as follows:

$$K_{diss} \geq [Ca^{+2}][SO_4^{-2}] = \gamma_{Ca} (Ca^{+2}) \gamma_{SO_4} (SO_4^{-2}) \quad (12)$$

The solubility of limestone is modeled using the solubility product rule and carbonic acid equilibria relationships. Since bicarbonate (HCO_3^-) is more easily measurable in the soil-solution system than carbonate (CO_3^{-2}), it is convenient to consider the overall reaction

The equilibrium equation is

$$K = \frac{[CaCO_3]_s [H_2CO_3]}{[Ca^{+2}] [HCO_3^-]^2} \quad (13)$$

The activity of carbonic acid is a constant if the partial pressure of carbon dioxide is constant.

$$\frac{[H_2CO_3]}{[H_2O][CO_2]} \approx \frac{[H_2CO_3]}{P_{CO_2(g)}} = K_o \quad (14)$$

At atmospheric equilibria the partial pressure of carbon dioxide is $10^{-3.5}$ atm., hence

$$[\text{H}_2\text{CO}_3] = K_o (P_{\text{CO}_2}) = K_o' \quad (15)$$

The first and second ionization constants of carbonic acid, K_1 and K_2 , are given by:

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1 \quad (16)$$

$$\frac{[\text{H}^+][\text{CO}_3^{-2}]}{[\text{HCO}_3^-]} = K_2 \quad (17)$$

combining Equations 15, 16, and 17 gives:

$$[\text{H}^+] = \frac{K_1 K_o'}{[\text{HCO}_3^-]} \quad (18)$$

$$[\text{CO}_3^{-2}] = \frac{K_2 [\text{HCO}_3^-]}{[\text{H}^+]} = \frac{K_2}{K_1 K_o'} [\text{HCO}_3^-]^2 \quad (19)$$

The solubility product constant of limestone is given by

$$K_{\text{Sp}} \geq \frac{[\text{Ca}^{+2}][\text{CO}_3^{-2}]}{[\text{CaCO}_3]_s} \quad (20)$$

Assuming that the activity of the solid phase, CaCO_3 , equals one and substituting Equation 19 for $[\text{CO}_3^{-2}]$, the expression for the carbonate equilibria is derived,

$$\frac{K_{\text{Sp}} K_1 K_o'}{K_2} \geq \frac{[\text{Ca}^{+2}][\text{HCO}_3^-]^2}{(\text{HCO}_3^-)^2} = \gamma_{\text{Ca}}(\text{Ca}^{+2}) \gamma_{\text{HCO}_3}^2 \quad (21)$$

In the PERCOL model, anion exchange is considered negligible. Anions other than those involved in slightly soluble salt or complex ion formation are considered to be non-reactive.

It should be noted that inherent in the model is the assumption that the influent seepage velocity is slow enough to allow chemical equilibria to be attained continuously throughout the system. Percolation velocities have generally been found to be slow enough to justify the use of this assumption at Hanford.

Microion Chemistry

The microions are assumed to be present in such small concentrations that they do not affect the macroions' chemical reactions or the sorption of other microions. The sorption of micro constituents is a specialized exchange reaction.

General ion exchange for a trace constituent in a macroion environment may be formulated as a replacement reaction:

Equation 22 expresses the competition between the micro and macroions for sorption sites on the soil. The mass action relationship for this system is

$$K_1 = \frac{(C_{\text{macro}})_{\text{eq.}} (A_{\text{micro}})_{\text{eq.}}}{(A_{\text{macro}})_{\text{eq.}} (C_{\text{micro}})_{\text{eq.}}} \quad (23)$$

Since the micro constituents are assumed to be present in minute quantities, the macro constituents essentially remain constant. Thus, it follows that a new constant is definable for a given macroion concentration

$$K_d = \frac{(A_{\text{micro}})_{\text{eq.}}}{(C_{\text{micro}})_{\text{eq.}}} \quad (24)$$

where

K_d = distribution coefficient (sorption coefficient)

$(A_{\text{micro}})_{\text{eq.}}$ = equilibrium trace concentration associated with the solid phase

$(C_{\text{micro}})_{\text{eq.}}$ = equilibrium trace concentration in the solution phase

Dropping the subscripts micro, the sorbed concentration becomes

$$A_{\text{eq.}} = K_d C_{\text{eq.}} \quad (25)$$

From Equation 25 the amount of sorption which will occur for a known soil-to-solution ratio can be calculated. Normally, the influent solution concentration (C_o), K_d , and soil-to-solution ratio (β) will be known and the equilibrium solution concentration and equilibrium soil concentration must be calculated. For an initially microion-free soil, the amount sorbed, Y_1 (amt./gm)

$$A_{\text{eq.}} = Y_1 = \frac{C_o - C_{\text{eq.}}}{\beta} \quad (26)$$

Solving Equation 26 for $C_{\text{eq.}}$ gives

$$C_{\text{eq.}} = C_o - Y_1 \beta \quad (27)$$

Combining Equations 26 and 25 gives

$$K_d = \frac{A_{\text{eq.}}}{C_o - Y_1 \beta} = \frac{Y_1}{C_o - Y_1 \beta} \quad (28)$$

Solving Equation 28 for Y_1 gives

$$Y_1 = \frac{K_d C_o}{1 + K_d \beta} \quad (29)$$

and $C_{eq.}$ is calculated from Equation 27.

