

Modelling Solute Transport, Chemical Adsorption and Cation Exchange

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SUMMARY We present an analytical model describing solute transport subject to nonlinear solute adsorption and demonstrate the exact correspondence of the model with water infiltration. The model is applied to experimental data from a laboratory Ca-K exchange experiment in which a solution containing Ca is passed through a column filled with K-saturated soil. The model, which is based on the assumption of local equilibrium of the solute between the adsorbed and liquid phases, fails to predict the spreading of the experimental breakthrough curve. Further analysis, however, suggests that chemical kinetic non-equilibrium exchange is occurring, thus violating the model assumption of local equilibrium.

0. NOTATION

a_i	$i = 1, 2, 3$, constants defined in (13), LT^{-1}
A_i	$i = 1, 2, 3$, arbitrary constants
c	normalized solute concentration in the aqueous phase
c_i	initial normalized solute concentration
c_0	normalized solute concentration in the influent solution
C	soil water capacity, L^{-1}
C_E	cation exchange capacity, charge M^{-1}
D	soil water diffusivity, L^2T^{-1}
D_0	diffusivity at the residual moisture content, L^2T^{-1}
D_s	dispersion coefficient, L^2T^{-1}
k	fundamental solution of the heat equation
\mathbf{k}	unit vector in the direction of positive z
K	hydraulic conductivity, LT^{-1}
K_N	Ca-K exchange selectivity coefficient at normality
N	
K_s	saturated hydraulic conductivity, LT^{-1}
L	column length, L
n	porosity
N	total normality in the liquid, charge L^{-3}
N_i	$i = Ca$ or K , species liquid normality, charge L^{-3}
\bar{N}_i	$i = Ca$ or K , normality in the solid, charge M^{-1}
p	function defined by (11)
P	Péclet number
Q	surface fluid flux, LT^{-1}
s	normalized solid phase concentration
t	time, T
u	total solute concentration (solid plus aqueous phases), ML^{-3}
v	mean solute velocity, LT^{-1}
x_i	$i = Ca$ or K , ionic fraction of the solute
\bar{x}_i	$i = Ca$ or K , ionic fraction of the adsorbed solute
z	distance below surface, L
γ	constant defined by (16b), $T^{-1/2}$
ζ	"location" variable in (10), $T^{1/2}$
η	boundary flux integral, $T^{1/2}$
$\bar{\eta}$	constant defined by (16c), $T^{-1/2}$
θ	moisture content
θ_i	initial moisture content
λ	boundary integral function

v	free parameter
ρ_b	soil bulk density, ML^{-3}
ψ	moisture tension, L

1. INTRODUCTION

Solute transport processes in the environment involve many complex phenomena. A solute may adsorb or exchange onto soil particles, or it may precipitate or react with other solutes, besides being advected and dispersed. The task of quantifying the possible physico-chemical transport and transformation mechanisms requires substantial contributions from the basic sciences of mathematics, chemistry, physics and biology.

Presently, there is a wide variety of models available for predicting of solute movement. These range from simple, analytical models of single species transport under steady flow conditions to multidimensional flow and multicomponent solute transport. At best, the simple models are useful for indicating the overall behaviour of the system. On the other hand, extensive site characterization and detailed knowledge of chemical reactions are needed for application of the multicomponent models. Furthermore, because each component must be described by its own transport equation, it might be necessary to have access to powerful computers to obtain model predictions (e.g., Liu and Narasimhan, 1989a,b; Barry, 1990).

The density of models in the range from simple to complex is not uniform. Indeed, there are gaps in the range, particularly when the transition from analytical to numerical models is considered. In the main, analytical solutions rely on linearity of the governing transport equation (e.g., van Genuchten and Alves, 1982; Barry and Sposito, 1988; Barry et al., 1989). There are severe difficulties when one attempts to find solutions for more realistic, nonlinear transport processes. One purpose of this paper is to generate exact analytical solutions for solute transport with a realistic adsorption or exchange isotherm. By deriving these results we provide a useful extension of the available analytical models. Also, because we account for nonlinearity, the results provide realistic test cases against which both numerical solutions and analytical approximations can be evaluated.

