

RAPID COMPUTATION OF SOLUTE TRANSPORT WITH NONLINEAR EQUILIBRIUM AND NONEQUILIBRIUM REACTIONS

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SUMMARY So-called mixing cell models have been used frequently to model solute transport coupled with reactions. The main advantage of these models is their conceptual simplicity. This allows them to be solved sequentially with chemical speciation models to predict chemical concentrations in combined reaction/transport problems. Mixing cell models are actually just explicit finite-difference solutions of the governing advection-dispersion equation. It can be shown that the inclusion of reactions in the "standard" mixing cell model degrades its second-order accuracy. We propose, therefore, an improved model which maintains second-order accuracy regardless of whether reactions are included. In addition, the improved model is unconditionally stable, unlike the standard scheme. We show that nonequilibrium reactions can also be included without difficulty. Next, we show that different boundary conditions can be incorporated into the mixing cell models. In particular, a third-type surface condition is considered. For this case, to maintain second-order accuracy of the improved model, it is necessary to dispense with the explicit nature of the scheme on the boundary. At other locations the scheme is still explicit. Other conditions, e.g., a finite mass of solute available at the surface, as would be the situation if a landfill was considered, can be handled in the same way. The method can easily be extended to cater for the multilayered porous media as well. Our results demonstrate that nonlinear reactions and transport can be modelled very efficiently and quickly.

INTRODUCTION

The mixing cell concept has been used frequently to predict migration of reactive and non-reactive solutes in soil and groundwater (Schweich and Sardin, 1981; Van Ommen, 1985; Rao and Hathaway, 1989; Dudley et al., 1991). Mixing cell models are easy to code and efficient to compute. They can be linked with chemical speciation models to simulate complex reactions coupled with transport.

Explicit finite-difference representations of the transport equation underlie the mixing cell concept. For tracer solutes, the standard model is second-order accurate in the space and time discretization. It can be shown that the inclusion of adsorption in the transport equation reduces the accuracy of the mixing cell model. We present an improved mixing cell model which maintains second-order accuracy. In addition, the improved model is unconditionally stable.

There are two types of predictive models used for analysing transport of reacting solutes (Rubin, 1983). In one, the reaction is sufficiently fast to be described by an equilibrium model. In the other type, the reaction is relatively slow and is quantified by a nonequilibrium model. We show that the improved method can cater for both cases. Also, different surface boundary conditions can be easily incorporated into the improved mixing cell model.

In reality soils are never homogeneous. Soil heterogeneity can be partially accounted for by considering mediums with different layers. Such porous media have been considered by a number of researchers (Shamir and Harleman, 1967; Selim, et al., 1977; Kreft, 1981; Barry and Parker, 1987; Barry et al., 1987). Here this problem is treated also using improved mixing cell model.

Our main purposes in this paper are to:

- (i) show that the improved mixing cell model can describe nonequilibrium reactions very efficiently;

- (ii) include different types of surface boundary condition in the numerical scheme; and

- (iii) show the use of the model in the case of a multilayered porous medium.

In the following section the governing equations with various surface and exit conditions and reactions are first described followed by improved mixing cell model.

GOVERNING MODEL

The governing one-dimensional solute transport equation with adsorption is given by (e.g., Yortsos, 1987):

$$\frac{\partial(S + C)}{\partial t} = D_s \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad (1)$$

(symbols are defined in the notation list). This equation describes solute transport subject to adsorption under steady flow conditions. The solid phase solute concentration, S , is assumed to be given as an equivalent fluid phase concentration. Initially, the normalised solute concentration in both the solid and liquid phases is taken as:

$$C(z,0) = S(z,0) = 0, \quad (2)$$

although the right-hand side can be non zero if necessary.

We consider next the different boundary conditions used to solve eqn. (1).

Entrance Boundary Conditions

One type of boundary condition is a constant concentration of solute at the soil surface,

$$C(0,t) = C_0. \quad (3a)$$

Equation (3a) is based on the assumption of a "well-mixed" solute reservoir at the entrance and assumes that the concentration is continuous across the inlet boundary (van Genuchten and Parker, 1984). Alternatively, eqn. (3a) is appropriate for describing the solute flux at $z = 0$ (Kreft and Zuber, 1978).