If the first equilibrium solution is entirely removed from the soil and a second increment of C_o is added, then the sorption will be

$$A_{eq.} = Y_2 + Y_1 \quad (30)$$

Substitution of Equation 30 into Equation 25 gives

$$Kd = \frac{Y_2 + Y_1}{C_o - Y_2 \beta_2} \quad (31)$$

Solving for Y_2 gives

$$Y_2 = \frac{Kd C_o - Y_1}{1 + \beta Kd} \quad (32)$$

Thus, from Equation 32 and the Kd one can calculate the sorption for all additional solution additions. However, the Kd is not constant but a measureable system parameter whose numerical value has been shown to be a function of the soil type and the equilibrium concentration of all of the macroions in solution.² The equilibrium concentration of macroions in each soil is determinable by the macroion portion of the PERCOL model for each pore volume of solution in each soil segment. A method of estimating the Kd as a function of all equilibrium macroion concentrations will now be described.

The investigation of the effects of the macroion variables on the Kd is amenable to factorial experimentation. Factorial experiments allow the study of the effects of several variables and their interactions in one experimental design.

As an example, the following procedure was used to calculate an empirical Kd function for the radionuclide strontium (^{85}Sr). It has been determined that the macroions in a typical Hanford soil solution which compete with strontium in the cation exchange-sorption reactions include Ca^{+2} , K^+ , Na^+ , and H^+ (pH).²

A 2^4 factorial, batch system, sorption experiment was set up to determine the effects of the above four variables on strontium sorption. Two levels of concentration for each variable, high (H) and low (L), were permuted to yield sixteen observations (see Table 1).

Table 1. PERMUTATIONS USED IN THE FACTORIAL DESIGN EXPERIMENT

Experiment Number	Ca^{+2}	K^+	Na^+	pH
1	H	H	H	H
2	H	H	H	L
3	H	H	L	H
4	H	H	L	L
5	H	L	H	H
6	H	L	H	L
7	H	L	L	H
8	H	L	L	L
9	L	H	H	H
10	L	H	H	L
11	L	H	L	H
12	L	H	L	L
13	L	L	H	H
14	L	L	H	L
15	L	L	L	H
16	L	L	L	L

The observed K_d values were statistically analyzed to yield the four main and twelve interaction effects of the variables studied. These sixteen effects are used as the linear regression coefficients in an equation describing K_d as a function of the four variables studied. pH above 6.5 was found to have little influence on strontium sorption and was neglected in further calculations.

The K_d predictor equation becomes

$$K_d(\text{Sr}) = aX_{\text{Ca}} + bX_{\text{Na}} + cX_{\text{K}} + dX_{\text{CaNa}} + eX_{\text{CaK}} + fX_{\text{NaK}} + gX_{\text{CaNaK}} \quad (33)$$

where $a, \dots, g$ are the coefficients derived from the factorial design experiment and $X(i)$ are normalized concentration variables covering the range of concentration (H-L) used in the factorial experiment. For example:

$$X_{Ca} = \frac{(Ca) - (H_{Ca} + L_{Ca})/2}{(H_{Ca} - L_{Ca})/2}$$

where

H_{Ca} = high calcium concentration used in the factorial design experiment;

L_{Ca} = low calcium concentration used in the factorial design experiment;

(Ca) = value of calcium concentration for which K_d is being calculated

The variable $X(i)$ will lie between ± 1 for any concentration within the range used in the factorial design experiment.

Equation 33 is an approximation of a phenomenon which is complex and often nonlinear. Therefore, to obtain a more accurate fit, the variables' concentration ranges were subdivided and separate factorial experiments were performed for each smaller range.

PERCOL PROGRAM

The computer program PERCOL was developed prior to the generalized transport models for the specific purpose of simulating soil column experiments and problems. It is a revision and extension of a program developed by Dutt⁵, which predicts the quality of water and breakthrough of contaminants at incremental lengths throughout a porous media column profile. This model determines concentration changes on the basis of chemical thermodynamic equilibria between the porous media and solution systems. The velocity of the percolating flow is unidirectional and normal to the cross section of the column, and is assumed to be slow enough to allow chemical equilibrium between the percolating solution and porous media. In soils from the Hanford Reservation studied in experimental columns it has been found that the effects of ion exchange, sorption, dissolution and precipitation are dominant over the effects of diffusion and dispersion. Therefore, diffusion and dispersion are neglected in this model, but are included in the more refined multidimensional

transport model. Other assumptions used in PERCOL are summarized in Table 2.

Table 2. ASSUMPTIONS INTRINSIC TO THE PERCOL MODEL

- a. Dispersion, diffusion and evaporation are neglected.
- b. Seepage velocity is slow enough for equilibrium to be attained.
- c. Cation exchange capacity is constant for each porous media type.
- d. Binary equations approximate the complex cation exchange in porous media.
- e. Equilibrium states are path independent.
- f. Anion exchange is negligible.
- g. Limestone and gypsum are considered to be the only slightly soluble salts present and their solubility is assumed to be that of the crystalline form.
- h. Undissociated calcium sulfate is the only complex ion formed.
- i. Activity coefficients follow the extended Debye-Huckel theory.
- j. Uniform moisture content is present.
- k. Microions' reactions are determined by the macroions present as described by factorial design regression coefficients.

PERCOL solves a one dimensional version of the transport equation, (Equation 34), using a Lagrangian coordinate system ($q=0$). Since diffusion and dispersion are neglected, the resultant equation becomes

$$\frac{\partial (\alpha C^k)}{\partial t} = r_s \quad (34)$$

where the reaction term r_s represents sorption for micro-ions and represents all chemical reactions for the macro-ions.

