

On the Equivalence of Two Conceptual Models for Describing Ion Exchange During Transport Through an Aggregated Oxisol

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Breakthrough curves (BTCs) of the cation $^{45}\text{Ca}^{2+}$, an anion $^{36}\text{Cl}^-$, and $^3\text{H}_2\text{O}$ were measured during miscible displacement through water-saturated soil columns packed with aggregates of an Oxisol. Two conceptual models were used to simulate the observed asymmetry and tailing in the BTCs caused by an apparent nonequilibrium situation in the porous medium. In both models the exchange process on one type of site was assumed to be instantaneous while the rate of isotopic exchange on another type of site was assumed to be either a diffusion-controlled process (model 1) or a first-order reversible kinetic process (model 2). Isotopic exchange in both models was described with a linear isotherm. It is shown that the two models are mathematically equivalent with respect to the derived BTCs.

INTRODUCTION

Kinetic studies with the batch equilibration method have suggested that ion exchange is an instantaneous process [Hissink, 1924; Borland and Reitemeier, 1950]. This should be expected since ion exchange is a physical stoichiometric process with ΔH values of about 2 kcal mol^{-1} , resembling dipole-dipole interactions [Helfferich, 1962]. The interdiffusion of counter ions from the solution to the exchanger and vice versa, called ion exchange, is probably the main step that limits instantaneous equilibrium. This suggests that diffusion to and from the exchange sites, rather than the actual exchange reaction itself, determines the apparent exchange rate [Helfferich, 1962]. Because of relatively small particles normally used in batch ion-exchange kinetic studies, and because of vigorous shaking, diffusion often can be eliminated as a rate-limiting step [Boyd et al., 1947; Helfferich, 1962]. However, in a system with flowing water, and especially in aggregated soils, the ion-exchange rate can be limited by the rate at which the ions are transported by diffusion to the exchange sites. Several researchers [Smith, 1968; Nkedi-Kizza et al., 1982] have shown that even if the point reaction is instantaneous, the global or space kinetics can be influenced by such variables as fluid velocity (which is related to residence time) or aggregate size (which determines the diffusion path length).

Boyd et al. [1947] recognized two potential rate-limiting steps for ion-exchange kinetics: (1) intradiffusion of counter ions within the ion exchanger (particle diffusion) and (2) interdiffusion of counter ions in the adherent films (film diffusion). In practice, either step can be rate limiting, and for some cases the rate may be affected by both steps [Boyd et al., 1947; Hiester and Vermeulen, 1948; Lapidus and Amundson, 1952].

Various empirical equations resembling chemical kinetic

rate laws have been used to describe the global kinetics of ion exchange [du Domaine et al., 1943; Thomas, 1944; Juda and Carron, 1948; Helfferich, 1962]. From a global (macroscopic) point of view, similar effects on chemical transport can be expected for certain rate laws that are based on diffusion mechanisms and for certain rate laws that are based on chemical kinetics [Hiester and Vermeulen, 1952; van Genuchten, 1981]. One kinetic rate equation that is applicable to heterogeneous exchange and macroscopically closely resembles diffusion-controlled exchange was proposed by Selim et al. [1976]. In this paper we shall demonstrate the mathematical equivalence of the physical nonequilibrium (diffusion) model of van Genuchten and Wierenga [1976] and the chemical nonequilibrium (kinetic) model of Selim et al. [1976]. The resulting simulations from the transport models will be applied to isotopic exchange of ^{45}Ca and ^{36}Cl during miscible displacement through an aggregated Oxisol.

THEORY

Model 1: Diffusion-Controlled Rate Law

This model was first proposed for nonadsorbed solutes by Coats and Smith [1964] and later extended to adsorbed solutes by van Genuchten and Wierenga [1976]. In this model the liquid phase of the soil is partitioned into "mobile" (macroporosity) and "immobile" (microporosity) regions. Convective-diffusive transport is confined to the mobile water phase, while transfer of solutes into and out of the immobile (nonmoving) soil-water region is assumed to be diffusion controlled. The rate of solute transfer into the immobile regions is taken to be proportional to the difference in concentration between the two liquid regions. The governing transport equations for the mobile and immobile water phases are, respectively

$$\theta_m \frac{\partial c_m}{\partial t} + f\rho \frac{\partial s_m}{\partial t} + \theta_{im} \frac{\partial c_{im}}{\partial t} + (1-f)\rho \frac{\partial s_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 c_m}{\partial z^2} - \theta_m v_m \frac{\partial c_m}{\partial z} \quad (1)$$

$$\theta_{im} \frac{\partial c_{im}}{\partial t} + (1-f)\rho \frac{\partial s_{im}}{\partial t} = \alpha_1 (c_m - c_{im}) \quad (2)$$

where c and s represent the concentrations associated with the liquid and solid phases of the soil, respectively, and where the subscripts m and im refer to the dynamic (mobile) and stag-

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nant (immobile) fluid regions. The parameter f represents the mass fraction of solid phase that is in direct contact with the mobile liquid phase. The remaining symbols in these and the following equations are defined in the notation list.

