

PENETRATION MODEL FOR DYNAMIC PERMEABILITY ANALYSIS

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ABSTRACT: A generalized one-dimensional discrete interface penetration model is presented for fluid propagation through a reactive porous medium during constant head infiltration. The model has been formulated to predict the consequences of changes in hydraulic conductivity produced by strong chemical interactions between the solid and fluid phases as a reacting fluid front advances. Analytical solutions are presented for the resulting transient potential gradients, interface locations, and volumetric flux response. Solution type curves are presented to illustrate the typical response of several reaction/interaction mechanisms. Characteristic laboratory responses are also discussed. The model is shown to be capable of reproducing commonly observed laboratory results and may provide insight into the mechanisms most responsible for hydraulic conductivity fluctuations. Although the analysis is based on relatively simple phenomenological assumptions, these results should also offer a logical point of departure for more detailed mechanistic modeling.

INTRODUCTION

It is well known that the chemical composition of infiltrating fluid can exert major impacts on the hydraulic conductivity of a porous medium. Numerous laboratory studies have been conducted in soil science, agricultural, environmental, geotechnical, water resources, and petroleum engineering applications to quantify these changes. Many other experiments, such as soil column attenuation studies, have been affected by unanticipated and undesirable changes in hydraulic conductivity. Although a great deal of the recent interest has concentrated on the problem of hazardous waste containment, undesirable domain interactions associated with irrigation, ground-water recharge, and land treatment systems remain important environmental considerations.

Several researchers have examined the potential physical impacts of leachates and full-strength hazardous wastes on the permeability of soils (Acar, et al. 1985; Brown and Anderson 1981; Cartwright, et al. 1977; Crim, et al. 1979; Dunn 1983; Dunn and Mitchell 1984; Gee, et al. 1980; Green, et al. 1981; Griffin and Shimp 1978). The primary focus of this work has been to assess the potential for "unexpected" increases in leakage from landfills, storage lagoons, and waste impoundments due to liner deterioration and dramatic conductivity increases. Many of these studies have concentrated on the impact of high-strength organic solvents, but inorganics such as full-strength acids and caustics have also been investigated (Gipson 1985; Lentz, et al. 1985; Nasiatka, et al. 1981; Peterson and Gee 1985). The typical result is that under hostile chemical conditions, soil permeabilities may be altered by orders of magnitude.

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A substantial body of work has also addressed the relationships between irrigation water quality and long-term hydraulic properties of soil (Alperovitch, et al. 1981; Frenkel, et al. 1978; McNeal and Coleman 1966; McNeal, et al. 1966; Park and O'Connor 1980; Quirk and Schofield 1955; Shainberg, et al. 1981; Yaron and Thomas 1968). Decreases in soil conductivity resulting from incompatible irrigation water can yield severe crop damage due to excessive water ponding. Similar impacts of wastewater composition on soil hydraulic conductivity must be considered in the design of land treatment systems (Burton, et al. 1981; Trick, et al. 1985). It has also been demonstrated that the inland extent of saltwater intrusions can be altered by dynamic changes in soil properties. Apparently, episodic changes in the ionic strength of pore water yield reversible and irreversible impacts on the aquifer's hydraulic conductivity (Goldenberg and Magaritz 1983; Goldenberg, et al. 1984; Mehnert and Jennings 1985). Attempts to associate these effects with soil mineralogy have been modestly successful.

The potential impact of acid rain and acid mine drainage on the hydraulic conductivity in sensitive watersheds has also been recognized as a new consideration in long-term water resources planning and management (Otte and Jennings 1984). Although soil acidification is a natural weathering process, accelerated acid leaching can yield rapid permeability changes. The fear is that these may alter watershed hydrology and soil productivity.

A significant number of studies on aquifer "sensitivity" to infiltrating solution composition may also be found in the petroleum engineering literature. The potential for drastic reductions in conductivity accompanying attempts at secondary or tertiary oil recovery have been recognized since the early 1950s (Hewitt 1963; Land and Baptist 1965; Smith and Hendrickson 1965; Neasham 1977; Shaughnessy and Kunze 1981).

Incorporating dynamic hydraulic conductivity changes into the analysis of these problems is an essential step in improving our predictive capabilities. The purpose of this paper is to present a generalized, one-dimensional, discrete interface penetration model capable of simulating the effects of conductivity changes that accompany the infiltration of a strongly reactive fluid. The writers fully realize that no simple phenomenological model can accommodate the diversity of the known (or suspected) physical impact mechanisms. The approach presented here does, however, offer the substantial advantage of leading to analytical solutions for the transient potential gradient, reacting interface location, and volumetric flux response. These solutions yield verifiable predictions that may be employed in the direct analysis of laboratory data. They have also proven to be capable of reproducing a wide variety of the transient responses actually observed in soil column studies.

BACKGROUND

Hydraulic conductivity, K , is a measure of the ease with which fluids pass through soil, and depends on both the soil matrix and fluid properties, as follows:

$$K = \frac{k\rho g}{\mu} \quad (1)$$

TABLE 1.—Mechanisms Causing Changes in Hydraulic Conductivity of Porous Medium

Number (1)	Mechanism (2)	Effect on effective porosity (3)	Effect on solid phase (4)	Effect on bulk hydraulic conductivity (5)
1	Dispersion 1 ^a	decrease	increase	decrease
2	Dispersion 2 ^b	increase	decrease	increase
3	Shrinking	increase	decrease	increase
4	Swelling	decrease	increase	decrease
5	Chemical precipitation	decrease	increase	decrease
6	Solid dissolution	increase	decrease	increase
7	Solid introduction	decrease	increase	decrease
8	Microbiological activity	decrease	increase	decrease
9	Sorption			
10	Gas generation	decrease	none	decrease
11	Gas dissolution/displacement	increase	none	increase

^aIncludes translocation and lodgment within sample.