The sorption relationship is based on an incremental change Δ in concentration sorbed on the soil. Defined in terms of initial or previous equilibrium states, these relationships are

$$A_{eq.} = A_o + \Delta \quad \text{and} \quad (35)$$

$$C_{eq.} = C_o - \beta \Delta \quad (36)$$

where

A_o = initial or previous equilibrium concentration in the solid phase,

C_o = initial or previous equilibrium concentration in the liquid phase,

Δ = incremental concentration change, and

β = soil to solution ratio.

Solving Equations 35 and 36 for the incremental change and applying Equation 25 yields

$$\Delta = \frac{KdC_o - A_o}{1 + \beta Kd} \quad (37)$$

Substitution of Δ into Equations 35 and 36 gives

$$A_{eq.} = A_o + \frac{KdC_o - A_o}{1 + \beta Kd} = \frac{A_o Kd\beta + KdC_o}{1 + \beta Kd} \quad \text{and} \quad (38)$$

$$C_{eq.} = C_o - \frac{(\beta KdC_o - A_o)}{1 + \beta Kd} = \frac{C_o + \beta A_o}{1 + \beta Kd} \quad (39)$$

Cation exchange expressions for the macroions are a combination of theoretical equations and empirical solid phase correction terms, as has been previously described. For example, the exchange reaction for sodium-calcium becomes

$$K^*_{Na-Ca} = \frac{\gamma_{Ca} (Ca)}{\gamma_{Na}^2 (Na)^2} \left\{ \frac{(Na_2X)}{(CaX)} \right\}^p \quad (40)$$

Since the solid phase activity parameter, p , is not an integer, a Newton-Raphson technique is applied to calculate the equilibrium concentrations. The activity coefficients are calculated from the extended Debye-Huckel theory (Equation 4). The equilibrium concentration of each constituent in Equation 40 may be expressed in terms of the initial concentrations and a finite concentration change, Δ . Using the conservation of mass principle, equations dependent only on Δ can be generated:

$$(Ca) = Ca_o^{+2} + \beta\Delta$$

$$(Na) = Na_o^{+} - 2\beta\Delta$$

$$(CaX) = CaX_o - \Delta$$

$$(NaX) = NaX_o + 2\Delta$$

Upon substitution the resultant algebraic expression is obtained:

$$\frac{\gamma_{Ca} (Ca_o^{+2} + \beta\Delta)}{\gamma_{Na}^2 (Na_o^{+} - 2\beta\Delta)} \left\{ \frac{(NaX_o + 2\Delta)}{(CaX_o - \Delta)} \right\}^p - K^*_{Na-Ca} = 0 \quad (41)$$

A subroutine (NEWTIT) determines the real root of the equation

$$f(\Delta) = 0$$

by the Newton-Raphson iterative technique. An initial estimate, Δ_o , the first derivative, $f'(\Delta)$, of Equation 41 and an error limit E are needed to start the iterative algorithm:

$$\Delta_1 = \Delta_0 + h_0$$

$$\Delta_2 = \Delta_1 + h_1$$

.

.

.

$$\Delta_{n+1} = \Delta_n + h_n$$

where

$$h_i = \frac{f(\Delta_i)}{f'(\Delta_i)}$$

Convergence is met when

$$f(\Delta_i) \leq E_{\max}$$

The calcium carbonate solubility equilibrium is also solved using the Newton-Raphson technique. The two calcium sulfate equilibria relations are solved by using the quadratic formula and extracting the one satisfactory root. The solubility product principle in terms of Δ is used to describe the gypsum equilibrium (Equation 24) where the concentration becomes

$$(\text{Ca}^{+2}) = \text{Ca}_o^{+2} + \Delta$$

$$(\text{SO}_4^{-2}) = \text{SO}_{4o}^{-2} + \Delta$$

and Δ = amount that dissolves (+) or precipitates (-). Substituting the above two equations into the solubility expression, a quadratic equation in terms of Δ is obtained,

$$\Delta^2 + (\text{Ca}_o^{+2} + \text{SO}_{4o}^{-2})\Delta + (\text{Ca}_o^{+2})(\text{SO}_{4o}^{-2}) - K_{\text{Sp}}/\gamma_{\text{Ca}}\gamma_{\text{SO}_4} = 0.$$

It follows that

$$\Delta = \frac{-(\text{Ca}_o^{+2}\text{SO}_4^{-2}) \pm [(\text{Ca}_o^{+2}\text{SO}_4^{-2})^2 - 4K_{\text{Sp}}/\gamma_{\text{Ca}} \gamma_{\text{SO}_4}]^{1/2}}{2}$$

The correct root is selected by requiring that all the chemical concentrations remain ≥ 0 . The aqueous undissociated calcium sulfate equilibrium expression is solved in an analogous fashion.

An iterative technique is used to simulate simultaneous equilibria of all constituents in the solution from the separate equations. After all the equilibria reactions are satisfied, PERCOL compares the final chemical concentration values with the previous values. If any solution constituent has changed by more than a given tolerance limit, the equilibrium values are set as the new initial concentrations and equilibrium calculations are repeated until all solution concentration changes satisfy the tolerance limit. When this requirement is met, equilibration is complete and the percolating solution is sent into the next soil subdivision. When the aliquot equilibrates with all the soil subdivisions, it exits as an effluent and a new aliquot is initiated at the top of the column. A User's Manual, BNWL-1720, details the application of the PERCOL computer program.