Isotopic exchange of ^{45}Ca and ^{36}Cl in both the dynamic and stagnant regions of the soil is assumed to be an instantaneous, linear, and reversible process. Therefore

$$s_m = K_D c_m \quad s_{im} = K_D c_{im} \quad (3)$$

and total adsorption is

$$s = f s_m + (1 - f) s_{im} \quad (4)$$

The transport equations reduce to

$$\begin{aligned} (\theta_m + \rho f K_D) \frac{\partial c_m}{\partial t} + [\theta_{im} + (1 - f) \rho K_D] \frac{\partial c_{im}}{\partial t} \\ = \theta_m D_m \frac{\partial^2 c_m}{\partial z^2} - \theta_m v_m \frac{\partial c_m}{\partial z} \end{aligned} \quad (5)$$

$$[\theta_{im} + (1 - f) \rho K_D] \frac{\partial c_{im}}{\partial t} = \alpha_1 (c_m - c_{im}) \quad (6)$$

The imposed initial and boundary conditions are

$$c_m(z, 0) = c_{im}(z, 0) = 0 \quad (7a)$$

$$\begin{aligned} -D_m \frac{\partial c_m}{\partial z} + v_m c_m|_{z=0} = v_m C_0 \quad 0 < \tau \leq t_0 \\ = 0 \quad t \geq t_0 \end{aligned} \quad (7b)$$

$$\frac{\partial c_m}{\partial z}(\infty, t) = \frac{\partial c_{im}}{\partial z}(\infty, t) = 0 \quad (7c)$$

Let us introduce the following dimensionless variables:

$$c_1 = c_m/C_0 \quad c_2 = c_{im}/C_0 \quad (8)$$

$$T = \frac{vt}{L} = \frac{v_m \phi_m t}{L} \quad \phi_m = \frac{\theta_m}{\theta} \quad (9)$$

$$x = z/L \quad (10)$$

$$P = \frac{v_m L}{D_m} \quad (11)$$

$$R = 1 + \frac{\rho K_D}{\theta} \quad (12)$$

$$\beta = \frac{\theta_m + f \rho K_D}{\theta + \rho K_D} = \frac{\phi_m R_m}{R} \quad R_m = 1 + \frac{f \rho K_D}{\theta_m} \quad (13)$$

$$\omega = \frac{\alpha_1 L}{q} \quad q = \theta_m v_m \quad (14)$$

Substitution of these variables into (5) and (6) gives the final form of the transport model:

$$\beta R \frac{\partial c_1}{\partial T} + (1 - \beta) R \frac{\partial c_2}{\partial T} = \frac{1}{P} \frac{\partial^2 c_1}{\partial x^2} - \frac{\partial c_1}{\partial x} \quad (15)$$

$$(1 - \beta) R \frac{\partial c_2}{\partial T} = \omega (c_1 - c_2) \quad (16)$$

Similarly, the initial and boundary conditions become

$$c_1(x, 0) = c_2(x, 0) = 0 \quad (17a)$$

$$\begin{aligned} -\frac{1}{P} \frac{\partial c_1}{\partial x} + c_1|_{x=0} = 1 \quad 0 < T \leq T_0 \\ = 0 \quad T > T_0 \end{aligned} \quad (17b)$$

$$\frac{\partial c_1}{\partial x}(\infty, T) = \frac{\partial c_2}{\partial x}(\infty, T) = 0 \quad (17c)$$

The analytical solution of (15), (16), and (17) is given elsewhere [van Genuchten and Wierenga, 1976].

Model 2: Surface Reaction Rate Law

Combined equilibrium and kinetic models to describe solute adsorption on heterogeneous solid surfaces were proposed independently by Selim *et al.* [1976] and by Cameron and Klute [1977]. This type of model was used later also by Rao *et al.* [1979] for pesticide adsorption and by De Camargo *et al.* [1979] and Hoffman and Rolston [1980] for phosphorus adsorption. In this model, two types of adsorption sites are hypothesized: type 1 sites that achieve instantaneous equilibrium and type 2 sites with time-dependent kinetic adsorption. At equilibrium, adsorption on both sites is described by linear equations:

$$s_1 = K_1 c = F K_D c \quad (18)$$

$$s_2 = K_2 c = (1 - F) K_D c \quad (19)$$

where the subscripts 1 and 2 now refer to type 1 (equilibrium) and type 2 (kinetic) sites respectively, and where F is the fraction of all sites that are type 1. Total adsorption at equilibrium is simply

$$s = s_1 + s_2 \quad (20)$$

Because type 1 sites are always at equilibrium, it follows from (18) that

$$\frac{\partial s_1}{\partial t} = F K_D \frac{\partial c}{\partial t} \quad (21)$$

The adsorption rate for the type 2 kinetic nonequilibrium sites is given by a linear and reversible first-order equation of the form

$$\frac{\partial s_2}{\partial t} = \alpha_2 [(1 - F) K_D c - s_2] \quad (22)$$

where the model-specific parameter α_2 now represents a first-order kinetic rate coefficient. The governing transport equations for model 2 are

$$\left[1 + \frac{F \rho K_D}{\theta} \right] \frac{\partial c}{\partial t} + \frac{\rho}{\theta} \frac{\partial s_2}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} \quad (23)$$

$$\frac{\partial s_2}{\partial t} = \alpha_2 [(1 - F) K_D c - s_2] \quad (24)$$

The initial and boundary conditions for model 2 are

$$c(z, 0) = s_2(z, 0) = 0 \quad (25a)$$

$$\begin{aligned} -D \frac{\partial c}{\partial z} + v c \Big|_{z=0} = v C_0 \quad 0 < t \leq t_0 \\ = 0 \quad t > t_0 \end{aligned} \quad (25b)$$

$$\frac{\partial c}{\partial z}(\infty, t) = \frac{\partial s_2}{\partial z}(\infty, t) = 0 \quad (25c)$$