The other commonly used surface condition is the mixed, or flux boundary condition, given by (Brenner, 1962):

$$VC(0,t) - D_s \frac{\partial C(0,t)}{\partial z} = VC_o. \quad (3b)$$

Equation (3b) results in a macroscopic discontinuity in concentration at $z = 0$.

Finite source boundary conditions are typically imposed in landfill modelling studies. It is assumed that the pollutant concentration in the landfill is initially C_o , and that this concentration decreases with time as leachate is transmitted through the soil by advective and dispersive flow. If the equivalent thickness of leachate in the landfill is h_f , and n_a is the porosity, then the surface concentration at any time, t , is given by (Rowe and Booker, 1985):

$$C(0,t) = C_o - \frac{n_a}{h_f} \int_0^t VC(0,\tau) - D_s \frac{\partial C(0,\tau)}{\partial z} d\tau. \quad (3c)$$

This entrance condition applies to a finite source of solute at the entrance boundary. Note that setting $h_f \rightarrow \infty$ recovers eqn. (3a). In the illustrative examples given below, boundary condition (3a) is used to solve the nonequilibrium problem and surface conditions (3b) and (3c) are used to solve the case of equilibrium reactions.

Exit Conditions

For a semi-infinite domain, we require that the solute concentration remains bounded throughout the soil profile, i.e. (van Genuchten and Parker, 1984):

$$\left. \frac{\partial C}{\partial z} \right|_{z \rightarrow \infty} = 0. \quad (4a)$$

For a finite column, the commonly used exit condition is given by (Brenner, 1962):

$$\left. \frac{\partial C}{\partial z} \right|_{z=L} = 0. \quad (4b)$$

In other words, eqn. (4b) assumes that the solute concentration is continuous across the exit boundary, although solute dispersion is negligible outside the porous medium. Another case of interest is the exit boundary condition for a soil column that is freely draining (Barry and Sposito, 1988):

$$C(L,0) = 0. \quad (4c)$$

Equation (4c) applies also in case of landfills, where base concentrations can be assumed zero when the groundwater velocity is quite large relative to the infiltrating solute (Rowe and Booker, 1985). This becomes the case of infinite dilution, and is a reasonable assumption given that flow rates in the unsaturated zone are typically much lower than those in the saturated zone. The incorporation of these boundary conditions into the mixing cell model is discussed below.

Adsorption

The relationship between solid and liquid phase solute concentration at equilibrium is given by the adsorption isotherm and is of the form:

$$S = f(C). \quad (5a)$$

A linear isotherm is given by

$$S = (R-1)C, \quad (5b)$$

where R is the retardation factor. An S-curve isotherm is (Barry, 1992)

$$S = k_4 \{ 1 - [1 + (k_2 C)^{k_1}]^{k_3} \}. \quad (5c)$$

The term $\partial S / \partial t$ in the left hand side of eqn. (1) describes the reaction process. When the reaction is sufficiently fast, the adsorption isotherm is written as an algebraic function of C , (eqn. 5) and so is used to eliminate the adsorbed phase concentration, S (Rubin, 1983; Clancy and Jennings, 1988). Such an operation gives rise to the equilibrium transport model. When the reaction process is insufficiently rapid, an additional differential rate equation must be used to solve (1). This results in the nonequilibrium transport model. A thorough discussion concerning classes of reactions can be found in the paper by Rubin (1983). Adsorption kinetics can be expressed mathematically as:

$$\frac{\partial S}{\partial t} = \alpha [f(C) - S]. \quad (6)$$

It should be noted that, at equilibrium, $\partial S / \partial t = 0$ and $S = f(C)$. Equations (1) and (6), together with appropriate boundary conditions, constitute a nonequilibrium transport model.

Improved Mixing Cell Model

Upon dropping second derivative term in the advective-dispersive equation, (1), one gets a pure advective transport equation given by:

$$\frac{\partial (C + S)}{\partial t} = -V \frac{\partial C}{\partial z}. \quad (7)$$

Finite-difference solutions of (7) produce numerical dispersion which is controlled to simulate solutions to (1).