MODEL VERIFICATION STUDIES

To verify the PERCOL model for some representative soils of the vadose zone of the Hanford Project, column studies were conducted to compare model predicted and measured trace solute (radionuclide) movement. Details of the exact experimental techniques used in the studies are given in an accompanying document (BNWL-1719). The initial column run (control run) was made with a saturated Tank Farm sandy loam soil, ^{85}Sr as the trace solute, a 25 cm column and a measured influent chemical system. System parameters which were varied with additional columns to verify the model include: 1) column length; 2) Cs as the trace radionuclide; 3) variable flow rate; 4) second soil (Burbank sand); and 5) a range of soil saturations. Soil properties for Tank Farm sandy loam and Burbank sand used in the column studies are given in Table 3. These soils represent the textural soil range which generally occurs in the vadose zone of the Hanford Reservation.

Table 3. PROPERTIES OF SOILS

<u>Soil</u>	<u>CaCO_3, mg/g</u>	<u>Silt, %</u>	<u>Clay, %</u>	<u>CEC (pH 7.0), meq/100g</u>	<u>pH in 0.01M, CaCl_2</u>
Burbank Sand	0.8	10.1	0.5	4.9	7.0
Tank Farm Sandy Loam	26.0	29.5	4.9	4.0	8.0

CONTROL COLUMN STUDY

Table 4 gives the column operational parameters for the control column using the Tank Farm sandy loam soil. This 25 cm column was run under saturated conditions. The simulated influent waste stream was near the ionic strength limit for which Davies' equation could be used to calculate activity coefficients.⁴ Figure 1 shows the normalized movement of ^{85}Sr (C/C_0) as a function of the column volumes

Table 4. SOIL COLUMN PARAMETERS FOR A 25 cm
TANK FARM SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	25.0 cm
Soil Volume	268 cm ³
Soil Weight	410 g
Cation Exchange Capacity	4.5 meq/100 g
CaCO ₃	2.6 x 10 ⁻⁴ moles/g
Flow Rate	1.1 cm/hr
Influent (Ca ⁺⁺)	4.40 meq/l
Influent (Na ⁺)	150 meq/l
Influent (K ⁺)	11.0 meq/l
Bulk Density	1.53 g/cm ³
Temperature	23 ± 3°C
Influent pH	7.0 ± .1
Soluble (Ca ⁺⁺)	5.9 x 10 ⁻³ meq/g
Soluble (Na ⁺)	2.4 x 10 ⁻² meq/g
Soluble (K ⁺)	4.1 x 10 ⁻⁴ meq/g
Soluble (Mg ⁺⁺)	3.7 x 10 ⁻³ meq/g
⁸⁵ Sr Influent	~2000 cpm/soil

of effluent solution. The solid line represents the movement predicted by the PERCOL model and the dots represent the laboratory measured data points. It can be seen that agreement between the predicted and measured trace Sr movement is good up to C/C₀ value of 0.8. Above a C/C₀ of 0.8 the predicted values become conservative in relation to the measured values, probably due to the slow diffusion of ⁸⁵Sr.

FIGURE 1. NORMALIZED EFFLUENT CONCENTRATION (C/C_0) OF ^{85}Sr FROM A 25 cm TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF COLUMN VOLUMES OF EFFLUENT SOLUTION. (Solid line represents model predicted curve and dots are measured data points.)

into some dead end pores which fail to transmit solution. However, this is not believed to be a serious handicap to the model since the disposal to ground sites almost never exceeds a C/C_0 of a few tens of percent. Figures 2, 3 and 4 show the movement of the influent macroions Na^+ , K^+ , and Ca^{++} as a function of column volumes of effluent solution. It can be seen that agreement between PERCOL model predicted and measured movement is generally good for K^+ and Na^+ but less so for Ca^{++} . The leveling of the Ca^{++} movement curve at 0.006 M is probably due to some unidentified solid Ca-phase more soluble than CaCO_3 and less soluble than CaSO_4 . Failure of the model to predict this plateau only nominally affects the trace ion movement. This effect was not found in the Burbank sand, and would rarely be expected in most natural soils.

FIGURE 2

EFFLUENT Na-CONCENTRATION

FIGURE 3

EFFLUENT K-CONCENTRATION

FIGURE 4

EFFLUENT Ca-CONCENTRATION

EFFLUENT CONCENTRATIONS FROM A SATURATED 25 cm TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF EFFLUENT COLUMN VOLUMES OF SOLUTION. (Solid line represents model predicted curve and dots are measured data points.)

COLUMN LENGTH STUDIES

Previous Hanford studies have shown the movement of radio-nuclides in soil columns to be independent of the column diameter and a function of column length.^{5,6} Thus, for any model to be viable it must account for this length dependence. Tables 5 and 6 give the column operational parameters for 50 and 100 cm columns. Figures 5 and 6 show the movement of ⁸⁵Sr as a function of the effluent column volumes of solution for the 50 cm and 100 cm columns, respectively. It can be seen that agreement between the PERCOL model predicted and measured ⁸⁵Sr movement is good. In both cases the number of microion segments chosen was one segment per cm of column length. Figures 7, 8, 9, 10, 11, and 12 show that the movement is in good agreement with that of the 25 cm control columns.

Essentially the same macroion agreement was found for all the additional saturated columns and thus only microion movement will be shown in the balance of the Tank Farm sandy loam saturated columns.