The following dimensionless variables are introduced for model 2:

$$c_1 = \frac{c}{C_0} \quad c_2 = \frac{s_2}{(1 - F) K_D C_0} \quad (26)$$

TABLE 1. Soil Column Data for Various Displacements Through the Ione Oxisol

Column No.	Experiment No.	Aggregate Diameter, mm	Concentration N	pH	Bulk Density ρ , g cm ⁻³	Water Content θ , cm ³ cm ⁻³	Flux q , cm h ⁻¹	Pulse T_1 Pore Volumes	Tracer
1	1	0.5-1	0.1	4	1.18	0.52	0.94	0.32	³⁶ Cl
1	2	0.5-1	0.01	4	1.18	0.52	0.94	0.44	³⁶ Cl
1	3	0.5-1	0.001	4	1.18	0.52	0.89	0.45	³⁶ Cl
2	4	0.5-1	0.01	4	1.09	0.56	0.25	0.31	³⁶ Cl
3	5	0.5-1	0.1	7	1.24	0.58	3.41	0.50	⁴⁵ Ca
3	6	0.5-1	0.1	7	1.24	0.58	0.25	0.38	⁴⁵ Ca
4	7	2-4.7	0.1	7	1.25	0.58	3.20	0.39	⁴⁵ Ca
4	8	2-4.7	0.1	7	1.25	0.58	0.26	0.35	⁴⁵ Ca

$$T = \frac{vt}{L} \quad x = \frac{z}{L} \quad (27)$$

$$P = \frac{vL}{D} \quad (28)$$

$$R = 1 + \frac{\rho K_D}{\theta} \quad R_m = 1 + \frac{F\rho K_D}{\theta} \quad (29)$$

$$\beta = \frac{\theta + F\rho K_D}{\theta + \rho K_D} = \frac{R_m}{R} \quad (30)$$

$$\omega = \frac{\alpha_2(1 - \beta)RL}{v} \quad (31)$$

Note that some of these variables (T , x , R) are the same as for model 1. Substitution of the dimensionless variables into (23) and (24) leads to the same dimensionless transport equations as for model 1 (equations (15) and (16)). Because the dimensionless boundary conditions are also the same, it follows immediately that the dimensionless analytical solutions for models 1 and 2 are identical.

MATERIALS AND METHODS

Miscible Displacement Studies

Breakthrough curves (BTCs) of ⁴⁵Ca, ³⁶Cl, and ³H₂O, applied together as a pulse to soil columns packed with an aggregated Oxisol, were measured under water-saturated, steady-flow conditions. Physical and chemical properties of the Ione Oxisol have been given elsewhere [Singer and Nkedi-Kizza, 1980; Nkedi-Kizza, 1979]. In summary, the soil is strongly aggregated, has a pH of 3.7, a cation exchange capacity (CEC) of 2 meq/100 g soil, an Fe₂O₃ content of 6.5%, a zero point of charge at pH 3.6, and has kaolinite as the predominant clay mineral. The soil was adjusted to a pH of either 4 or 7 and separated into aggregate fractions of 0.5–1.0 and 2.0–4.0 mm in diameter. Each aggregate fraction was first saturated with 0.1 N CaCl₂ and then packed separately into Plexiglas cylinders, 45 cm² in cross-sectional area and 5 cm long. Details of the procedure used to adjust the soil pH, the pH of the applied solution concentrations, the simultaneous determination of the three isotopes in one sample, and the miscible displacement experiments themselves are given by Nkedi-Kizza [1979]. The BTCs were measured using 0.1, 0.01, and 0.001 N CaCl₂ solutions that were adjusted to the final pH of the soil. The pulse solutions of CaCl₂ were spiked with ⁴⁵Ca, ³⁶Cl, and ³H₂O, each giving about 5 nCi/ml. Table 1 summarizes column data for the various displacement experiments. The displacements through the same column were run in the same order as presented in the table. For example, for

column 1 the experiments were run from experiment 1 through 3.

Model Parameter Estimation

The analytical solution of (15)–(17) contains the four independent parameters P , R , β , and ω . Experimental methods currently are unavailable to measure parameters β and ω independently. The initial estimates of P , β , and ω for ³⁶Cl or ⁴⁵Ca breakthrough curves were obtained by curve fitting the analytical solution to the experimental effluent curves of ³H₂O. The nonlinear curve-fitting program of *van Genuchten* [1981] was used for this purpose and for estimating R , β , and ω of ³⁶Cl⁻ and ⁴⁵Ca²⁺ effluent curves. For BTCs obtained from the same experiment for ³H₂O, ³⁶Cl⁻, and ⁴⁵Ca²⁺, the estimated parameter P from ³H₂O effluent curves was not optimized during the estimation of the remaining parameters (R , β , and ω) for ³⁶Cl⁻ or ⁴⁵Ca²⁺. Thus the task was reduced to estimating three parameters (R , β , and ω).