In the standard mixing cell model, the temporal derivative is approximated by forward differencing and the advective term is approximated by backward differencing. The standard mixing cell solution has a truncation error of $O(\Delta z^2, \Delta t)$ and the following scheme is proposed which is still explicit but is more accurate than the standard model. In this scheme the advective term is approximated by the average of the backward difference approximations at the (i,j) and $(i,j+1)$ grid points as in the conventional Crank-Nicolson scheme (e.g., Noye, 1982). After simplification, the improved scheme is given by

$$(2 + C_r)C(i,j+1) + 2S(i,j+1) = 2[C(i,j) + S(i,j)] + C_r[C(i-1,j) - C(i,j) + C(i-1,j+1)], \quad (8)$$

where we use the notation $C(z,t) = C(i\Delta z, j\Delta t) = C(i,j)$, while

$$C_r = \frac{V\Delta t}{\Delta z} \quad (9)$$

is the Courant number. At equilibrium, the solid phase concentration is given by:

$$S(i,j+1) = f[C(i,j+1)]. \quad (10)$$

By making use of (10), (8) reduces to an equation with $C(i,j+1)$ as the only unknown. In the case of nonequilibrium adsorption, the finite-difference analog of (6) is given by:

$$S(i,j+1) = \frac{\frac{\alpha \Delta t}{2} \{f[C(i,j+1)] + f[C(i,j)]\}}{1 + \frac{\alpha \Delta t}{2}} + \frac{\left(1 - \frac{\alpha \Delta t}{2}\right) S(i,j)}{1 + \frac{\alpha \Delta t}{2}} \quad (11)$$

Equations (8) and (11), when combined, again result a single equation with $C(i,j+1)$ as the only unknown. Next we show that eqns. (8) and (11), the improved mixing cell model, are consistent.

By making use of the third-order Taylor series expansion in eqn. (8), we get:

$$\frac{\partial(C+S)}{\partial t} = \frac{V \Delta z}{2} \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} + O(\Delta z \Delta t, \Delta z^2, \Delta t^2), \quad (12)$$

i.e., the error is $O(\Delta z \Delta t, \Delta z^2, \Delta t^2)$. In this scheme the numerical dispersion introduced is $V \Delta z/2$. When the transport equation (1) is to be solved by eqn. (8), the relation $D_s = V \Delta z/2$ is imposed, thus fixing the spatial step length.

Similarly, eqn. (11) reduces to:

$$\frac{\partial S}{\partial t} = \alpha [f(C) - S] + O(\Delta t^2), \quad (13)$$

and so eqns. (12) and (13) are consistent with respect to truncation error.

Since a stability analysis is possible only for simple cases, the scheme obtained by combining eqns. (8) and (11) was checked for stability using numerical experiments. In all cases the scheme was found to be unconditionally stable. Unlike the standard scheme, this allows large time steps to be used without the solution being corrupted by roundoff errors. The improved mixing cell is unconditionally stable when adsorption is not considered (Bajracharya and Barry, 1992).

Incorporation of Surface Boundary Conditions

The incorporation of eqn. (3a) is straightforward so only conditions (3b) and (3c) are considered below. The entrance condition (3b) is incorporated at $z = 0$ by the central difference approximation (Noye, 1982). This reduces to a system of equations in two unknowns at the first two grid points. The system of equations is:

$$\left(1 + \frac{C_r}{2} + \frac{C_r V \Delta z}{D_s}\right) C(0,j+1) - \frac{C_r}{2} C(1,j+1) + S(0,j+1) = \left(1 - \frac{C_r}{2} - \frac{C_r V \Delta z}{D_s}\right) C(0,j) + \frac{C_r}{2} C(1,j) + \frac{2 C_r V \Delta z}{D_s} C_0 + S(0,j) \quad (14a)$$

and

$$-\frac{C_r}{2} C(0,j+1) + \left(1 + \frac{C_r}{2}\right) C(1,j+1) + S(1,j+1) = \frac{C_r}{2} C(0,j) + \left(1 - \frac{C_r}{2}\right) C(1,j) + S(1,j). \quad (14b)$$

Equations (10), (14a), and (14b) are used to compute the concentration at $z = 0$. At the rest of the locations, the scheme reduces to a single equation in one unknown.