Table 5. SOIL COLUMN PARAMETERS FOR A 49 cm
TANK FARM SANDY LOAN SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	49.2
Column Volume	529 cm ³
Cation Exchange Capacity	4.5 meq/100 g
Soil Weight	823 g
CaCO ₃	2.6 x 10 ⁻⁴ moles/g
Flow Rate	2.1 cm/hr
Influent (Ca ⁺⁺)	4.52 meq/l
Influent (Na ⁺)	152 meq/l
Influent (K ⁺)	10.3 meq/l
Bulk Density	1.56 g/cm ³
Soluble (Ca ⁺⁺)	5.9 meq/g
Soluble (Na ⁺)	24 meq/g
Soluble (K ⁺)	0.41 meq/g
Soluble (Mg ⁺⁺)	3.7 meq/g
⁸⁵ Sr Influent	~2000 cpm/ml (~0.9 x 10 ⁻³ μ Ci/ml)

Table 6. SOIL COLUMN PARAMETERS FOR A 114 cm
TANK FARM SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	114.4 cm
Column Volume	1230 cm ³
Cation Exchange Capacity	4.5 meq/100 g
Soil Weight	1926 g
CaCO ₃	2.6 x 10 ⁻⁴ moles/g
Flow Rate	2.1 cm/hr
Influent (Ca ⁺⁺)	4.14 meq/l
Influent (Na ⁺)	142 meq/l
Influent (K ⁺)	9.9 meq/l
Bulk Density	1.57 g/cm ³
Temperature	23 ± 3°C
Influent pH	7.0 ± 0.1
Soluble (Ca ⁺⁺)	5.9 meq/g
Soluble (Na ⁺)	24 meq/g
Soluble (K ⁺)	0.41 meq/g
Soluble (Mg ⁺⁺)	3.7 meq/g
⁸⁵ Sr Influent	~2000 cpm/ml (~0.9 x 10 ⁻³ μCi/ml)

Cs COLUMN STUDY

Table 7 gives the column operational parameters for a ¹³⁴Cs movement study. Figure 13 shows the movement of ¹³⁴Cs as a function of the column volumes of effluent solution. It can be seen that the agreement between the PERCOL model predicted and measured Cs movement is good. It should be noted that Cs is generally sorbed to a greater extent than Sr, and C/C₀ of 0.5 Cs occurs at 15 column volumes compared with about 7 column volumes with Sr (Fig. 1). This occurred even though the influent K⁺ was 0.15 M and K⁺ is known to have a highly competitive effect on the sorption Cs. If the influent K⁺ concentration were the same as for the column shown in Figure 1, a very large number of column volumes would be necessary to obtain measureable ¹³⁴Cs breakthrough.

FIGURE 5. NORMALIZED EFFLUENT CONCENTRATION (C/C_0) OF ^{85}Sr FROM A 49 cm TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF EFFLUENT COLUMN VOLUMES SOLUTION (Solid line represents model predicted curve and dots are measured data points.)

FIGURE 6. NORMALIZED EFFLUENT CONCENTRATION (C/C_0) OF ^{85}Sr FROM A 114 cm TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF COLUMN VOLUMES EFFLUENT SOLUTION. (Solid line represents model predicted curve and dots are measured data points.)

FIGURE 7. EFFLUENT
Na-CONCENTRATION

FIGURE 8. EFFLUENT
K-CONCENTRATION

FIGURE 9. EFFLUENT
Ca-CONCENTRATION

EFFLUENT CONCENTRATIONS FROM A 49 cm TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF EFFLUENT COLUMN VOLUMES OF SOLUTION. (Solid lines represent model predicted curve and dots measured data points.)

FIGURE 10. EFFLUENT
Na-CONCENTRATION

FIGURE 11. EFFLUENT
K-CONCENTRATION

FIGURE 12. EFFLUENT
Ca-CONCENTRATION

EFFLUENT CONCENTRATIONS FROM A 114 cm TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF EFFLUENT COLUMN VOLUMES OF SOLUTION. (Solid line represents model predicted curve and dots measured data points.)

Table 7. COLUMN PARAMETERS FOR A TANK FARM
SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	24.2 cm
Soil Weight	364.1 g
Soil Volume	232.8 g/cm ³
Flow Rate	0.50 cm/hr
Bulk Density	1.56 g/cm ³
Temperature	23 ± 3°C
Influent (K ⁺)	0.15 <u>M</u>
Influent (Na ⁺)	0.05 <u>M</u>
Influent (Ca ⁺⁺)	0.01 <u>M</u>
Influent ¹³⁴ Cs	≈ 2000 cpm/ml
CaCO ₃	2.6 x 10 ⁻⁴ moles/g
Soluble (Ca ⁺⁺)	5.9 meq/g
Soluble (Na ⁺)	24 meq/g
Soluble (K ⁺)	0.41 meq/g
Soluble (Mg ⁺⁺)	3.7 meq/g

FIGURE 13. NORMALIZED MOVEMENT OF ¹³⁴Cs (C/C₀) THROUGH A TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF COLUMN VOLUMES OF THROUGHPUT SOLUTION. (Solid line is model predicted movement and dots are data points.)

VARIABLE FLOW RATE COLUMN STUDY

To check the effect of flow rate on the PERCOL model, variable flow rates of half and double the control were applied at various times during a column run. Table 8 gives the column operational parameters for the variable flow rate column. Figure 14 shows the normalized movement of ^{85}Sr as a function of the effluent column volumes of solution. It can be seen that agreement between the PERCOL model predicted and the measured ^{85}Sr movement is good. Small perturbations in the data are noticeable immediately after changing the flow rate; however, these effects were short-lived and had no measureable effect upon the overall movement curve. The lack of effect of flow rate variation strongly suggests that the equilibrium assumption of the model is adequate for the measured systems.