RESULTS AND DISCUSSIONS

Breakthrough Curves

Figures 1–8 show measured and calculated BTC for either ³⁶Cl⁻ or ⁴⁵Ca²⁺. The measured BTC for each experiment is represented by solid circles, while the simulated BTC is shown as a solid line. Table 2 summarizes the dimensionless parameter values obtained using model simulations for each experiment. For Figures 1–3, BTCs were obtained from the same column, except that the carrier concentration was reduced from 0.1 N to 0.001 N CaCl₂. The retardation factor for all three displacements is greater than 1 for ³⁶Cl⁻, implying sorp-

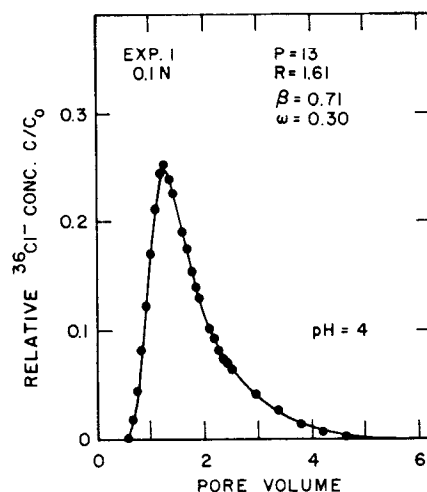


Fig. 1. Observed (solid circles) and fitted (solid lines) breakthrough curves for experiment 1: ³⁶Cl in 0.1 N CaCl₂.

TABLE 2. Fitted Values for the Dimensionless Parameters P , R , β , and ω

Column No.	Experiment No.	P	R	β	ω	Tracer
1	1	13	1.61 ± 0.04	0.71 ± 0.02	0.30 ± 0.10	^{36}Cl
1	2	13	1.89 ± 0.06	0.73 ± 0.03	0.69 ± 0.19	^{36}Cl
1	3	13	4.46 ± 0.08	0.74 ± 0.10	0.59 ± 0.10	^{36}Cl
2	4	13	1.89 ± 0.34	0.88 ± 0.12	0.16 ± 0.12	^{36}Cl
3	5	8	2.88 ± 0.07	0.67 ± 0.03	1.74 ± 0.34	^{45}Ca
3	6	8	2.39 ± 0.19	0.67 ± 0.03	1.55 ± 0.34	^{45}Ca
4	7	4	1.83 ± 0.11	0.57 ± 0.03	0.18 ± 0.02	^{45}Ca
4	8	4	1.60 ± 0.20	0.57 ± 0.03	0.59 ± 0.13	^{45}Ca

Fitted values include the 95% confidence interval.

tion at $\text{pH} = 4$. It should be pointed out that the method of *van Raij and Peech* [1972] used to determine the zero point of charge (ZPC) of the Ione Oxisol [Nkedi-Kizza, 1979] tends to give lower ZPC (lower pH) than that obtained by anion retention. *Espinoza et al.* [1975] found ZPC resulting from nitrate retention to be significantly higher than that obtained by the method of *van Raij and Peech* [1972]. Thus it is not surprising that $^{36}\text{Cl}^-$ is sorbed by the Ione Oxisol at $\text{pH} = 4.0$. From the R values in Table 2, it is clear that the sorption of trace amounts of $^{36}\text{Cl}^-$ in the system increases with a decrease in solution concentration of the carrier solution (Figures 1–3). A similar trend of data was obtained by *Persaud et al.* [1983] for sorption and leaching of Na^+ and Li^+ in decreasing concentrations of $\text{Ca}(\text{NO}_3)_2$. During the model simulations the Peclet number value of 13 initially obtained for the $^3\text{H}_2\text{O}$ effluent curve for experiment 1, was used for BTCs in Figures 1–3. The only parameters optimized were R , β , and ω .

In Figure 4 the BTC of ^{36}Cl in a column packed with aggregate of the same size as for column 1 is presented. The experiment was run at a flux 4 times less with 0.01 N CaCl_2 as carrier solution. Thus the Peclet number of 13 was fixed for this simulation, since *Nkedi-Kizza et al.* [1983] found a linear relationship between the dispersion coefficient D_m and velocity v_m . The R and β values obtained for this experiment are not significantly different from those of experiment 2, which was run under similar conditions except for the flux. Thus R and β values obtained from experiment 2 could have been used to describe the BTC for experiment 4 (Table 2).

Figures 5 and 6 show BTCs of ^{45}Ca for the same column,

but experiment 5 was run at a flux 14 times greater than that of experiment 6. Again as for ^{36}Cl effluent curves, the P value of 8 for both experiments was obtained from the $^3\text{H}_2\text{O}$ effluent curve simulation. Thus only the parameters R , β , and ω were optimized for experiment 5. Since *Nkedi-Kizza et al.* [1983] pointed out that the best estimate of β is from high flow velocity experiments, the β value from experiment 5 was used to simulate BTC for experiment 6. Thus the parameters R and ω were optimized to simulate the BTC for experiment 6. It should be pointed out that the R value for experiment 5 is higher than that for experiment 6. Since K_d is not a function of velocity, the possible explanation is that the pH for experiment 5 might have been somewhat higher than that of experiment 6. Since CEC is a function of pH in this soil, the higher pH would increase K_d and thus R .