It is widely recognized that mass fluxes of solute and water in porous media are related mathematically (Barnes, 1986, 1989). There exists a large body of research literature on water infiltration and movement in soil under unsaturated conditions. The governing model for unsaturated flow is a strongly nonlinear Fokker-Plank equation (Richards, 1931). Because of the relationship between fluxes of water and solute, the diffusivity and conductivity functions of Richards' equation correspond to a particular nonlinear adsorption isotherm. It appears that the results derived for soil-water movement can be applied to the transport of a solute undergoing transformation due to a nonlinear adsorption isotherm (hereafter referred to as adsorptive solute transport).

In this paper we shall demonstrate the correspondence between infiltration and adsorptive solute transport. By using new solutions for Richards' equation derived from application of the Lie-Bäcklund transform method, we generate a fully analytical solution for adsorptive solute transport. The isotherm for which the transformation is applicable has enough free parameters to allow it to be fitted to a sizable class of isotherms. We explore an application of the results using data from a laboratory experiment featuring K-Ca exchange.

2. THEORETICAL DEVELOPMENT

2.1 The Correspondence Between Water Infiltration and Solute Transport

The governing equation for a solute undergoing transport in a porous medium subject to an equilibrium adsorption isotherm is (e.g., Bryant *et al.*, 1986):

$$\frac{\partial u}{\partial t} = \nabla \cdot (D_s \nabla c - vck), \quad (1a)$$

where

$$u = c + s(c). \quad (1b)$$

The dispersion coefficient, D_s , and solute velocity, v , are assumed to be scalar constants, as is the porosity, n , and vertical advection only is permitted. The aqueous phase concentration, c , in (1b) is assumed to be normalized, as is the adsorbed concentration, s . Observe that (1a) can be rewritten as:

$$\frac{1}{A_2} \frac{\partial u}{\partial t} = \nabla \cdot \left[\frac{D_s}{A_2} (c + A_2 A_3) \nabla \ln(c + A_2 A_3) - \frac{v(c + A_2 A_3)}{A_2} k \right]. \quad (2)$$

Richards' equation for water infiltration can be formulated in terms of moisture tension, ψ , or water content, θ . The ψ -formulation is (e.g., Huyakorn *et al.*, 1984):

$$C \frac{\partial \psi}{\partial t} = \nabla \cdot [K(\psi) \nabla \psi - K(\psi)k], \quad (3a)$$

where the soil water capacity, C , is defined by:

$$C = \frac{d\theta}{d\psi}. \quad (3b)$$

Equations (1a) and (3a) map onto each other by the prescription (cf. Lantz, 1970; Yortsos, 1987):

$$v\psi = D_s \ln(c + A_2 A_3), \quad (4a)$$

$$A_2 K(\psi) = v(c + A_2 A_3) \quad (4b)$$

and

$$A_1 + A_2 \theta = c + s(c). \quad (4c)$$

Equation (4) generalizes the transformation used by Barnes (1986). Equations (4a) and (4b) imply:

$$K(\psi) = \frac{v}{A_2} \exp\left(\frac{v\psi}{D_s}\right). \quad (4d)$$

Richards' equation can be formulated with water content as the dependent variable instead of ψ , so long as K and ψ are single-valued functions of θ (Philip, 1969, §2). In this case we have:

$$\frac{\partial \theta}{\partial t} = \nabla \cdot [D(\theta) \nabla \theta - K(\theta)k], \quad (5a)$$

where the soil water diffusivity, $D(\theta)$, is defined by

$$D(\theta) = K(\theta) \frac{d\psi}{d\theta}. \quad (5b)$$

Of course, the conductivity in (5) is a suitable transformation of that in (3a). We can map (1) directly onto (5) if we wish. The required mapping consists of (4b) with $K(\psi)$ replaced by $K(\theta)$, and (4c) together with:

$$D(\theta) = D_s \left[1 + \frac{ds(c)}{dc} \right]^{-1}. \quad (6)$$

2.2 Bäcklund Transformation

For a class of diffusivity and conductivity functions, the one-dimensional form of (5a) can be linearized as shown by Fokas and Yortsos (1982) and Rogers *et al.* (1983). This transformation was utilized for the case of constant flux at the soil surface by Broadbridge *et al.* (1988), Broadbridge and White (1988), Sander *et al.* (1988) and Warrick *et al.* (1990). More recently, Barry and Sander (1991) have extended these results to include the case of an arbitrary time dependence in the surface flux. A summary of these results is presented below.

2.2.1 The Infiltration Model and Solution

Barry and Sander (1991) have considered the one-dimensional form of (5a):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[D(\theta) \frac{\partial \theta}{\partial z} - K(\theta) \right], \quad z > 0, t > 0 \quad (7a)$$

subject to

$$\theta(z, 0) = \theta_i(z), \quad z > 0 \quad (7b)$$

and

$$Q(t) = K(\theta) - D(\theta) \frac{\partial \theta(0, t)}{\partial z}, \quad t > 0. \quad (7c)$$

If $D(\theta)$ and $K(\theta)$ are defined by:

$$D(\theta) = \frac{D_0}{(1 - v\theta)^2}, \quad (8)$$

and

$$K(\theta) = \frac{K_s \theta (1 - v)}{(1 - v\theta)} \quad (9)$$

respectively, then (7) can be solved exactly. Applications of the solution for constant flux infiltration have been presented by *White and Broadbridge* (1988). For a time-dependent flux, the solution satisfying (7) through (9) is (*Barry and Sander*, 1991):

$$v\theta(z,t) = 1 + \frac{K_s(1-v)p(\zeta,t)}{\sqrt{D_0}} \left[\frac{\partial p(\zeta,t)}{\partial \zeta} \right]^{-1} \quad (10a)$$

with

$$(v-1)K_s z(\zeta,t) = \ln[p(\zeta,t)]D_0. \quad (10b)$$

The function p is defined by:

$$p(\zeta,t) = \int_0^\infty k[\zeta - \eta(t) - \zeta',t]p(\zeta',0) d\zeta' - \int_0^t \frac{[\zeta - \eta(t) + \eta(t')]}{2(t-t')} k[\zeta - \eta(t) + \eta(t'),t-t']\lambda(t') dt' \quad (11a)$$

where $\lambda(t)$ is given by the solution of

$$\frac{\lambda(t)}{2} + 1 = \int_0^\infty k[\eta(t) + \zeta,t]p(\zeta,0) d\zeta + \int_0^t \frac{\partial k[\eta(t') - \eta(t),t-t']}{\partial a} \lambda(t') dt', \quad (11b)$$

$k(a,b)$ is the fundamental solution of the heat equation:

$$k(a,b) = \frac{\exp\left(-\frac{a^2}{4b}\right)}{\sqrt{4\pi b}} \quad (11c)$$

and $p(\zeta,0)$ is:

$$p(\zeta,0) = \exp\left[\frac{K_s(v-1)}{\sqrt{D_0}} \int_0^\zeta [1 - v\theta_i(\zeta')]^{-1} d\zeta' \right]. \quad (11d)$$

Last, $\eta(t)$ is defined by the integral:

$$\eta(t) = \int_0^t \frac{K_s(v-1) - vQ(t')}{\sqrt{D_0}} dt'. \quad (11e)$$

2.3 Solution for One-Dimensional Adsorptive Solute Transport

The one-dimensional form of (1a) is:

$$\frac{\partial [c + s(c)]}{\partial t} = D_s \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z}, \quad z, t > 0. \quad (12a)$$

Suitable boundary and initial conditions used in the solution of (12) are (e.g., *Barry et al.*, 1983):

$$c(z,0) = c_i(z), \quad z > 0 \quad (12b)$$

and

$$vc(0,t) - D_s \frac{\partial c(0,t)}{\partial z} = vc_0(t), \quad t > 0. \quad (12c)$$