^bIncludes translocation out of sample.

^cDependent on specific type of reaction.

where K = hydraulic conductivity (LT^{-1}); k = intrinsic permeability (L^2); ρ = fluid density (ML^{-3}); μ = viscosity of the fluid ($ML^{-1}T^{-1}$); and g = acceleration due to gravity (LT^{-2}). In principle, the intrinsic permeability depends only on the soil matrix properties (pore size distribution, pore shape, pore arrangement, tortuosity, grain specific surface, etc.).

From Eq. 1, it may be seen that changes in hydraulic conductivity during the displacement of pore liquids may result from differences in fluid properties (ρ, μ), or induced changes in the intrinsic permeability (k). Mechanisms thought to be responsible for intrinsic permeability modifications are listed in Table 1. Mechanisms 1–4 alter conductivity by modifying the available pore space. These are primarily a result of physical changes in the structure and distribution of the clay portion of the solid matrix. Chemical precipitation, solid dissolution, cation exchange, and gas generation or dissolution are dependent on the concentrations of the chemical species in the soil-liquid interactions that occur as the systems tend toward equilibrium. Solid introduction and microbiological activity are functions of the liquid characteristics (total suspended solids, organic type and concentration, and initial biomass concentration), and act to reduce porosity by adding mass to the solid phase.

DESCRIPTION OF PROBLEM

The purpose of this paper is to provide a reasonably simple, generalized model for predicting the consequences of hydraulic conductivity changes during constant potential infiltration. It is assumed that these changes are the result of a chemically reactive liquid introduced at time $t = t_0$ at space location $x = 0$ (i.e., into the top of a permeameter col-

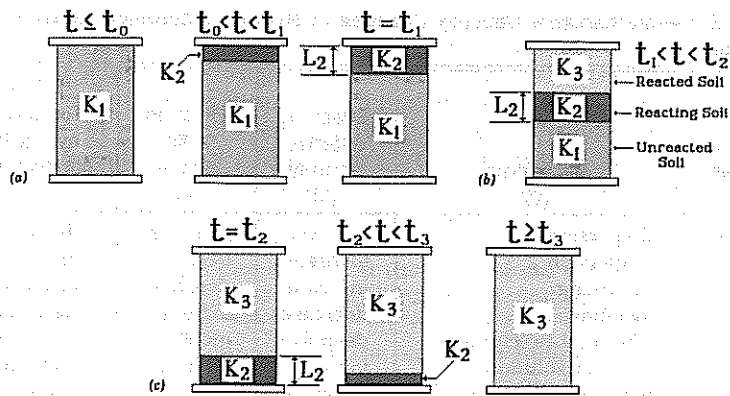


FIG. 1.—Idealized Three-Stage Flow Experiment: (a) Stage I—Growth of Reacting Zone; (b) Stage II—Vertical Transport of Reacting Zone; (c) Stage III—Completion of Reacting Zone Penetration

umn). The model was originally developed to simulate conductivity changes that result from the penetration of acid solutions through soils containing a reactive carbonate component. The origin of the modeling approach can easily be described in these terms.

As an acid penetrates soil, chemical interactions between the solid and liquid phases result in physical changes in the soil matrix. Since the chemical neutralizing reactions retard the advance of the acid front, the dissolution of the carbonate portion and the generation of gas occur at some point behind the advancing liquid front. As these reactions continue, the neutralizing capacity of the soil is depleted and the pH declines to that of the acidic influent. Dissolution and gas generation cease at some distance behind the advancing liquid front. Laboratory observations of these phenomena led to the development of a discrete interface model in which the domain is divided into three transient zones: (1) The unreacted zone in which the soil has not yet been physically affected by the soil-liquid interactions; (2) the reacting zone in which physical transformations are actively occurring; and (3) the reacted zone in which chemical interactions and physical transformations have stabilized.

Although developed for soil-acid interaction, it appears that the model provides a general method for analyzing the results of many soil-liquid flow experiments. The analysis is based on a domain of length, L , and cross-sectional areas, A , initially containing a saturated, homogeneous, isotropic porous medium. Constant potential boundary conditions are applied at the top ($x = 0$) and bottom ($x = L$) of the domain. The general flow experiment may be idealized as occurring in the following three stages, as shown in Fig. 1:

Stage I: Growth of Reacting Zone.—The soil of the domain exhibits an initially unreacted saturated hydraulic conductivity of K_1 at time $t = t_0$ when a new fluid is introduced. As the fluid passes through the soil, chemical reactions induce a “reacting” hydraulic conductivity, K_2 . With

continued introduction of the liquid, the reacting zone grows to a maximum thickness, L_2 at time $t = t_1$ when the chemical reactions near the source are completed and the soil reaches a steady state hydraulic conductivity, K_3 . [See Fig. 1(a)]

Stage II: Transport of Reacting Zone.—The reacting zone of constant thickness, L_2 , and hydraulic conductivity, K_2 , propagates through the domain until the front reaches the end of the domain ($x = L$) at time $t = t_2$. [See Fig. 1(b).]

Stage III: Completion of Reaction.—When the reacting front reaches the end of the domain, the thickness of the reacting zone begins to reduce as the reacted zone continues to grow. At time $t = t_3$, the soil is completely reacted. [See Fig. 1(c).]

ANALYSIS OF FLOW DURING STAGE I: $t_0 \leq t \leq t_1$

Calculation of the transient location of the reacting interface $X_{II}(t)$, the hydraulic potential at this interface $\phi(X_{II}(t), t)$, and the bulk transient volumetric flux from the domain, $Q(t)$, is accomplished as follows.