BURBANK SAND COLUMN STUDY

The Burbank sand has a low-exchange capacity so a column run was made using this as a second porous media. Table 9 gives the column operational parameters for the Burbank sand. Figure 15 shows the normalized movement of ^{85}Sr as a function of effluent solution volume. It can be seen that the agreement between PERCOL model predicted and measured ^{85}Sr movement is good. Figures 16 and 17 show the movement of macroion Ca^{++} , Na^{+} , and K^{+} as a function of effluent volume. It can be seen that agreement between PERCOL model predicted and measured macroion movement is generally good for all three ions. In contrast to the Tank Farm sandy loam, no Ca^{++} plateau was observed which is again an indication that an additional solid Ca phase may exist in the saline Tank Farm sandy loam soil. The agreement of this data and Tank Farm sandy loam data with PERCOL model data is a strong indication that the PERCOL model is adequate for describing the movement of trace Sr and Cs in the saturated porous media of the Hanford system.

UNSATURATED COLUMN STUDIES

To more fully verify the model, it was checked for operation under unsaturated conditions. A group of unsaturated soil columns was run as a function of saturation. Tables 10, 11, 12, 13, and 14 give the column operational parameters for 96%, 75%, 62%, 52%, and 45% saturations. Figures 18, 19, 20, 21, and 22 show the normalized movement of ^{85}Sr as a function of effluent column volumes of solution. It can be seen that the agreement between the PERCOL model and measured ^{85}Sr movement is generally good. The maximum disagreement for the five columns at a C/C_0 of 0.5 is about 6%, which is within experimental error considering the many parameters which are measured in the system. There is no

Table 8. COLUMN PARAMETERS FOR A TANK FARM
SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	24.9 cm
Soil Weight (Air Dry)	438.8 g
Soil Volume	267.73 cm ³
Flow Rate	(a) 1.02 cm/hr ¹ (b) 2.08 cm/hr ¹ (c) .51 cm/hr ¹
Bulk Density	1.6 g/cm ³
Temperature	23 ± 3°C
Influent (K ⁺)	.0103 <u>M</u>
Influent (Na ⁺)	.1420 <u>M</u>
Influent (Ca ⁺⁺)	.00208 <u>M</u>
Influent ⁸⁵ Sr	≈ 2000 cpm/ml
Influent pH	7.0
CaCO ₃	2.57 x 10 ⁻⁴ moles/g
CaSO ₄ ·2H ₂ O	3.1 x 10 ⁻⁷ moles/g
Soluble (Ca ⁺⁺)	5.9 x 10 ⁻³ meq/g
Soluble (Na ⁺)	2.4 x 10 ⁻² meq/g
Soluble (K ⁺)	4.1 x 10 ⁻⁴ meq/g
Soluble (Mg ⁺⁺)	3.7 x 10 ⁻³ meq/g
Soluble (SO ₄ ⁼)	1.2 x 10 ⁻⁴ meq/g
Soluble (NO ₃ ⁻)	2.9 x 10 ⁻⁴ meq/g

¹ See Fig. 14

Table 9. COLUMN PARAMETERS FOR A BURBANK SAND SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	100 cm
Column Volume	1080 cm ³
Soil Weight (Oven Dry)	1785 gms
C.E.C.	4.8 meq/100 g
CaCO ₃	8 x 10 ⁻⁶ moles/gm
Flow Rate	1.02 cm/hr
Influent Ca	0.0020 <u>M</u>
Influent Na	0.10 <u>M</u>
Influent K	0.050 <u>M</u>
Bulk Density	1.65 g/cm ³
Temperature	23.5 ± 3°C

FIGURE 14. NORMALIZED MOVEMENT OF ⁸⁵Sr THROUGH A TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF COLUMN VOLUMES OF THROUGHPUT SOLUTION. (Solid line is model predicted movement and dots are data points.)

FIGURE 15. RELATIVE
MOVEMENT OF ^{85}Sr

FIGURE 16. EFFLUENT
Ca-CONCENTRATION

FIGURE 17. EFFLUENT K and
Na-CONCENTRATIONS

RELATIVE MOVEMENT AND EFFLUENT CONCENTRATIONS FROM A BURBANK SATURATED SAND SUBSOIL AS A FUNCTION OF EFFLUENT VOLUME. (Solid lines represent model predicted curves and dots are measured data points.)

Table 10. COLUMN PARAMETERS FOR AN UNSATURATED
TANK FARM SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Saturation	96%
Soil Weight	147 gms
Soil Volume	90.8 cm ³
Bulk Density	1.62 gms/cm ³
Column Length	10.0 cm
Flow Rate	0.22 cm/hr
Temperature	23 $\pm$ 5°C
CaCO ₃	2.6 x 10 ⁻⁴ moles/g
pH	7.0
Soluble (Ca ⁺⁺)	5.9 meq/g
Soluble (K ⁺)	0.41 meq/g
Soluble (Mg ⁺⁺)	3.7 meq/g
Soluble (Na ⁺)	24 meq/g
Soluble (SO ₄ ⁻)	.12 meq/g
Soluble NO ₃ ⁻)	.29 meq/g
Influent (K ⁺)	5.1 x 10 ⁻³ <u>M</u>
Influent (Ca ⁺⁺)	2.1 x 10 ⁻³ <u>M</u>
Influent (Na ⁺)	1.45 x 10 ⁻¹ <u>M</u>
Influent (⁸⁵ Sr)	~2000 cpm/ml