As we have noted already, this model can be mapped onto either the head or water content forms of Richards' equation, together with appropriate boundary conditions. If, for example, the water content form is used, then the results in §2.2.1 can be used to derive an exact solution for (12). The specific forms of the diffusivity and conductivity functions in (8) and (9) restrict the adsorption isotherm for which exact results can be obtained. This isotherm is (*Barry and Sander*, 1991):

$$s(c) = \frac{\sum_{i=0}^2 a_i c^i}{K_s A_2 (v-1) - v A_2 v A_3 - a_2 c}, \quad (13a)$$

where

$$a_0 = K_s A_1 A_2 (v-1) - v A_2 A_3 (A_2 + v A_1), \quad (13b)$$

$$a_1 = K_s A_2 (1-v) + v v (A_2 A_3 - A_1) - A_2 v \quad (13c)$$

and

$$a_2 = v v. \quad (13d)$$

The flux boundary conditions, (12c) and (7c) are equivalent under this mapping if:

$$A_2 Q(t) = v [c_0(t) - A_2 A_3] \quad (14a)$$

and

$$D_s = \frac{D_0 v}{K_s (1-v)}. \quad (14b)$$

3. APPLICATION

The theory contained in §2 has yet to be compared with experimental data. A suitable experiment was carried out by *Schweich et al.* (1983). These authors presented experimental results for Ca-K exchange during soil column miscible displacement experiments. Typical of the data they report is the case of a column initially filled with K-saturated soil. This column was subjected to an influent solution containing Ca at a fixed normality under the condition of steady flow. Relevant soil and column data are presented in Table 1. Both physical and chemical parameters are needed to obtain predictions using the model in §2. Both types of data are provided by *Schweich et al.* (1983).

Although these data are derived from independent experiments, we recognize that the parameter values are possibly not truly independent.

Schweich et al. (1983) analyzed their experiment using a simple mixing-cell model. In this model, the column is divided into a group of batch cells in series. At each time step, the contents of each cell are advected and mixed to simulate the transport process in the column. We shall refer to the results of this model in the following.

3.1 Physical Parameters

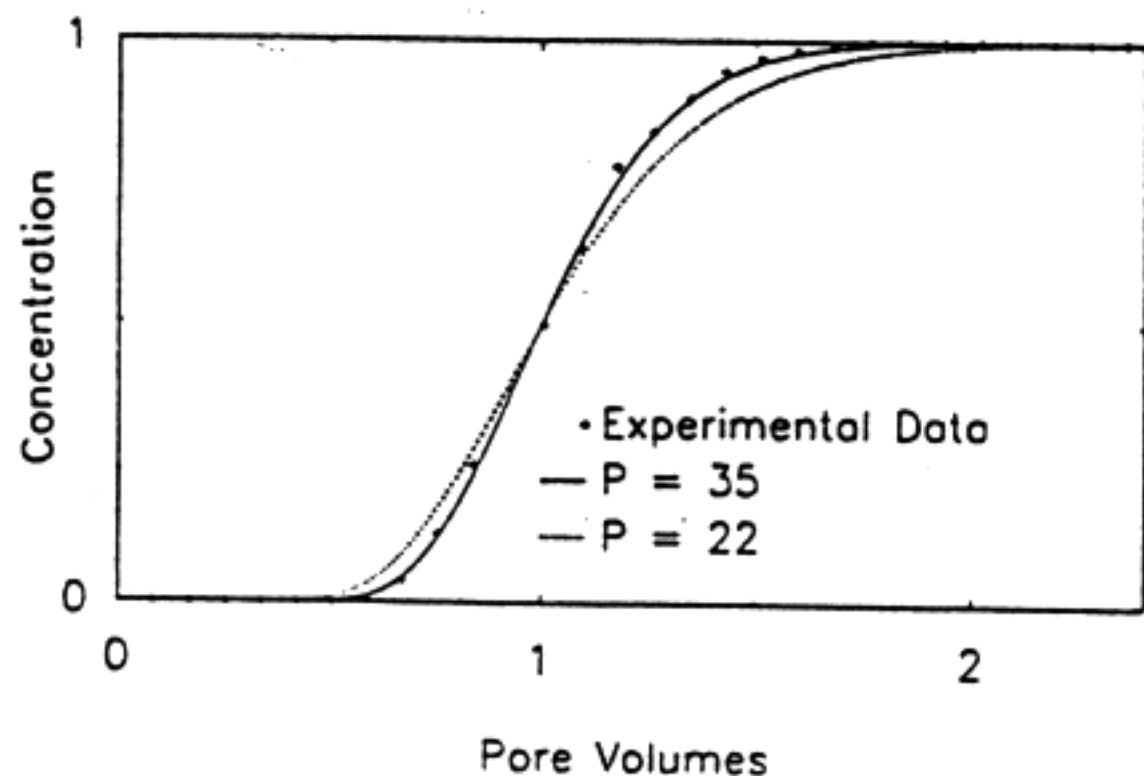
Schweich et al. (1983, Figure 5) carried out a miscible displacement experiment where Ca in the influent solution was exchanged on a Ca-saturated soil. The breakthrough curve from this experiment can be analyzed as for a tracer displacement experiment. The appropriate analytical solution from *van Genuchten and Alves* (1982, §A2) was fitted to the data with the result as displayed in Figure 1. We obtain a good fit for $P = 35$.