The Darcy flow velocity through a multilayered saturated soil is given by (Bear 1972)

$$q = \frac{-\Delta\phi}{M \sum_{j=1}^M \frac{D_j}{K_j}} \quad (2)$$

in which D_j = thickness of layer j ; K_j = saturated hydraulic conductivity of layer j ; $\Delta\phi$ = the total change in potential across the strata; and M = the number of layers in the strata. Since the model assumes constant potential boundary conditions at the top and bottom of the domain, letting $\phi(X = 0, t) = \phi_1$ and $\phi(X = L, t) = \phi_2$ yields a constant potential differential $\Delta\phi = \phi_1 - \phi_2$.

Applying Eq. 2 to the two-layered strata shown in Fig. 1(a) and using the notation defined in Fig. 2 yields the following result:

$$q = \frac{K_1 K_2 (\phi_1 - \phi_2)}{K_1 X_{II}(t) + K_2 [L - X_{II}(t)]} \quad (3)$$

Since the Darcy velocity, q , divided by the effective porosity, η , represents the actual interstitial velocity, v , or the rate at which the fluid front is passing through the domain, the rate at which the reacting front is advancing must be less than or equal to q/η . This assumes that there is a discrete front interface and that no dispersion occurs ahead of the interface. The rate of the reacting front advance may be expressed as follows:

$$\frac{dX_{II}(t)}{dt} = \frac{\alpha q}{\eta} \quad (4)$$

in which α = the reacting front control function. For the analysis presented here, α will be taken to be a constant. It should be obvious that the functional form of α is dependent on the unique physical and chemical characteristics of the solid and liquid phases, and will change for

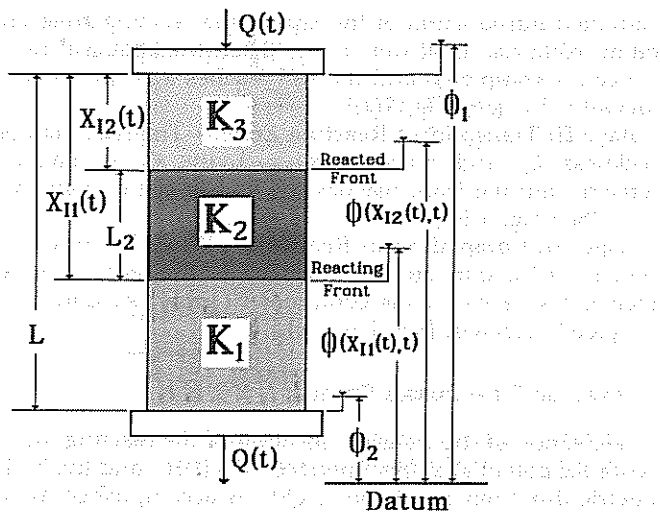


FIG. 2.—Definition Sketch for Column Analysis Notation

each specific class of soil-liquid problems studied. To create a generalized model to simulate a broad range of soil-liquid problems, the selection of α as a constant or simple integrable function is necessary. It will be shown that for the soil-acid problem, a constant α value appears to be a reasonable assumption.

Substituting q from Eq. 3 into Eq. 4, separating, and integrating yields

$$\int_0^{X_{11}(t)} \{K_1 X_{11}(t) + K_2[L - X_{11}(t)]\} dX_{11}(t) = \frac{\alpha}{\eta} K_1 K_2 (\phi_1 - \phi_2) \int_{t_0}^t dt \dots \dots \dots (5)$$

or $\left(\frac{K_1 - K_2}{2}\right) X_{11}^2(t) + (K_2 L) X_{11}(t) - \frac{\alpha}{\eta} K_1 K_2 (\phi_1 - \phi_2) (t - t_0) = 0 \dots \dots \dots (6)$

Note that this yields a quadratic equation that can be solved for $X_{11}(t)$. The volumetric flux, $Q(t)$, through each domain segment is given by

$$Q(t) = \frac{K_1 A [\phi(X_{11}(t), t) - \phi_2]}{L - X_{11}(t)} \dots \dots \dots (7)$$

$$Q(t) = \frac{K_2 A [\phi_1 - \phi(X_{11}(t), t)]}{X_{11}(t)} \dots \dots \dots (8)$$

Therefore, interface flux continuity yields

$$\phi(X_{11}(t), t) = \frac{K_1 X_{11}(t) \phi_2 + K_2 [L - X_{11}(t)] \phi_1}{K_1 X_{11}(t) + K_2 [L - X_{11}(t)]} \dots \dots \dots (9)$$

ANALYSIS OF FLOW DURING STAGE II: $t_1 < t < t_2$

Fig. 2 shows the conditions existing during Stage II used to calculate the location of the reacting front, $X_{11}(t)$; the reacted front, $X_{12}(t)$; potential

at the front locations, $\phi(X_{11}(t), t)$ and $\phi(X_{12}(t), t)$; and the transient volumetric flux, $Q(t)$.

As before, applying Eq. 2 to the three-layered strata of Fig. 2 yields

$$q = \frac{K_1 K_2 K_3 (\phi_1 - \phi_2)}{K_1 K_2 X_{12}(t) + K_1 K_3 L_2 + K_2 K_3 [L - X_{12}(t) - L_2]} \dots \dots \dots (10)$$

in which L_2 = the thickness of the reacting zone, $L_2 = X_{11}(t) - X_{12}(t)$. The rate of the reacted front advance may be represented by

$$\frac{dX_{12}(t)}{dt} = \frac{\beta q}{\eta} \dots \dots \dots (11)$$

in which β = the reacted front control function. Similar to α , the β function depends on the physical and chemical characteristics of the solid and liquid phases. For the results presented here, it is assumed that β is a constant and equal to α . This requires that the reacting zone thickness, L_2 , remains constant during Stage II.