Table 11. COLUMN PARAMETERS FOR AN UNSATURATED
TANK FARM SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Saturation	75%
Column Length	18.3 cm
Soil Weight	284 g
Soil Volume	166 cm ³
Flow Rate	2.27 ml/hr
Bulk Density	1.71 g/cm ³
Temperature	23 $\pm$ 3°C
CaCO ₃	2.6 x 10 ⁻⁴ moles/g
pH	7.0
Soluble (Ca ⁺⁺)	5.9 meq/g
Soluble (Mg ⁺⁺)	3.7 meq/g
Soluble (K ⁺)	0.41 meq/g.
Soluble (Na ⁺)	24 meq/g
Influent Na ⁺	0.146 <u>M</u>
Influent K ⁺	0.0021 <u>M</u>
Influent Ca ⁺⁺	0.0054 <u>M</u>

Table 12. COLUMN PARAMETERS FOR AN UNSATURATED
TANK FARM SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Saturation	64%
Column Length	18.3 cm
Soil Weight	271 g
Soil Volume	166 cm ³
Flow Rate	2.34 ml/hr
Bulk Density	1.63 g/cm ³
Temperature	23 $\pm$ 3°C
CaCO ₃	2.6 x 10 ⁻⁴ moles/g
pH	7.0
Soluble (Ca ⁺⁺)	5.9 meq/g
Soluble (Mg ⁺⁺)	3.7 meq/g
Soluble (K ⁺)	0.41 meq/g
Soluble (Na ⁺)	24 meq/g
Influent (Na ⁺)	0.13 <u>M</u>
Influent (K ⁺)	0.066 <u>M</u>
Influent (Ca ⁺⁺)	0.0022 <u>M</u>
Influent ⁸⁵ Sr	~2000 cpm/ml

Table 13. COLUMN PARAMETERS FOR AN UNSATURATED
TANK FARM SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Saturation	52%
Soil Weight	276 g
Soil Volume	166 cm
Flow Rate	0.22 cm/hr
Bulk Density	1.66 g/cm ³
Temperature	23 $\pm$ 3°C
CaCO ₃	2.6 x 10 ⁻⁴ moles/g
pH	7.0
Soluble (Ca ⁺⁺)	5.9 meq/g
Soluble (K ⁺)	3.7 meq/g
Soluble (Mg ⁺⁺)	0.41 meq/g
Soluble (Na ⁺)	24 meq/g
Soluble (SO ₄ ⁼)	0.12 meq/g
Soluble (NO ₃ ⁻)	0.29 meq/g
Influent (K ⁺)	0.01 <u>M</u>
Influent (Ca ⁺⁺)	0.002 <u>M</u>
Influent (Na ⁺)	0.15 <u>M</u>
Influent (⁸⁵ Sr)	~2000 cpm/ml

Table 14. COLUMN PARAMETERS FOR AN UNSATURATED TANK
FARM SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Saturation	45%
Length	5.1 cm
Soil Weight	71.13 gms
Soil Volume	46.30 cm ³
Bulk Density	1.57 g/cm ³
Temperature	23 $\pm$ 3°C
CaCO ₃	2.6 x 10 ⁻⁴ moles/g
pH	7.0
Influent (CaCl ₂)	0.13 <u>M</u>
Influent (KCl)	0.009 <u>M</u>
Influent (NaCl)	0.231 <u>M</u>
Saturation	45.2%
Flow Rate	0.055 cm/hr
Soluble (Ca ⁺⁺)	5.9 x 10 ⁻³ eq/g
Soluble (Mg ⁺⁺)	3.7 x 10 ⁻³ eq/g
Soluble (K ⁺)	4.1 x 10 ⁻⁴ eq/g
Soluble (Na ⁺)	2.4 x 10 ⁻² eq/g

FIGURE 18

FIGURE 19

MOVEMENT OF ^{85}Sr THROUGH AN UNSATURATED TANK FARM SANDY LOAM SOIL COLUMN. (Solid curve is model predicted curve and dots are measured data.)

FIGURE 20

FIGURE 21

FIGURE 22

MOVEMENT OF ^{85}Sr THROUGH AN UNSATURATED TANK FARM SANDY LOAM SOIL COLUMN. (Solid curve is predicted movement and dots are measured data points.)

apparent reduction of sorption as a function of saturation in these systems. To obtain lower saturations at which sorption may be reduced for the Tank Farm sandy loam soil or any finer textured media, a prohibitively long experimental time would be required (in the order of a year). At the low tensions and saturation of such soils only a limited amount of solution will be transmitted per unit area and the sorption of radionuclides in these zones is probably negligible in an actual field percolation system. Figures 23, 24, and 25 show the movement of macroions Na^+ , K^+ , and Ca^{++} as a function of column effluent volumes for the 73% saturation column. It can be seen that the unsaturated movement of these macroions is in general agreement with those in the saturated systems.

FIGURE 23. EFFLUENT Na-CONCENTRATION FROM AN UNSATURATED (75%) TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF EFFLUENT COLUMN VOLUMES OF SOLUTION. (Solid line represents model predicted curve and dots measured data points.)

FIGURE 24. EFFLUENT K-CONCENTRATION

FIGURE 25. EFFLUENT Ca-CONCENTRATION

EFFLUENT CONCENTRATIONS FROM AN UNSATURATED TANK FARM SANDY LOAM SOIL COLUMN AS A FUNCTION OF EFFLUENT COLUMN VOLUMES OF SOLUTION. (Solid line represents model predicted curve and dots measured data points.)

ERROR AND SENSITIVITY ANALYSIS

An error analysis was made to estimate the maximum laboratory analytical errors of each parameter measurement which could be expected from triplicate analyses. These maximum estimated analytical errors were used to perform a sensitivity analysis of the PERCOL model and the effect of these errors on the predicted movement of ^{85}Sr through the Tank Farm sandy loam and Burbank sand soils was determined. Tables 15 and 16 list the results of the analyses. The percentage deviation of effluent column volume at a C/C_0 of 0.5 from that predicted by the measured parameter was selected as the quantitative measure of the variation.