TABLE 1

SOIL AND EXPERIMENTAL APPARATUS DETAILS

$\frac{\rho_b}{n}$	1.48 g ml ⁻¹
L	20 cm
column diameter	2.6 cm
C _E	25 × 10 ⁻³ meq g ⁻¹
P	35
N	28 meq gm ⁻¹
K _N	exp(2.1 - 2.1x _{Ca})

From the data contained in Figure 5 of Schweich *et al.* (1983) we estimate the pore space in the column to be 67.5 ml, as opposed to the value of 69 ml reported. Also, Schweich *et al.* (1983) applied their mixing-cell model to these data and arrived at the estimate $P = 22$. The solution of van Genuchten and Alves (1982, §A2) for $P = 22$ is shown in Figure 1 as well. It is apparent that this value for P does not yield an adequate description of the experimental data. Part of the difference between our results and the results of Schweich *et al.* (1983) may be due to inaccurate digitizing of the original data, but errors in digitizing can only account for a small portion of the difference.

Figure 1. Breakthrough curve used to determine P .

3.2 The Adsorption Isotherm

Schweich *et al.* (1983) report that the equilibrium partitioning of the solute between the adsorbed and aqueous phases can be described by:

$$K_N = \frac{\bar{x}_{Ca} x_K^2}{\bar{x}_K^2 x_{Ca}} \quad (15a)$$

where

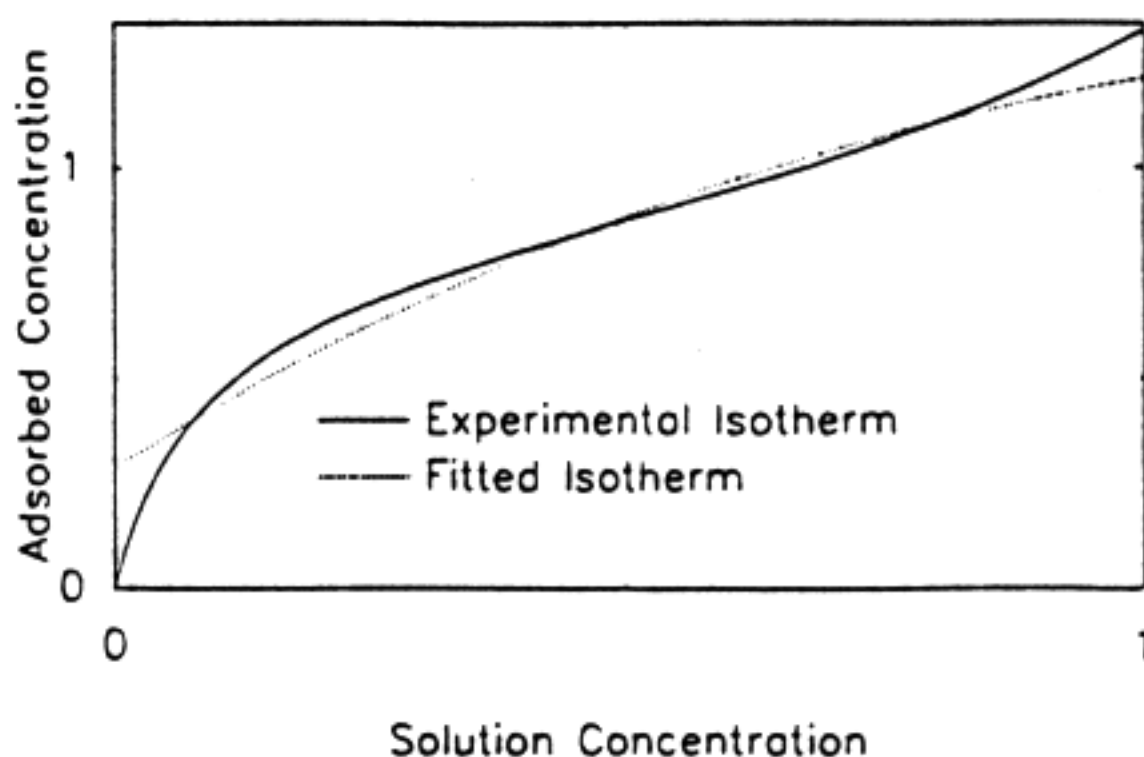
$$\bar{x}_K = \frac{N_K}{C_E} \quad (15b)$$

and

$$x_K = \frac{N_K}{N} \quad (15c)$$

Similar definitions apply to Ca. All results will be presented in terms of the normalized aqueous phase concentration, as given by (15c). The information in Table 1 and (15) can be used to derive the adsorption isotherm for the soil and solution normality used in the experiment, as displayed in Figure 2. In this figure the adsorbed phase concentration has been converted to the normalized solution phase concentration scale.