Substitution of Eq. 10 into Eq. 11 and integrating over space from zero to $X_{12}(t)$ and over time from t_1 to t yields a quadratic equation, which can be solved for the location of the reacted front:

$$\left[\frac{K_2(K_1 - K_3)}{2}\right] X_{12}^2(t) + \{K_3[K_2 L + L_2(K_1 - K_2)]\} X_{12}(t) - \frac{\alpha}{\eta} K_1 K_2 K_3 (\phi_1 - \phi_2) (t - t_1) = 0 \dots \dots \dots (12)$$

By applying continuity of flux across interfaces and Darcy's Law, the solution of the following set of equations yields values for the interface potentials and resulting volumetric flux [$\phi(X_{11}(t), t)$; $\phi(X_{12}(t), t)$; and $Q(t)$]:

$$\phi(X_{11}(t), t) = \frac{K_2 K_3 \phi_1 [L - X_{12}(t) - L_2] + \phi_2 [K_1 K_3 L_2 + K_1 K_2 X_{12}(t)]}{K_2 K_3 [L - X_{12}(t) - L_2] + [K_1 K_3 L_2 + K_1 K_2 X_{12}(t)]} \dots \dots \dots (13)$$

$$\phi(X_{12}(t), t) = \frac{K_2 \phi(X_{11}(t), t) X_{12}(t) + K_3 \phi_1 L_2}{K_2 X_{12}(t) + K_3 L_2} \dots \dots \dots (14)$$

$$Q(t) = \frac{K_3 A [\phi_1 - \phi(X_{12}(t), t)]}{X_{12}(t)} \dots \dots \dots (15)$$

ANALYSIS OF FLOW DURING STAGE III: $t_2 \leq t \leq t_3$

The analysis of flow during the final stage of the experiment is accomplished similarly to the procedure described for Stage I. Using the two-layer system of Fig. 1(c) and the notation defined in Fig. 2, the solution to the following set of equations yields the values for interface location, interface potential, and volumetric flux [$X_{12}(t)$; $\phi(X_{12}(t), t)$; and $Q(t)$]:

$$\left(\frac{K_2 - K_3}{2}\right) X_{12}^2(t) + (K_3 L) X_{12}(t) - \frac{(K_2 - K_3)}{2} (L - L_2)^2 - K_3 L^2 + K_3 L_2 - \frac{\alpha}{\eta} K_2 K_3 (\phi_1 - \phi_2) (t - t_2) = 0 \dots \dots \dots (16)$$

$$\phi(X_{I2}(t), t) = \frac{K_2 X_{I2}(t) \phi_2 + K_3 [L - X_{I2}(t)] \phi_1}{K_2 X_{I2}(t) + K_3 [L - X_{I2}(t)]} \quad (17)$$

$$Q(t) = \frac{K_3 A [\phi_1 - \phi(X_{I2}(t), t)]}{X_{I2}(t)} \quad (18)$$

TRANSIENT BULK HYDRAULIC CONDUCTIVITY, $K(t)$

The bulk domain hydraulic conductivity as a function of time (or non-dimensional pore volume) can be calculated from Darcy's Law using the value of $Q(t)$ determined from Eqs. 8, 15, or 18:

$$K(t) = \frac{Q(t)L}{A(\phi_1 - \phi_2)} \quad (19)$$

Although the conductivity throughout the entire domain is constant at the beginning and end of the simulation, bulk values calculated during the course of the experiment represent averaged values resulting from the transient location of the discrete interfaces. This is equivalent to calculating (at any time) the average hydraulic conductivity of a multilayered saturated soil (McWhorter and Sunada 1977):

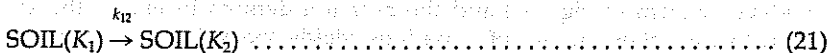
$$K(t) = \frac{\sum_{j=1}^M D_j(t)}{\sum_{j=1}^M \frac{D_j(t)}{K_j}} \quad (20)$$

where the values of $D_j(t)$ correspond to the thicknesses of the unreacted, reacting, and reacted zones.

SIMULATING INTERACTION KINETICS

Each soil-liquid interaction experiment is uniquely defined by the specific mechanisms of the phase interactions and the rate at which those interactions alter hydraulic conductivity. In order to better describe these rate-dependent transformations, the magnitudes of the reacting front control function, α , and the reacting zone thickness, L_2 , may be adjusted to account for mechanism interaction kinetics.

The change in soil conductivity from unreacted K_1 to reacting K_2 may be thought of as the following irreversible physical transformation:



where k_{12} = the transformation rate constant. The capacity of this transformation governs the magnitude of the difference between K_1 and K_2 . The rate at which the transformation occurs relative to the fluid velocity governs the separation of the reacting front from the infiltrating fluid front, $X_L(t)$. This behavior is governed by the magnitude of α . Since the rate of movement of the fluid front is equal to the interstitial velocity, as $\alpha \rightarrow 1.0$ the location of the infiltrating liquid and reacting fronts will

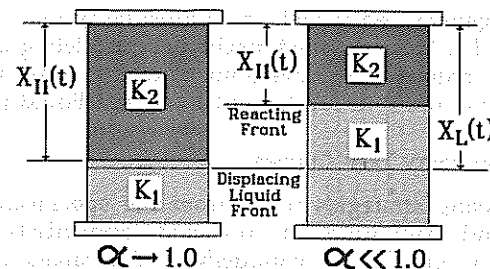


FIG. 3.—Mobility of Reacting Front Relative to Displacing Liquid Front

be identical (see Fig. 3). This simply implies that the transformation from K_1 to K_2 occurs at a high rate relative to bulk fluid flow. When $\alpha \ll 1.0$, the liquid front penetrates the soil ahead of the reacting front, simulating a time lag between fluid introduction and a more gradual conductivity change.