In the case of the finite source boundary condition, eqn. (3c) is first differentiated with respect to time to yield

$$\frac{\partial C(0,t)}{\partial t} = -\frac{n_a}{h_f} \left[V C(0,t) - D_s \frac{\partial C(0,t)}{\partial z} \right]. \quad (15a)$$

Writing eqn. (15a) in finite-difference form with a forward difference in time and a centred difference in space and making use of eqn. (8), we get two sets of equations with two unknowns as follows

$$\left[1 + \frac{C_r}{2} + \frac{C_r}{2} \left(\frac{4 h_f \Delta z}{n_a D_s \Delta t} + \frac{2 V \Delta z}{D_s} \right)\right] C(0,j+1) - \frac{C_r}{2} C(1,j+1) = \left[1 - \frac{C_r}{2} + \frac{C_r}{2} \left(\frac{4 h_f \Delta z}{n_a D_s \Delta t} - \frac{2 V \Delta z}{D_s} \right)\right] C(0,j) + \frac{C_r}{2} C(1,j) \quad (15b)$$

with (14b) representing the other equation of the set. Note that no adsorption is assumed to take place at $z = 0$. However adsorption proceeds at $z = 0^+$. Equations (14b) and (15b) are used to compute the concentration at $z = 0$.

Boundary Layer Correction

In the mixing cell model, no exit condition can be specified and the solution obtained is that for a semi-infinite system. At the exit, the boundary condition is often taken as eqn. (4b). Parlange and Starr (1975) have shown that the effect of eqn. (4b) is to increase solute concentration in the profile in the region $z \approx L$. Solutions found for semi-infinite column can be corrected to account for this small concentration increase. When $P < 4$, the relatively short column length produces a significant increase in solute concentration throughout the soil profile and eqn. (1) must be solved directly using eqn. (4b). For $P > 4$ it is possible to approximate the effect of eqn. (4b) using a boundary layer correction. We find, following a similar procedure to that employed by Barry et al. (1986), that the corrected solution to a finite column is, for $P > 4$

$$C^*(z,t) = C(z,t) - \frac{\exp[\beta(z-L)]}{\beta} \frac{\partial C}{\partial z} \Big|_{z=L} \quad (16a)$$

where C is the solution obtained for a semi-infinite spatial domain. The corrected solid phase concentration is

$$S^* = f(C^*). \quad (16b)$$

Since eqns. (16a) and (16b) must satisfy eqn. (1), the value of β is closely approximated by

$$\beta = \frac{V}{2D} \left[1 + \sqrt{1 - \frac{4\gamma D}{V}} \right], \quad (16c)$$

where γ is,

$$\gamma = \frac{\frac{\partial^2 C}{\partial z^2} \Big|_{z=L} - \frac{D_s \partial^3 C}{V \partial z^3} \Big|_{z=L}}{\frac{\partial C}{\partial z} \Big|_{z=L}}. \quad (16d)$$

This boundary layer correction is applied when condition (4b) is imposed.

Similarly, for the case of zero concentration at the column exit, another boundary layer correction can be obtained. In

this case, the effect of eqn. (4c) is to decrease the solute concentration in the profile near $z \approx L$. We find that the corrected solution to a finite column is, for $P > 4$

$$C^*(z,t) = C(z,t) - \exp[\beta'(z-L)] C(L,t), \quad (17a)$$

where β' is given by

$$\beta' = \frac{V}{2D} \left[1 + \sqrt{1 + \frac{4\gamma'D}{V^2}} \right], \quad (17b)$$

while γ' is

$$\gamma' = \frac{D_s \left. \frac{\partial^2 C}{\partial z^2} \right|_{z=L} - V \left. \frac{\partial C}{\partial z} \right|_{z=L}}{C(L,t)}. \quad (17c)$$

This correction is applied when exit condition (4c) is used. Equations (16d) and (17c) are incorporated by using a centred finite-difference scheme for the first, second and third spatial derivatives.

Layered Porous Media

The same advective-dispersive equation (1) is used to describe transport and reaction of chemical species in layered media. The case of a two-layered medium is treated here. This problem can be easily solved by treating each layer to be semi-infinite, in which case the mixing cell model can be directly applied using the same equation for each layer. The exit concentration in one layer gives the entrance concentration for the next, i.e., continuity of concentration. Shamir and Harleman (1967) also used this approach. In the exact solution, the additional constraint at the interface between the two layers is the continuity of mass flux. The results of the time-moment analysis given by Barry and Parker (1987) and Barry et al. (1987) were used to obtain the following condition for the mixing cell solution to be close to the exact solution

$$\left| \frac{d_1 d_2 - d_1^2 [1 - \exp(-P_1)] - d_2^2 [1 - \exp(-P_2)]}{d_1 l_1 + d_2 l_2} \right| \ll 1 \quad (18)$$

where $d_i = D_i/V_i^2$, $l_i = L_i/V_i$, $P_i = V_i L_i/D_i$, $i = 1, 2$. The condition used to obtain eqn. (18) is that the ratio of the difference of the variances of the exact solution and the mixing cell solution to the variance of the exact solution should be small. Note that condition (18) is valid for nonreactive and linearly adsorbing solutes only. However, our numerical checks demonstrate that it is reasonable for nonlinear reactions as well.