The isotherm, (13), for which we can obtain exact analytical results was fitted to the experimental isotherm. This fit is plotted also in Figure 2. It was obtained with the parameters: $v = 2.79$ cm hr⁻¹, $K_S = 1.10$ cm hr⁻¹, $\nu = 0.0270$, $A_1 = 0.191$, $A_2 = 0.215$ and $A_3 = 0.178$.

Figure 2. Adsorption isotherm for the experiment of Schweich *et al.* (1983), together with a fit of (13).

3.3 Predictions of the Model

Schweich *et al.* (1983) used a constant flux of solute as the surface boundary condition for their experiment. Thus we take the right side of (12c) as being constant, i.e., $c_0 = 1$. The initial condition was a uniform concentration in the soil column, so $c_i = 0$ in (12a). Under these conditions, (11) yields, for p :

$$p(\zeta, t) = \frac{1}{2} \exp[\gamma(\tau\gamma - \zeta + \bar{m})] \operatorname{erfc}\left(\frac{2\tau\gamma - \zeta + \bar{m}}{\sqrt{4t}}\right) - \frac{1}{2} \exp[(\gamma + \bar{\eta})(\tau\gamma + \zeta)] \operatorname{erfc}\left(\frac{2\tau\gamma + \zeta + \bar{m}}{\sqrt{4t}}\right) + \frac{1}{2} \left[\exp(\zeta\bar{\eta}) \operatorname{erfc}\left(\frac{\zeta + \bar{m}}{\sqrt{4t}}\right) + \operatorname{erfc}\left(\frac{\zeta - \bar{m}}{\sqrt{4t}}\right) \right] \quad (16a)$$

where

$$\gamma = \frac{K_S(1 - \nu)}{(1 - \nu\theta_i)\sqrt{D_0}} \quad (16b)$$

and

$$\bar{\eta} = \frac{K_S(\nu - 1) - \nu Q}{\sqrt{D_0}} \quad (16c)$$

The value of Q is known from (14a). We use (4c), (7b), (12b) and (13) to compute $\theta_i = 0.459$, with this value used in (16b).