Similarly, the change in soil conductivity from the reacting state (K_2) to the reacted state (K_3) may be described by an irreversible physical transformation:



where k_{23} = a second transformation rate constant. The rate of the transformation from K_2 to K_3 relative to the transformation of K_1 to K_2 governs the thickness of the reacting zone, L_2 . As shown in Fig. 4, if k_{23} is nearly equal to k_{12} , the reacting zone thickness will be small. If this transformation occurs gradually, a large zone thickness will develop. For k_{23} greater than or equal to k_{12} , no reacting zone will develop, and the conductivity transformation will occur rapidly from K_1 to K_3 . For k_{12} greater than k_{23} , the reaction zone thickness, L_2 , will continue to grow throughout the experiment. For the solutions presented here, it has been assumed that there is a constant reacting zone thickness during Stage II.

The rate at which hydraulic conductivity changes actually occur is a complex function of the types and rates of solid-liquid chemical inter-

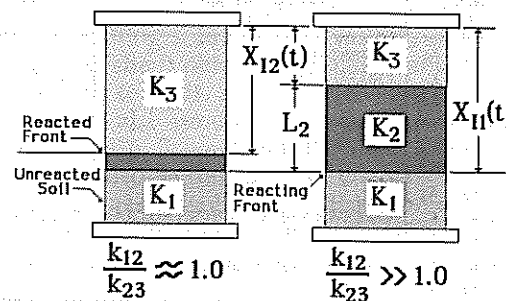


FIG. 4.—Effect of Physical Transformation Kinetics on Thickness (L_2) of Reacting Zone

actions. In this generalized model, these must be simulated by the magnitude of α and L_2 . More detailed mechanistic modeling of specific soil-liquid problems requires the development of the constitutive relationships that relate α and β to fundamental soil and liquid properties.

HYDRAULIC CONDUCTIVITY TYPE CURVES

Distinct modeling strategies result from the specification of unique combinations and magnitudes of unreacted conductivity (K_1), reacting conductivity (K_2), and reacted conductivity (K_3) values, as well as the reacting front control function, α , and reacting zone thickness, L_2 . In general, the resulting solution forms, denoted as hydraulic conductivity type curves [$K(t)$ versus t], may be divided into four categories: (1) Type curve A, an overall continuous increase in hydraulic conductivity; (2) type curve B, an overall continuous decrease in hydraulic conductivity; (3) type curve C, an initial decrease followed by a recovery of hydraulic conductivity; and (4) type curve D, an initial increase followed by an eventual permanent decrease in hydraulic conductivity.

The interaction mechanisms thought to produce each category are summarized in Table 2. Hydraulic conductivity type curves shown later in Figs. 5–8 were generated from simulations using $\phi_1 = 100$ cm, $\phi_2 = 10$ cm, $A = 5.00$ cm², $L = 10.0$ cm, and $\eta = 0.40$. However, the relative behavior illustrated remains independent of all of these. The results are presented as normalized hydraulic conductivity, $K(t)/K_1$, versus non-dimensional time (pore volumes). It should be noted that normalized conductivity is directly proportional to the measured volumetric flux (the primary experimental observation).

Type Curve A: Increasing Hydraulic Conductivity.—Solutions predicting a general increase in conductivity due to the solid-liquid interactions are shown in Figs. 5(a–d). Increases of this type are often caused by flocculation or shrinking of the clay fraction within the soil matrix, or dissolution of the solid phase.

TABLE 2.—Reaction Mechanisms Represented by Hydraulic Conductivity Type Curves

Type curve (1)	Case number (2)	Case (3)	Reaction mechanism (4)	Reference where type curve response was observed (5)
A	1	$K_1 = K_2 = K_3$	nonreactive	5,12,17,23,29,34,42
	2	$K_1 < K_2 = K_3$	CSH,SD,GDD	
	3	$K_1 = K_2 < K_3$		
	4	$K_1 < K_2 < K_3$		
B	5	$K_1 > K_2 = K_3$	CD,CSW,CP,SI,MA,GG	1,5,10,14,17,19,23,38,40,44,45
	6	$K_1 = K_2 > K_3$		
	7	$K_1 > K_2 > K_3$		
C	8	$K_1 = K_3 < K_2$	CD,CSW,CP,SI,MA,GG/CSH,SD,GDD	5,11,23,34,40,46,47,49
	9	$K_1 > K_2 < K_3$		
D	10	$K_1 = K_3 < K_2$	CSH,SD,GDD,/CD,CSW,CP,SI,MA,GG	
	11	$K_1 < K_2 > K_3$		

Note: CD = Clay dispersion; CSW = Clay swelling; SD = Solid dissolution; MA = Microbiological activity; GDD = Gas dissolution/displacement; CSH = Clay shrinkage; CP = Chemical precipitation; SI = Solid introduction; GG = Gas generation.