COMPARISON WITH CRANK-NICOLSON SCHEME

The results of kinetic nonequilibrium simulations are first discussed followed by the results obtained by incorporating the time-dependent surface boundary conditions. The two layer problem is then discussed considering linear and nonlinear adsorption isotherms.

Kinetic Nonequilibrium

The problem solved by the improved mixing cell is eqn. (1) with initial condition (2), the boundary conditions (3a), (4a) and an S-curve isotherm given by (5c). The reactive transport problem was also solved by the Crank-Nicolson method [error of $O(\Delta z^2, \Delta t^2)$]. The Crank-Nicolson scheme

is a common way to solve (1) numerically. The set of nonlinear algebraic equations, obtained upon applying the method, was solved by iteration. Note that the spatial domain used in the Crank-Nicolson scheme was large enough so that the results were unaffected by the exit condition imposed.

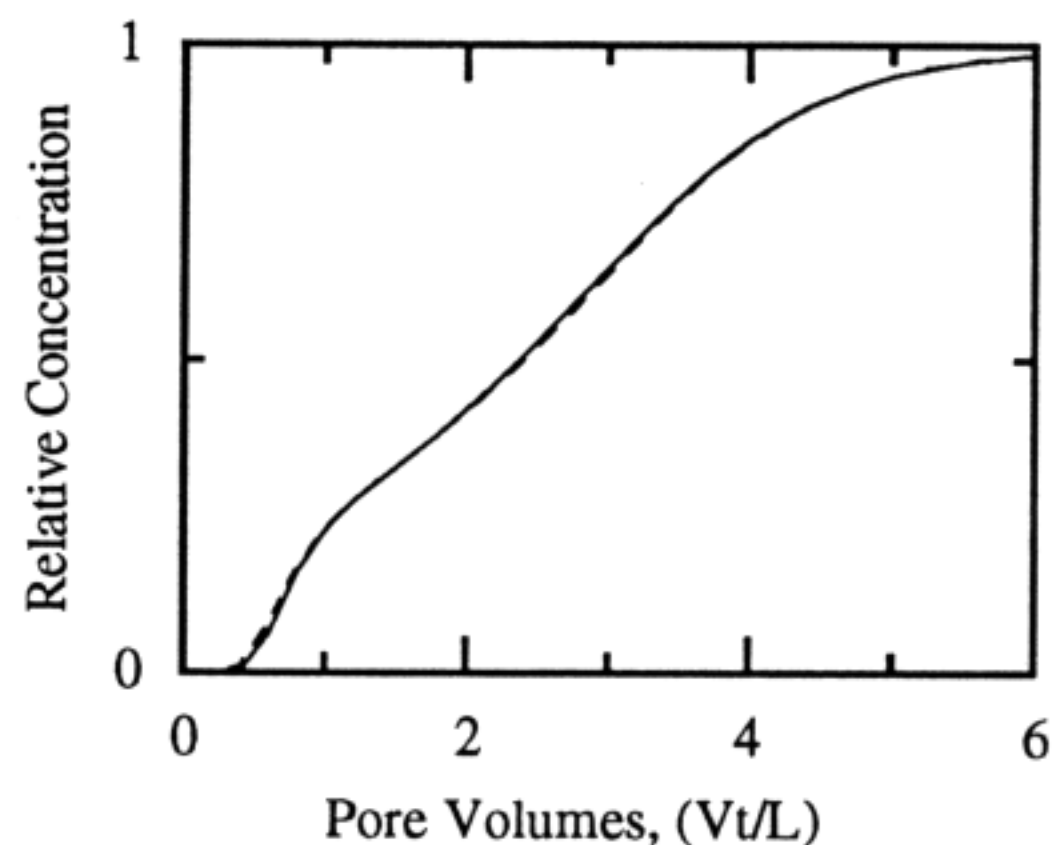


Figure 1. Comparison of the predictions of the improved mixing cell model (dashes) with those of the Crank-Nicolson scheme (line) for the S-curve eqn. (5c) ($P = 16$, $\alpha L/V = 1.6$, $k_1 = 3$, $k_2 = 3.375$, $k_3 = -2$, $k_4 = 1.5299$).