From Tables 15 and 16 it can be seen that input variation in CaCO_3 content; cation exchange capacity; soluble Ca^{++} , Na^+ , and K^+ ; influent Ca^{++} and Na^+ ; and exchange parameters had negligible effect on the predicted movement of Sr. The PERCOL model is most sensitive to variations in the empirical Sr-sorption equations for both the Tank Farm sandy loam and Burbank sand soils. Sample quartering and replication has been found to minimize this possible error. The second most sensitive parameter is the bulk density of both soils. With care, laboratory bulk densities can be measured to less than 3%, which minimizes this error. Influent K^+ concentration had essentially no effect in the case of the Tank Farm sandy loam, but significant effect in the case of the Burbank sand. The difference may be due to the greater dependence of exchange capacity on the illite content and a greater K^+ selectivity of the Burbank sand. With care, influent K^+ can be measured to $\pm 1\%$ to minimize this error.

The above analysis gives a qualitative evaluation of the effects of natural variations in the porous media of the Hanford Reservation's hydrogeologic system on the movement of trace radionuclides. The parameter to which the model is most sensitive must be measured with the greatest accuracy. In the laboratory, the developed analytical techniques are sufficient for the measurement of all the model parameters.

Table 15. BURBANK SAND SUBSOIL PARAMETERS VARIED TO
DETERMINE THEIR EFFECT ON THE MOVEMENT OF
EFFLUENT ^{85}Sr

Run	Parameter	Mean Value	Variation Value %	Volume Variation %
1.	C.E.C.	4.8 meq/100g	-17%	<0.5
2.	C.E.C.	4.8 meq/100g	+25%	<0.5
3.	KNa-K	5.9	-17%	<0.5
	MNa-K	1.03	-12%	
4.	KNa-K	5.9	+14%	<0.5
	MNa-K	1.03	+36%	
5.	KCa-Na	0.97	+24%	<0.5
	MCa-Na	1.13	+13%	
6.	KCa-Na	0.97	- 6%	<0.5
	MCa-Na	1.13	-24%	
7.	KCa-Mg	0.11	+10%	<0.5
	MCa-Mg	3.05	-17%	
8.	KCa-Mg	0.11	-18%	<0.5
	MCa-Mg	3.05	+21%	
9.	Bulk density (ρ_b)	1.65	- 6%	+14%
10.	Bulk density (ρ_b)	1.65	- 3%	+ 7%
11.	Soluble (Ca^{++})	0.12 meq/l	-75%	<0.5
12.	Soluble (Ca^{++})	0.12 meq/l	+1000%	<0.5
13.	Soluble (Mg^{++})	0.36 meq/l	+100%	<0.5
14.	Soluble (Mg^{++})	0.36 meq/l	-50%	<0.5
15.	Influent (Na^+)	0.10 M	-40%	<0.5
16.	Influent (Na^+)	0.10 M	+20%	<0.5
17.	Sorption Equation	Mean Kds	Max. Kds	-14%
18.	Sorption Equation	Mean Kds	Min. Kds	+48%
19.	CaCO_3	7.9×10^{-6} moles/g	-98%	<0.5
20.	CaCO_3	7.9×10^{-6} moles/g	+2500%	<0.5
21.	Influent Ca	0.002 moles/l	-10%	<0.5
22.	Influent Ca	0.002 moles/l	+10%	<0.5
23.	Influent K	0.050 moles/l	+30%	+50%
24.	Influent K	0.050 moles/l	-30%	-65%

Table 16. TANK FARM SANDY LOAN SUBSOIL PARAMETERS VARIED
TO DETERMINE THEIR EFFECT ON THE MOVEMENT OF
EFFLUENT ^{85}Sr

Run	Parameter	Mean Value	Variation Value %	Volume Variation %
1.	C.E.C.	4.5 meq/100g	+124	<0.5
2.	C.E.C.	4.5 meq/100g	-82	<0.5
3.	KNa-K	8.23	-100	<0.5
	MNa-K	1.15	-100	<0.5
4.	KNa-K	8.23	+104	<0.5
	MNa-K	1.15	-103	<0.5
5.	KCa-Na	2.24	+177	<0.5
	MCa-Na	0.494	+119	<0.5
6.	KCa-Na	2.24	-68	<0.5
	MCa-Na	0.494	-173	<0.5
7.	KCa-Mg	1.26	+101	<0.5
	MCa-Mg	1.23	+102	<0.5
8.	KCa-Mg	1.26	-98	<0.5
	MCa-Mg	1.23	-98	<0.5
9.	Bulk Density (ρ_b)	1.62	+104	+37
10.	Bulk Density (ρ_b)	1.62	-97	-4
11.	Influent (Na^+)	$1.52 \times 10^{-1} \text{M}$	+120	+12
12.	Influent (Na^+)	1.52×10^{-1}	-80	-13
13.	Influent (Ca^{++})	2.26×10^{-3}	+125	+3
14.	Influent (Ca^{++})	2.26×10^{-3}	-90	-8
15.	Influent (K^+)	1.03×10^{-2}	+130	+4
16.	Influent (K^+)	1.03×10^{-2}	-70	-4
17.	CaCO_3	2.57×10^{-4} moles/g	+1000	<0.5
18.	CaCO_3	2.57×10^{-4} moles/g	-100	-8
19.	Sorption Equation	Mean Kds	Max. Kds	+11
20.	Sorption Equation	Mean Kds	Min. Kds	-47

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