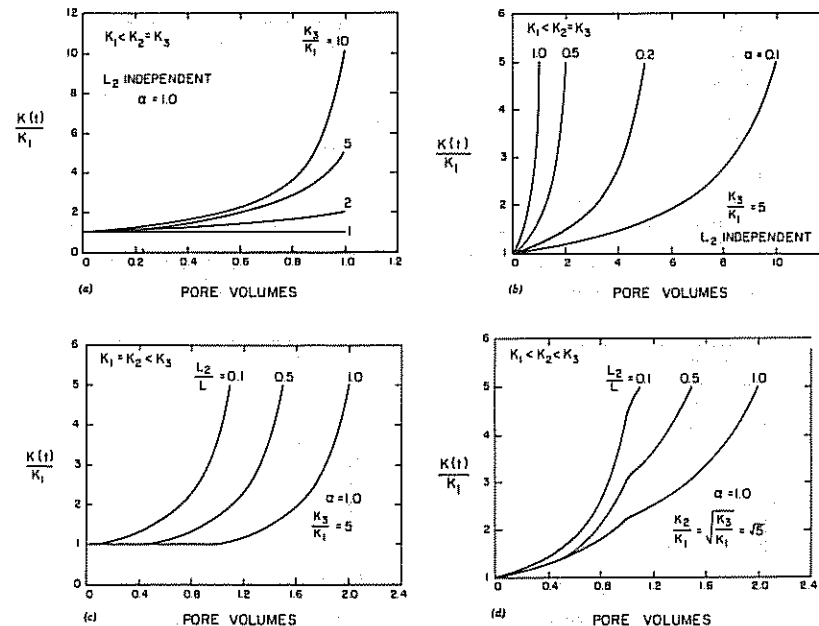


FIG. 5.—Type Curve A—Increasing Bulk Hydraulic Conductivity for: (a) Increasing K_3/K_1 Ratio; (b) Decreasing α ; (c) Increasing L_2/L , $K_1 = K_2$; (d) Increasing L_2/L , $K_1 \neq K_2$

Goldenberg and Magaritz (1983) obtained similar results after displacing fresh water with seawater in a granular soil containing 11% silt and clay. Similar results were obtained for a sandy dunal soil in which a CaCl_2 solution of high ionic strength was replaced by one of low ionic strength. Compacted clay soils, which were initially saturated and permeated with a standard aqueous solution of 0.01N CaSO_4 and subsequently with concentrated organic solutions of methanol or xylene, have shown increased conductivity with time (Brown and Anderson 1981). Type curve A has also been observed from laboratory studies of natural clay and compacted calcium bentonite/sand mixtures exposed to sulfuric acid and acidic mill tailing solutions by Nasiatk, et al. (1981). Mundell and Jennings (unpublished) obtained similar results by exposing Maryland coastal plain soils to acids. Acid reactions with sandstone and limestone rock cores have also produced similar results (Lund, et al. 1976; Fogler and McCune 1976; Schechter and Gidley 1969).

Type curve A may also be indicative of changes in hydraulic conductivity that result from gas dissolution or displacement within a partially saturated soil, or the infiltration of a high density and/or low viscosity fluid into a nonreactive soil.

Figs. 5(a–d) show the relative effects of the essential coefficients (K_1 , K_2 , K_3 , α , and L_2) on the increasing conductivity solution. In general, as α decreases or L_2 increases, the type curve shifts toward greater pore volumes.

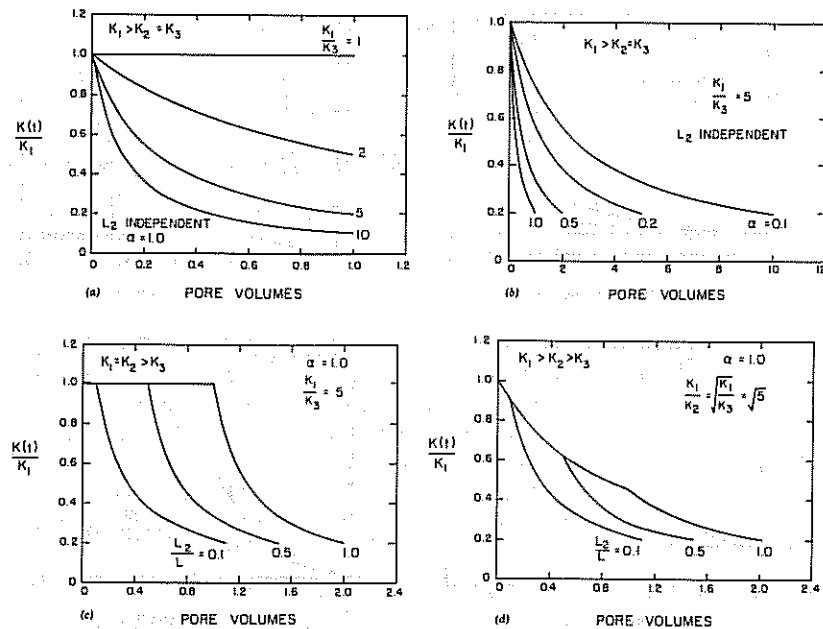


FIG. 6.—Type Curve B—Decreasing Bulk Hydraulic Conductivity for: (a) Increasing K_1/K_3 ; (b) Decreasing α ; (c) Increasing L_2/L , $K_1 = K_2$; (d) Increasing L_2/L , $K_1 \neq K_2$

Type Curve B: Decreasing Hydraulic Conductivity.—Decreases in hydraulic conductivity may be simulated as shown in Figs. 6(a–d). This type of response generally results from a decrease or blockage in available pore space due to clay dispersion or swelling, chemical precipitation, microbial growth, or gas generation. This response has been the most commonly documented and has been observed in studies on the effects of several inorganic liquids (Frenkel, et al. 1978; Griffin and Shimp 1978; Park and O'Connor 1980; Shainberg, et al. 1981), low and high concentrations of organic liquids (Acar 1985; Brown and Anderson 1981; Green, et al. 1981), organic-nutrient solutions (Allison 1947; Frankenberger, et al. 1979; Gupta and Swartzendruber 1962), acids (Dunn and Michell 1984; Nasiatka, et al. 1981), and saltwater solutions (Goldenberg and Magaritz 1983; Mehnert and Jennings 1985). This response may also result from the introduction of a low density and/or high viscosity fluid into a non-reactive soil.

Figs. 6(a–d) show the effects of α and L_2 and the relative magnitudes of K_1 , K_2 , and K_3 on the resulting solution. As with type A curves, decreasing α or increasing L_2 causes the change of the bulk hydraulic conductivity to occur at greater pore volumes.