In Figures 7 and 8 the BTCs for ^{45}Ca are presented for experiments run through the soil column packed with aggregates of 2–4.7 mm in diameter. Experiment 7 was run at a flux 12 times larger than that of experiment 8. The P value of 4 (Table 2) was obtained from $^3\text{H}_2\text{O}$ simulations of effluent curves for both experiments. Thus initially, the parameters R , β , and ω were optimized for experiment 7 and the β value obtained was used in simulating the BTC for experiment 8. Thus only the parameters R and ω were optimized for experiment 8. From Table 2 the R values for experiments 7 and 8 are not significantly different; thus both BTC could not be simulated using the same values of the parameters P , R , and β .

The most inconsistent parameter in all these simulations is ω . This parameter seems to be influenced by aggregate size,

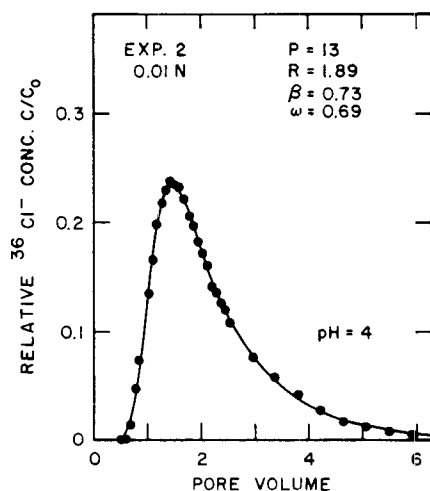


Fig. 2. Observed (solid circles) and fitted (solid lines) breakthrough curves for experiment 2: ^{36}Cl in 0.01 N CaCl_2 .

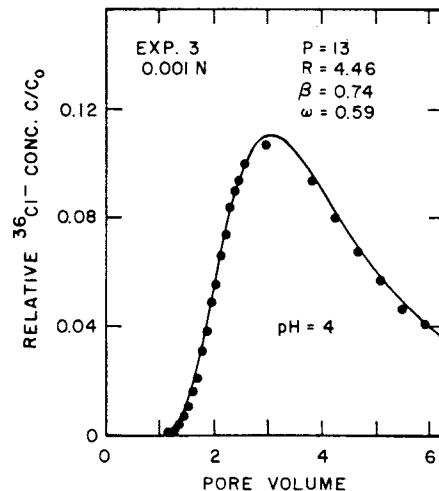


Fig. 3. Observed (solid circles) and fitted (solid lines) breakthrough curves for experiment 3: ^{36}Cl in 0.001 N CaCl_2 .

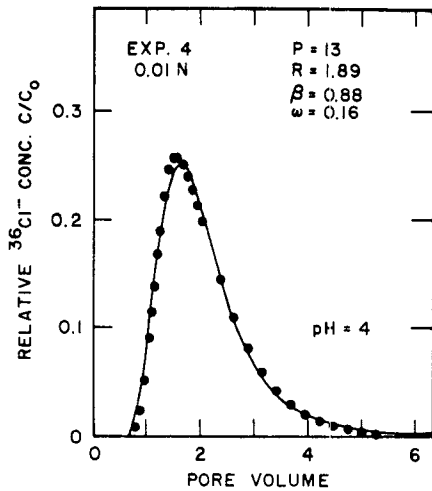


Fig. 4. Observed (solid circles) and fitted (solid lines) breakthrough curves for experiment 4. Conditions are similar to experiment 3 but flux is 4 times slower.

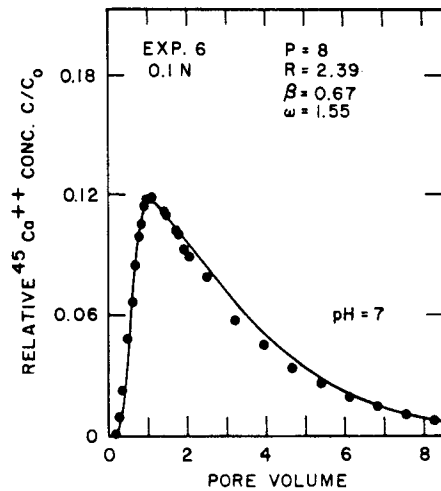


Fig. 6. Observed (solid circles) and fitted (solid lines) breakthrough curves for experiment 6. Conditions are similar to experiment 5 but flux is 14 times slower.

flux, and concentration of carrier solution. Rao *et al.* [1980] have pointed out that for a given ionic species, ω is not a constant but a function of aggregate size, flux, and mobile water. In this study we find ω to be a function of solution concentration also. It seems more work is needed to characterize ω with respect to the nature of porous medium and experimental conditions imposed on the system.

Estimates for the Original Model Parameters

Table 2 gives the fitted values of the four dimensionless parameters (P , R , β , and ω) in the general transport model. Of these, the column Peclet number P can be viewed approximately as the ratio of the residence times for diffusive (L^2/D_m or L^2/D) and convective transport (L/v_m or L/v). From Table 2 it is apparent that the same P value can be used to simulate effluent curves run through the same column even if flux and solution concentration are varied. The data presented with respect to P confirm earlier data presented by Nkedi-Kizza *et al.* [1983] for $^3\text{H}_2\text{O}$ and ^{36}Cl leached simultaneously through the same column.

The retardation factor R reflects the effects of adsorption during transport through the Ione soil. The parameter β de-

scribes the maximum degree of nonequilibrium in the system, either in a physical (model 1) or chemical-kinetic sense (model 2). Finally, the mass transfer coefficient ω describes the rate at which equilibrium is obtained from the initial nonequilibrium situation; the larger ω is, the sooner equilibrium is obtained.