Predictions for the fitted isotherm in Figure 2 can now be calculated using (10) and (16). In Figure 3 we present the predictions of this model and the experimental data collected by Schweich *et al.* (1983, Figure 4). The prediction for $P = 35$, given by the solid line in Figure 3, does not replicate the spreading of the breakthrough curve, although the mean breakthrough position is predicted accurately. Breakthrough curves for $P = 22$ and 15 are displayed as well. We note that the initial portion of the experimental breakthrough data is predicted quite well for $P = 22$. On the other hand, the latter portion is fitted well by the curve produced using $P = 15$. We point out that our prediction for $P = 22$ is reasonably close to the result produced by the numerical scheme

of Schweich *et al.* (1983), although the latter curve is not reproduced here.

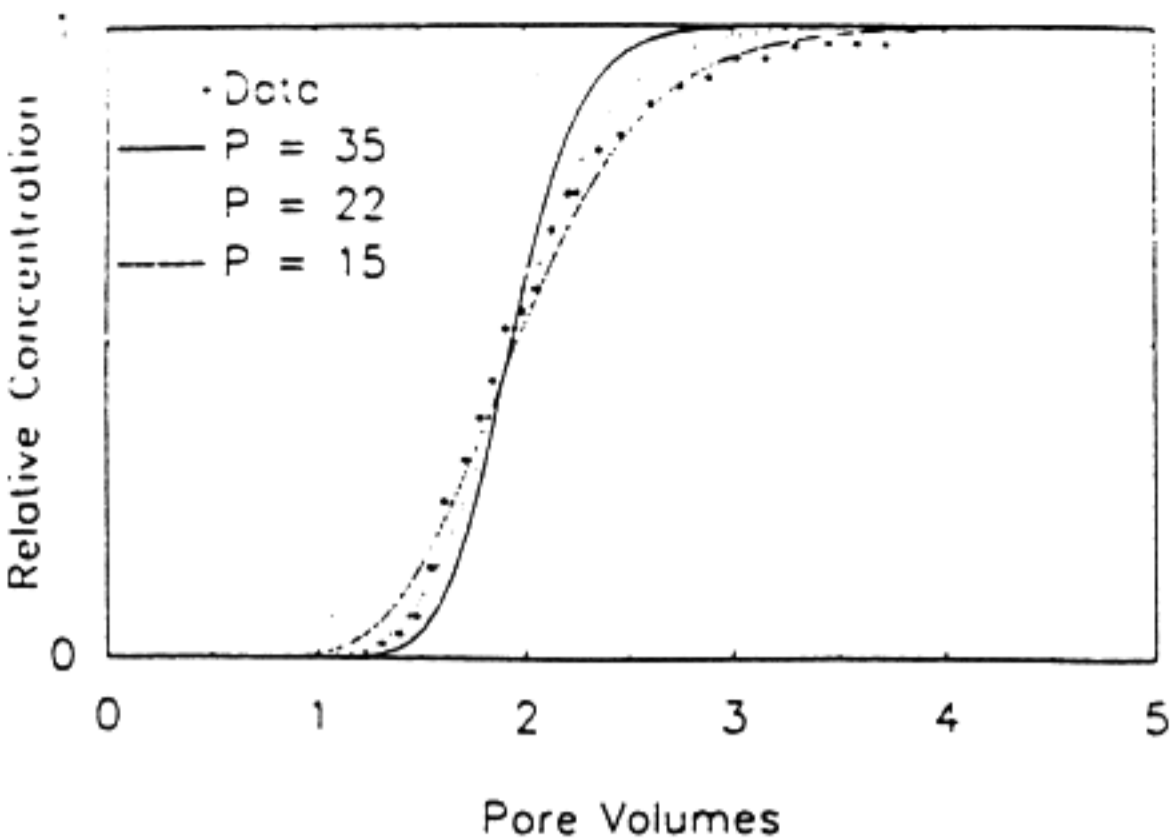


Figure 3. Experimental and predicted breakthrough curves for Ca-K exchange during a miscible displacement.