We considered a nonlinear S-curve isotherm to test the accuracy of the mixing cell model. This isotherm represents qualitatively the isotherms likely to be encountered in practice. The breakthrough curve predictions of the Crank-Nicolson scheme and those obtained from the improved mixing cell model are compared in Figure 1. It is clear that the mixing cell model predictions are in excellent agreement with the Crank-Nicolson scheme.

Time Dependent Boundary Conditions

We show, in Figures 2a and 2b, the mixing cell and the Crank-Nicolson solutions for the transport equation (1), with the S-curve isotherm (same as used in Figure 1) and entrance boundary conditions (3b) and (3c), and exit conditions (4b) and (4c) respectively at a dimensionless time $V^2 t/D_s = 40$. Note that, the boundary layer correction, eqn. (16a), was applied to the mixing cell solution in Figure 2a whereas eqn. (17a) was applied in the mixing cell solution in Figure (2b).

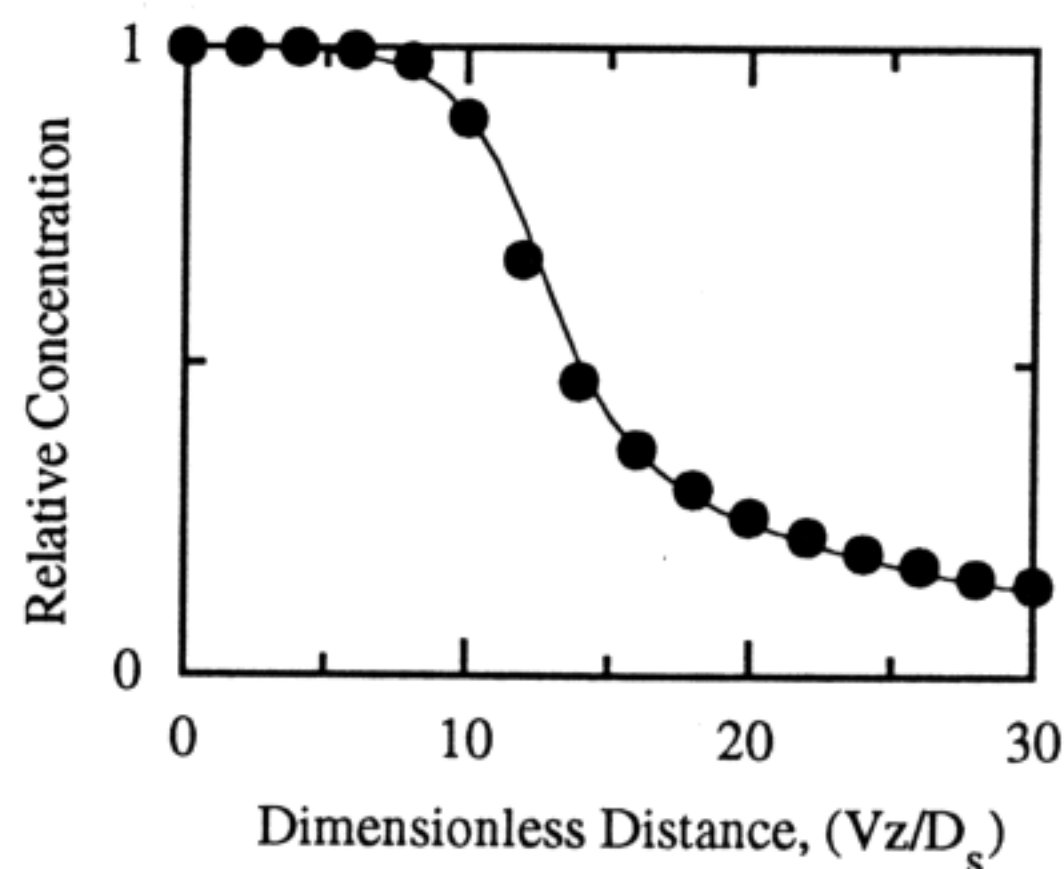


Figure 2a. Concentration profiles simulated using the mixing cell (solid circles) and Crank-Nicolson scheme (line) considering boundary conditions (3b) and (4a) ($P = 30$, $V^2 t/D_s = 40$).