Once the dimensionless parameters have been quantified, estimates for the original parameters in the two conceptual models can be derived by appropriately inverting the dimensionless quantities. Table 3 gives the inverted expressions that can be used as a guide for deriving estimates for the original parameters. Use of this table is straightforward, except with respect to the inverted expressions for the dimensionless parameter β in model 1. This parameter contains the unknown quantities ϕ_m (fraction of water considered to be mobile) and f (fraction of adsorption sites located in the dynamic region). For example, from Table 2 we have

$$\phi_m = \beta R - f(R - 1) \quad (32)$$

This equation shows that, first, an estimate of f is needed before ϕ_m can be calculated from β or, conversely, that an estimate for ϕ_m is needed before f can be calculated.

At least four alternative procedures can be followed to

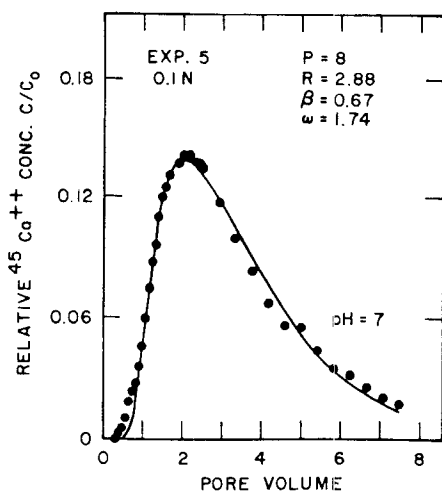


Fig. 5. Observed (solid circles) and fitted (solid lines) breakthrough curves for experiment 5: ^{45}Ca in 0.1 N CaCl_2 and aggregates of 0.5–1.0 mm in diameter.

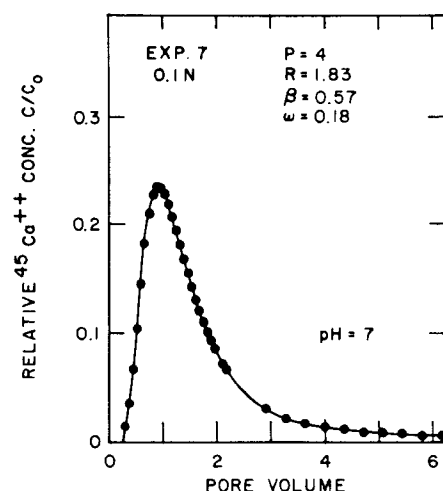


Fig. 7. Observed (solid circles) and fitted (solid lines) breakthrough curves for experiment 7: ^{45}Ca in 0.1 N CaCl_2 and aggregates of 2–4.7 mm in diameter.

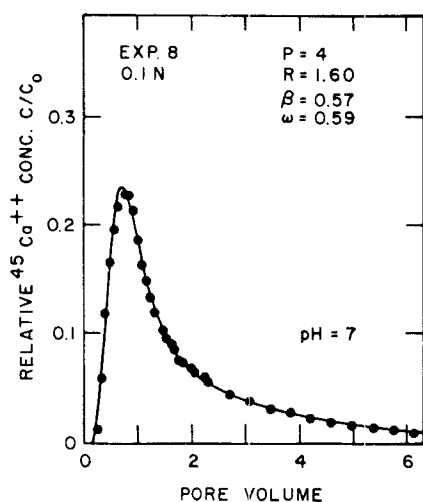


Fig. 8. Observed (solid circles) and fitted (solid lines) breakthrough curves for experiment 8. Conditions are similar to experiment 7 but flux is 12 times slower.

obtain estimates for ϕ_m and f . One method would be to carry out displacement experiments on the same soil column and at the same flow velocity but with a tracer that does not interact or only weakly interacts with the solid phase [Gaudet *et al.*, 1977; De Smedt, 1979]. This approach yields an estimate for ϕ_m that should be characteristic for the prevailing aggregate size and flow velocity. A second approach would be to obtain BTCs from the same soil column using two chemicals that are adsorbed by similar sorption sites but at different strengths. Assuming ϕ_m and f to be the same for the two chemical-soil combinations, the procedure would lead to two simultaneous equations in two unknowns, the solution of which yields estimates for ϕ_m and f [van Genuchten and Clearly, 1979].

As a third approach, one could simply assume that f equals zero, thereby assuming that tracer adsorption takes place only in the stagnant region of the soil, i.e., inside the aggregates [Bolt, 1979; Nkedi-Kizza *et al.*, 1982]. This assumption appears realistic for those soils in which the interior surface area of the aggregates is much larger than the exterior surface area. The assumption that $f = 0$, however, is less realistic for soils that are only weakly aggregated. In fact, for the limiting case when all soil water becomes mobile, all adsorption sites would become completely inaccessible for the chemical in the displacing fluid.