4. DISCUSSION

The model we presented in §2 is based on the assumption of local equilibrium between the solute in the liquid and in the exchanger. This means, of course, that the rate of transfer between the solution and exchanger phases is very rapid. The results of the model, as shown in Figure 3, do not agree very well with the experimental data for $P = 35$. On the condition that our analysis of the experiment is correct, we are led to conclude that the model assumptions are not appropriate.

It has pointed out by numerous authors (e.g., Parker and van Genuchten, 1984, §4) that there are models of non-equilibrium adsorption that are mathematically equivalent to models of physical non-equilibrium due to widely varying pore water velocities. For example, the "two-site" adsorption model (Cameron and Klute, 1977) comprises both equilibrium adsorption and first-order kinetic non-equilibrium adsorption. This chemical non-equilibrium model is identical with the model for the transport of solute in a medium with mobile and immobile zones, with a linear transfer rate between each zone.

By itself, the fact that our equilibrium model does not predict the data well is not sufficient to indicate that the local equilibrium assumption is invalid. We must also consider the effect of deviation from local equilibrium. The main effect is an enhanced spreading of the breakthrough curve. Barry and Sposito (1989, §1.2) showed that the enhanced breakthrough curve spreading of the mobile-immobile solute transport model is exactly reproduced by a tracer-type convection-dispersion equation with a time-dependent dispersion coefficient. This result suggests that we examine the experimental breakthrough curve for evidence of time-dependence in the dispersion coefficient required to model the data.

We have already seen in Figure 3 that the data could be reasonable well modelled by P changing from $P = 22$ (around 1 pore volume) to $P = 15$ (around 2.5 pore volumes). However, the tracer data in Figure 1 showed that $P = 35$ for this experiment. Since P is inversely proportional to the dispersion coefficient, and pore volumes are proportional to time, it is clear that the experimental data contained in Figure 3 reveal a non-equilibrium process is operational. The tracer experiment

(Figure 1) rules out physical non-equilibrium. We suggest, therefore, that Ca-K ion exchange kinetics are the cause of the enhanced spreading of the breakthrough curve plotted in Figure 3.

Apart from the local equilibrium assumption, we have assumed that it is permissible to use an approximation to the true adsorption isotherm, rather than the experimental isotherm presented by Schweich *et al.* (1983). Although the fit of the approximate isotherm is acceptable, the effect of the deviations should be ascertained. Perturbations of the approximate isotherm in Figure 2 produced only minor changes in predicted breakthrough curves. Certainly, the enhanced spreading exhibited by the data was not observed. However, we recognise that a numerical solution of (12) with $s(c)$ given by (15) will demonstrate conclusively whether the approximate isotherm in Figure 2 is adequate. We leave this step to a future analysis.

5. CONCLUSIONS

The main purpose of this research was to show the correspondence between the models for infiltration and nonlinear adsorption and to use this correspondence to predict adsorptive solute transport. The transport model is based on the assumption of local equilibrium between solute in the aqueous phase and the exchanger. We used the model to reanalyze data from the Ca-K exchange experiments of Schweich *et al.* (1983). In contrast to the original analysis, which was based on a simple numerical model, the present results indicate that the Ca-K exchange in this experiment does not conform to the assumption of local equilibrium. There is no evidence of physical non-equilibrium, and the breakthrough curve data reveal that a local equilibrium model with a time-dependent dispersivity is sufficient to simulate the data. This behaviour is characteristic of kinetic non-equilibrium in the exchange process.

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7. ACKNOWLEDGEMENTS

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