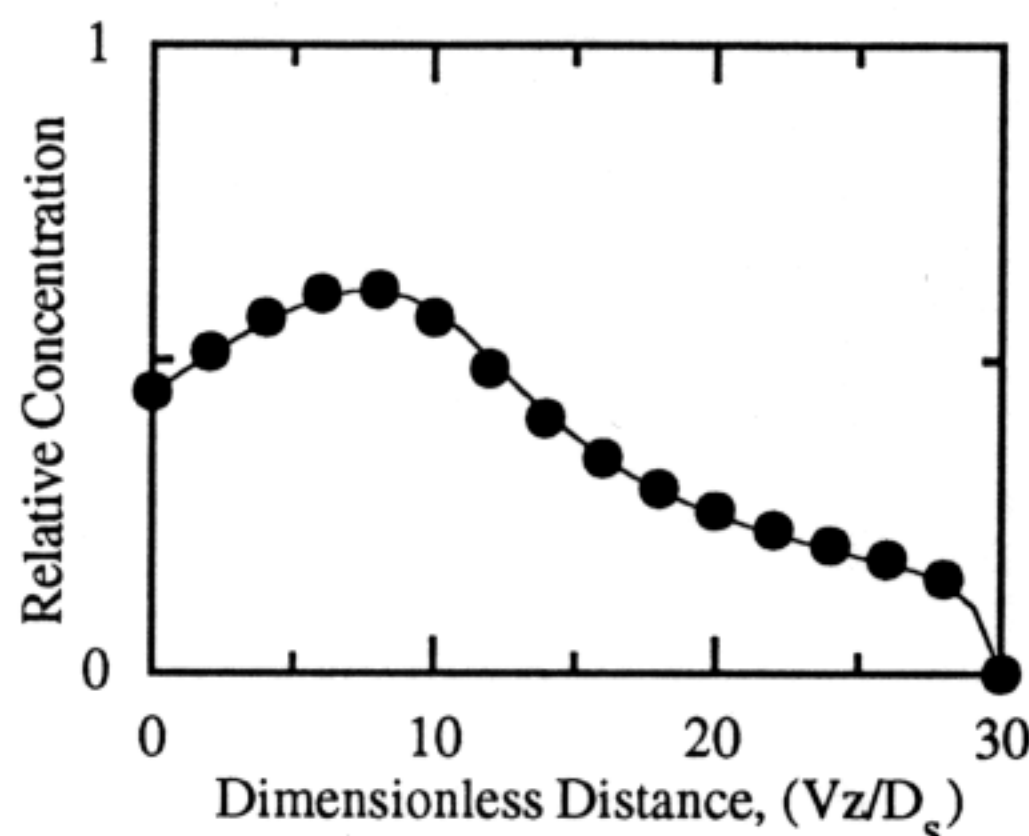


Figure 2b. Concentration profiles simulated using mixing cell (solid circles) and Crank-Nicolson scheme (line) considering boundary conditions (3c) and (4b) ($P = 30$, $Vh_f/D_s = 20$, $n_a = 0.4$, $V^2t/D_s = 40$).

Observe that the mixing cell predictions are close to the Crank-Nicolson solution. It is also found that the mixing cell solution was faster by at least an order of magnitude as compared with the time taken by the Crank-Nicolson scheme.

Two Layered Porous Media

Equation (1) is solved with the initial condition (2) and with a pulse type of surface boundary condition (3a) for the adsorption isotherm given by eqn. (5). For the linear isotherm it was found that the expression on the left hand side of the inequality of eqn. (18) had to be less than 0.0312 in order to get the accurate solutions using mixing cell models. This corresponds approximately to a layer Peclet number of 16. For the nonlinear isotherm followed by linear adsorption isotherm, the layer Peclet number of 16 also gave results close to that obtained from the exact solution using Crank-Nicolson scheme. Note that, at the interface, continuity of concentration as well as mass flux were assumed in the Crank-Nicolson solution where as only continuity of concentration was considered in the mixing cell solution.