Type Curve C: Hydraulic Conductivity Decrease/Increase.—Figs. 7(a–c) show the response that may result from sequential mechanisms as a liquid passes through soil. The sequence of pore volume reduction mechanisms (clay dispersion, clay swelling, chemical precipitation, or

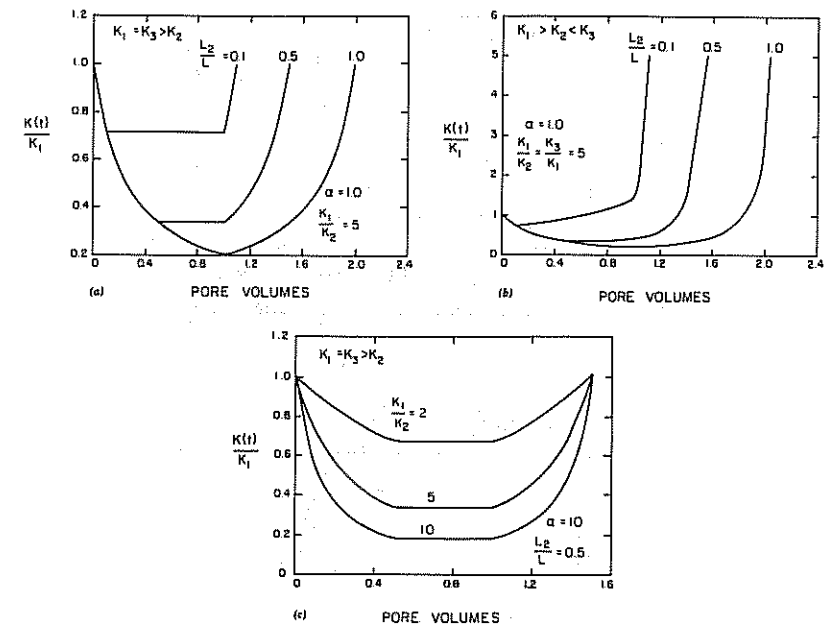


FIG. 7.—Type Curve C—Decrease/Increase of Bulk Hydraulic Conductivity for: (a) Increasing L_2/L , $K_1 = K_3$; (b) Increasing L_2/L , $K_1 < K_3$; (c) Increasing K_1/K_2 , $K_1 = K_3$

gas generation) followed by pore volume increasing mechanisms (clay flocculation or shrinkage, solid dissolution, or gas dissolution or displacement) has been proposed in several studies as a possible explanation of the observed fluctuations in hydraulic conductivity. Initial dispersion of clay size particles followed by subsequent flushing of the pores (observed as loss of clay from the column) was measured by Pupisky and Shainberg (1979). Clay dispersion or swelling followed by shrinkage has been proposed to explain similar trends observed when organic liquids such as xylene (Brown and Anderson 1981), phenol or acetone (Acar, et al. 1985) are used as permeants. Acidic infiltrations into sandstone and limestone have also produced similar results (Smith and Hendrickson 1965; Farley, et al. 1970; Shaughnessy and Kuntz 1981). Walsh (1983) has suggested that this may be the result of multiple precipitation/dissolution fronts propagating through the sample. It has also been suggested that the introduction of acids into calcareous soils may initiate gas generation and clay dispersion prior to solid dissolution and gas displacement.

Curve Type D: Hydraulic Conductivity Increase/Decrease.—The responses typical of sequential mechanisms causing an initial pore volume increase followed by a pore volume decrease are shown in Figs. 8(a–b). The mechanisms for generating results of this type are the same as those required to produce type C, given that one reverses the sequence order. Mundell and Jennings (unpublished) observed type D experi-

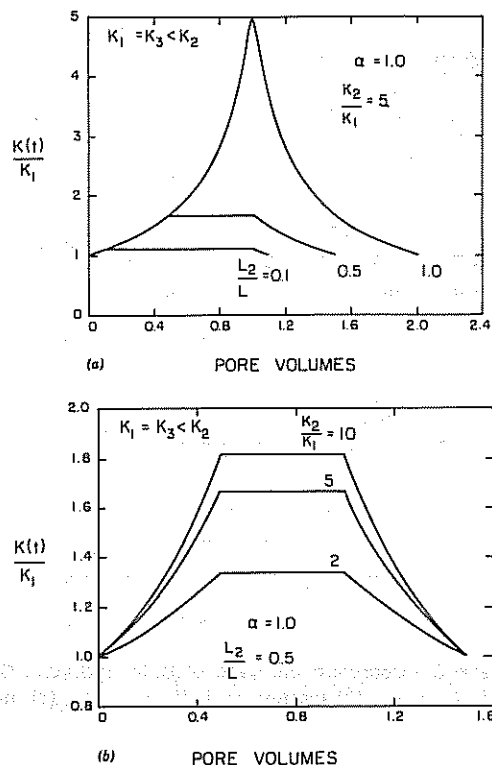


FIG. 8.—Type Curve D—Increase/Decrease of Bulk Hydraulic Conductivity for: (a) Increasing L_2/L ; (b) Increasing K_2/K_1

mental results for acid infiltration into a reactive Atlantic coastal plain soil.

EXAMPLE ACID REACTION-INDUCED CONDUCTIVITY CHANGES

The physical effect of acid infiltration on a soil is strongly related to the buffering or acid neutralizing capacity (ANC) of the soil. If the ANC is insignificant, little or no reaction between the acid and soil may occur. However, if the ANC is large, major structural modifications of the soil matrix can result as the acid is being neutralized.

ANC quantifies the ability of a soil to neutralize acids measured in milliequivalents (meq) of H^+ per mass of soil (meq/100 g) exchanged or transformed into aqueous complexes. This is generally measured by a dynamic acid titration of the soil (Jennings, et al. 1984; Kramer, et al. 1981; Otte and Jennings 1984).