A fourth approach, and the one followed here, assumes that f and ϕ_m are numerically equal and that they are similar functions of the physical makeup of the soil (mainly aggregate size). When ϕ_m is small and large quantities of relatively immobile water are stored inside the aggregates, one may assume that only a few of the adsorption sites are readily accessible for the displacing chemical (f is small). On the other hand, when all soil water becomes mobile ($\phi_m = 1$), one may assume that most of the adsorption sites are also readily accessible

($f = 1$). In that case, model 1 would then reduce to the classical convective-diffusive transport model [Lindstrom *et al.*, 1967]. A possible situation that may not conform to this description would be the leaching process through soils with extremely dense aggregates that have large internal surface areas but, at the same time, contain only little intraaggregate water [Bolt, 1979]. The assumption that f equals ϕ_m leads to the simple equation

$$\phi_m = f = \beta \quad (33)$$

Using (33), it is now possible to obtain estimates for the original parameters in model 1. The various estimates are given in Table 4. Note that the K_D values for the two models are the same (R is the same). The dependency of the sorption coefficient K_D (for isotopic exchange) on solution concentration is evident from Table 2 while comparing experiments 1–3 for ^{36}Cl . The dispersion increases with velocity, and the fraction of "sites" at equilibrium decreases with an increase in aggregate size. The mass transfer coefficient α_1 or the first-order kinetic coefficient α_2 seems to become larger with an increase in flux. Since the residence time of a solute in a porous medium is a measure of the time available for diffusive mass exchange between the stagnant and mobile water regions in the porous medium, α should decrease with a decrease in flux as indicated in Table 3. This is a result of an increase in time over which α is calculated [Rao *et al.*, 1980].

Mathematical Equivalence of Models 1 and 2

The theoretical sections show that the two conceptually different models 1 and 2 can be put into the same dimensionless form. In this study we have measured only breakthrough curves. The dimensionless dependent variable $c_1(x, T)$, evaluated at $x = 1$, describes in mathematical terms these breakthrough curves for both models. Therefore the models are mathematically equivalent with respect to their BTCs. However, the two models are not equivalent with respect to measurements inside the column. For example, the dependent dimensionless concentration variable c_2 for model 1 is associated with a certain fraction of the liquid phase, while for model 2, it refers to a fraction of the solid phase. Furthermore, the variable c_1 itself is associated with different parts of the porous medium inside the column: mobile liquid in model 1 and total liquid in model 2. It follows therefore that only careful (microscopic) determinations of certain parameters (in situ) inside the column (c , c_1 , s_1) could be used to verify the conceptual basis of the two models. However, such a verification cannot be made by using only measured effluent curves.

From this it follows that the measured BTCs in this study cannot be used to differentiate between the exact physical and chemical aspects of the apparent nonequilibrium situation inside the column. The question immediately arises whether such a differentiation between physical and chemical aspects is possible, important, and really needed. Model 1 is con-

TABLE 3. Expressions for the Original Parameters in Models 1 and 2 in Terms of the Dimensionless Parameters P , R , β , and ω

	P	R	β	ω
Model 1	$D_m = (qL)/(0_m P)$	$K_D = [\theta(R - 1)]/\rho$	$\phi_m = \beta R + f(R - 1)$ $f = (\beta R - \phi_m)/(R - 1)$	$\alpha_1 = (\omega q)/L$
Model 2	$D = (vL)/P$	$K_D = [\theta(R - 1)]/\rho$	$F = (\beta R - 1)/(R - 1)$	$\alpha_2 = (\omega v)/[(1 - \beta)RL]$

TABLE 4. Derived Values for the Original Parameters in Models 1 and 2

Experiment No.	Model 1				Model 2				Tracer
	D_m , $\text{cm}^2 \text{h}^{-1}$	K_D , $\text{cm}^3 \text{g}^{-1}$	f	α_1 , h^{-1}	D , $\text{cm}^2 \text{h}^{-1}$	K_D , $\text{cm}^3 \text{g}^{-1}$	F	α_2 , h^{-1}	
1	0.98 ± 0.02	0.26 ± 0.01	0.71 ± 0.02	0.06 ± 0.02	0.70	0.26 ± 0.01	0.23 ± 0.08	0.25	^{36}Cl
2	0.95 ± 0.04	0.39 ± 0.02	0.73 ± 0.03	0.13 ± 0.04	0.70	0.39 ± 0.02	0.43 ± 0.10	0.49	^{36}Cl
3	0.94 ± 0.14	1.52 ± 0.03	0.74 ± 0.10	0.11 ± 0.02	0.66	1.52 ± 0.03	0.66 ± 0.13	0.17	^{36}Cl
4	0.20 ± 0.01	0.46 ± 0.10	0.88 ± 0.12	0.01 ± 0.01	0.17	0.46 ± 0.10	0.75 ± 0.42	0.06	^{36}Cl
5	5.48 ± 0.34	0.88 ± 0.03	0.67 ± 0.03	1.19 ± 0.24	3.67	0.88 ± 0.03	0.49 ± 0.05	2.15	^{45}Ca
6	0.40 ± 0.02	0.65 ± 0.09	0.67 ± 0.03	0.08 ± 0.02	0.27	0.65 ± 0.09	0.43 ± 0.10	0.17	^{45}Ca
7	12.10 ± 0.67	0.39 ± 0.06	0.57 ± 0.03	0.12 ± 0.02	6.90	0.39 ± 0.06	0.05 ± 0.00	0.25	^{45}Ca
8	0.98 ± 0.02	0.27 ± 0.08	0.57 ± 0.03	0.03 ± 0.01	0.56	0.27 ± 0.08	0.03 ± 0.00	0.08	^{45}Ca

Derived values include the 95% confidence interval where desirable.