Dissolution of the buffering mineral fraction occurs during soil acidification. In addition, a two-step mechanism describing soil acidification (or weathering) has been proposed involving a rapid surface exchange of adsorbed cations with the H^+ ion, followed by a slower, diffusion-

controlled decomposition reaction for the penetration and exchange of H^+ with crystalline cations of soil silicates (Oster and Shainberg 1979; Shainberg 1973). A more detailed description of this process is given in Shainberg (1973).

Since the interstitial velocity is the rate at which the fluid front is moving, the total amount of acid (E_s) supplied to the soil in one unit of time may be expressed as

$$E_s = v\eta NA(\Delta t) \dots \dots \dots (23)$$

where N = the normality of the acid; and A = the cross-sectional area. Each unit volume of soil can neutralize E_N total equivalents of acid:

$$E_N = \rho_s A(ANC)\Delta X \dots \dots \dots (24)$$

in which ρ_s = the bulk soil density. The acid reaction at any point in the domain is completed when no additional H^+ supplied by the acid can react with the soil. Therefore, equating the total equivalents supplied to the neutralizing capacity yields

$$v\eta N\Delta t = \rho_s(ANC)\Delta X \dots \dots \dots (25)$$

or, in general, the acid front advances at the velocity

$$\frac{dX}{dt} = \frac{\eta N v}{\rho_s(ANC)} \dots \dots \dots (26)$$

By comparing Eq. 26 with Eq. 4 it can be seen that the front penetration control function α would be given by $\eta N / [\rho_s(ANC)]$. This assumes that the movement of the reacted front causing the transformation of conductivity from K_2 to K_3 occurs at the same rate that the ANC of the soil is consumed.

In order to test this assumption, a permeameter column of soil with a bulk soil density of 1.67 g/cm³ and a measured ANC of 262 meq/100 g (based on a titration to pH = 3.5) was penetrated with a 0.05 normal H_2SO_4 solution. Comparison of the observed hydraulic response with the model simulation is shown in Fig. 9. The laboratory data indicate a very small initial rise in the bulk conductivity followed by a decrease until about 42 pore volumes, and then an increase to a final value approaching 3.6 times the initial conductivity. The acid was observed to break through at approximately 180 pore volumes, after which conductivity stabilized. The transient decrease in bulk conductivity is most likely the result of gypsum ($CaSO_4 \cdot 2H_2O$) precipitation within the reacting zone ahead of a calcium carbonate/gypsum dissolution front. Considering the assumptions made, the interface penetration model simulates the observed laboratory response quite well. The model initially underestimates the rate of conductivity increase after conductivity reaches a minimum. This is most likely due to the discrete interface assumption. Observations of the reacted zone front during the experiment revealed that the acid advanced through several preferential pathways, causing higher conductivity channels to develop ahead of the reacted front. This would tend to increase the rate at which the conductivity transformation occurred.

Adjustment of α to a value of 0.0075 corresponding to an ANC of

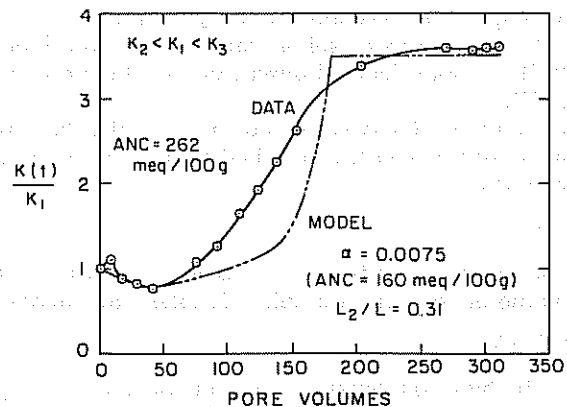


FIG. 9.—Experimental and Predicted Transient Bulk Hydraulic Conductivity for Acid-Soil Interaction System: 0.05 NH_4SO_4 Infiltrating Previously Saturated 5:1 Mixture of Fine Ottawa Sand and Edwards Marl (Otte and Jennings 1984)

approximately 160 meq/100 g is required to most accurately predict observed breakthrough. This indicates that the movement of the discrete interfaces preceded the full (batch) measured ANC consumption. Subsequent experiments on this and other carbonate rich soils indicate that measured ultimate ANC of a batch system will consistently underestimate acid breakthrough and conductivity transformation of column studies. There are several possible explanations for this.

The response appears to be primarily due to the transport of dissolved buffering carbonate complexes out of the domain at a pH above the titration end point. Chemical equilibrium calculations suggest that as much as one third of the domain ANC may have been transported out of the column (predominantly as HCO_3^-) prior to full utilization. Peterson and Gee (1985) have also suggested that the release of hydrogen ions during precipitation reactions may add to the early breakthrough observed in some soil columns. In addition, soil-water suspension ratio differences between columns and batch measurements of ANC may contribute to this apparent disagreement. Recent evidence has indicated that titrations of dilute soil-water suspensions overestimate actual ANC by allowing reactions to attain an uncharacteristically high degree of completion.

CONCLUSIONS

A generalized one-dimensional discrete interface penetration model, which simulates fluid propagation through reactive porous media during constant head infiltration, has been presented. This simple phenomenological formulation permits consideration of the changes in hydraulic conductivity that result from complex chemical interactions of the soil matrix and the infiltrating liquid. The resulting analytical solutions appear to encompass the observations of a wide range of experimental studies. The model is shown to be a useful tool for analyzing the results of soil column permeability data, and may provide insights into the types

of mechanisms responsible for the hydraulic conductivity transformations.

ACKNOWLEDGMENTS

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