ceptually pleasing since it has an equivalent formulation for nonadsorbing systems [Gaudet *et al.*, 1977; Coats and Smith, 1964]. On the other hand, adsorption in this model is described with the assumption that the solid phase is homogeneous and hence that adsorption on all sites occurs with the same strength and at the same (equilibrium) rate. This assumption may not be realistic for usually heterogeneous soil systems. It appears more likely that the mechanisms of both models are present simultaneously in many soil systems. Thus the macroscopically oriented and semiempirical dimensionless transport model can be used without having to delineate the exact physical and chemical processes that operate in the system in a microscopic fashion. However, it should not be alarming to see that both models can be used to predict isotopic exchange during transport in an aggregated porous medium. We may emphasize once more that isotopic exchange is instantaneous and that both models are empirical in nature with regard to describing ionic diffusion to inaccessible sites in the system. Rigorously, diffusion of ionic species to inaccessible sites or regions in the porous medium should have been described by Fick's second law of diffusion, if the shape and sizes of aggregates were known exactly.

SUMMARY AND CONCLUSIONS

This paper evaluated two conceptual models that describe isotopic exchange of ^{36}Cl or ^{45}Ca during transport through water-saturated aggregated soil columns. In both models, exchange on one type of sorption sites was assumed to be instantaneous, while the rate of exchange on another type of sites was assumed to be either a diffusion-controlled process (model 1) or a first-order reversible kinetic process (model 2). At equilibrium, isotopic exchange in both models was described with a linear reversible isotherm. By introducing appropriate dimensionless variables, both models could be put into exactly the same dimensionless form. The resulting dimensionless transport model contains two dependent variables (c_1 and c_2) and four independent parameters (P , R , β , and ω).

Because the effluent curves in both models could be described by the same dependent variable (c_1), it follows that the two models are equivalent with respect to their breakthrough curves. Therefore both models were equally successful in describing the measured BTCs. However, the two dependent variables define conceptually different quantities in the two models. For example, c_2 in model 1 describes the average solution concentration of the immobile liquid zone, while c_2 in model 2 defines the adsorbed concentration associated with type 2 (kinetic) nonequilibrium sites. This shows that micro-

scopic measurements inside the column must be carried out to verify the conceptual basis of the two models.

In most cases the parameters R , β , and ω were estimated by curve fitting them to measured BTCs. The parameter P was obtained from $^3\text{H}_2\text{O}$ effluent curves and was therefore not optimized during model simulations and was found to be dependent only on physical characteristics of the porous medium (mainly aggregate size). The retardation factor R , which was defined similarly for the two models, depended mainly on $p\text{H}$ and total electrolyte concentration of the feed solution. The parameter ω was found to be a function of both the physical (aggregate size, flow velocity) and chemical characteristics (e.g., total solute concentration) of the system, and the parameter β was a function of aggregate size.

It is suggested that the difference between diffusion-controlled adsorption (model 1) and two-site kinetic adsorption (model 2) is of little practical importance when describing ion exchange during transport through aggregated sorbing media. Both models generate macroscopically the same total concentration distribution ($c_i + s_i$) in the system.

NOTATION

- c solution concentration, nCi/cm^3 (model 2).
- C_0 input concentration, nCi/cm^3 .
- c_1 dimensionless solution concentration of "mobile" liquid phase (model 1) or of total liquid phase (model 2).
- c_2 dimensionless solution concentration of "immobile" liquid phase (model 1) or adsorbed concentration for type 2 kinetic sites (model 2).
- c_{im} average concentration of immobile liquid phase, nCi/cm^3 .
- c_m average concentration of mobile liquid phase, nCi/cm^3 .
- D apparent diffusion coefficient of total liquid phase, cm^2/h (model 2).
- D_m apparent diffusion coefficient of mobile liquid phase, cm^2/h (model 1).
- f mass fraction of adsorption sites in dynamic region (model 1).
- F fraction of adsorption sites in equilibrium with solution concentration (model 2).
- K_1, K_2 distribution coefficients for type 1 (equilibrium) and type 2 (kinetic) sites, cm^3/g (model 2).
- K_D distribution coefficient for linear adsorption, cm^3/g .
- L column length, cm .
- P column Peclet number.
- q volumetric flux density, cm/h .
- R retardation factor.

- R_m retardation factor for dynamic region (model 1) or type 1 equilibrium sites (model 2).
 s total adsorbed concentration, nCi/g.
 s_1, s_2 adsorbed concentrations associated with type 1 (equilibrium) and type 2 (kinetic) sites, nCi/g (model 2).
 s_{im}, s_m adsorbed concentrations in the dynamic and stagnant regions of the soil, respectively, nCi/g (model 1).
 t time, hours.
 t_1 time of applied concentration pulse, hours.
 T pore volume.
 T_0 dimensionless pulse time.
 v average pore-water velocity, cm/h.
 v_m average pore-water velocity in mobile liquid region, cm/h (model 2).
 x dimensionless distance.
 z distance, cm.
 α_1 first-order mass transfer coefficient, per hour (model 1).
 α_2 first-order kinetic rate coefficient, per hour (model 2).
 β dimensionless partition coefficient.
 θ volumetric water content.
 θ_m volumetric water content in mobile region.
 ρ bulk density, g/cm³.
 ϕ_m fraction of liquid phase that is considered to be mobile (model 1).
 ω dimensionless mass transfer coefficient.

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