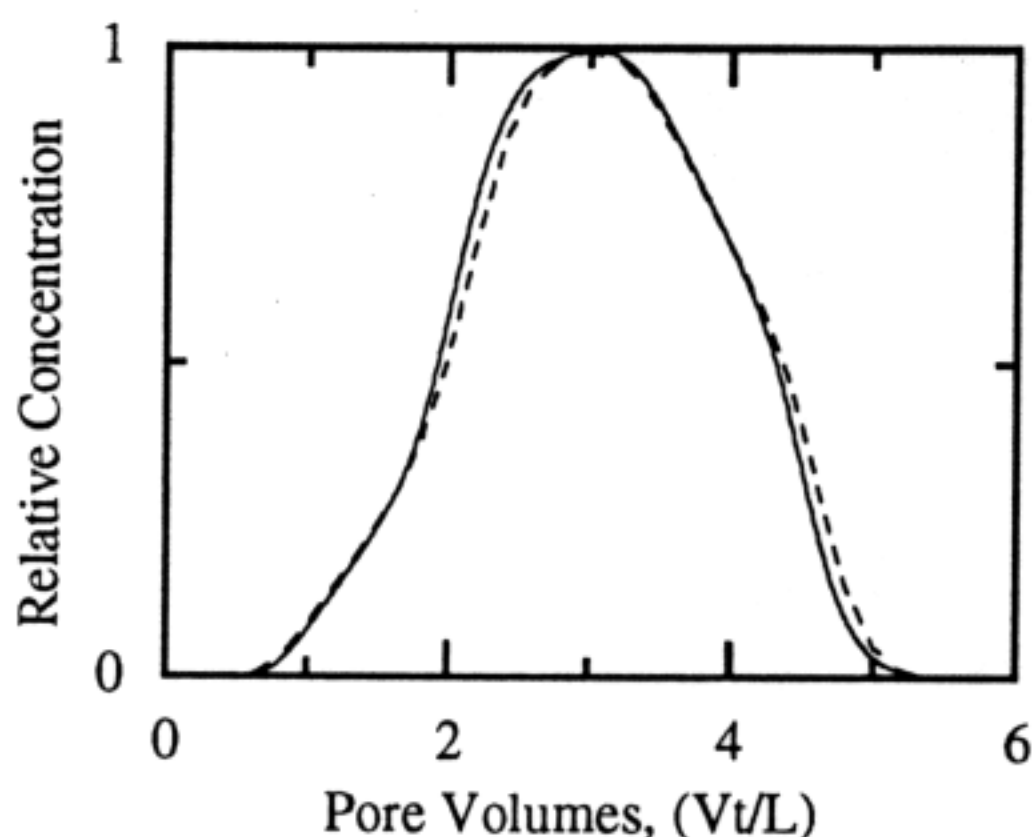


Figure 3. Breakthrough curves simulated using the mixing cell (dashes) and Crank-Nicolson scheme (line) considering boundary conditions (3a) and (4b) ($P = 50$, $R = 1.145$).

The results for a two layered porous medium are shown in Figure 3 for the nonlinear S-curve followed by linear

isotherm. The constants of the S-curve used were the same as those shown in the figure caption of Figure 1. A retardation factor, $R = 1.145$ was used for a linear isotherm and $V_1L_1/D_1 = V_2L_2/D_2 = 16$. The input considered was a pulse type with a duration of 2.4 pore volumes. The case of two layers is presented here but the scheme can be applied for any number of layers.

CONCLUSIONS

It has been demonstrated that the improved mixing cell model is second-order accurate even when reactions are included. Because the improved mixing cell is unconditionally stable, it allows a larger time step to be used than the standard mixing cell model, with a commensurate reduction in computation time. Not surprisingly, it was found that the Crank-Nicolson scheme requires at least an order of magnitude more time than the mixing cell computation.

The boundary conditions (3b) and (3c) when incorporated in the improved mixing cell model remove the explicit nature of the scheme at the entrance boundary. At the rest of the locations the scheme is still explicit.

Mixing cell models have been used to simulate finite column miscible displacement experimental results without boundary layer correction. We have demonstrated that mixing cell models can be used to simulate finite columns with different exit conditions by making use of boundary layer corrections. We have shown also that different surface conditions can be incorporated without difficulty and that the case of finite source boundary condition, which is often used in the landfill modelling studies, can be successfully simulated by the mixing cell model. The improved mixing cell can be successfully applied for the case of a multilayered porous medium. For mixing cell models to give accurate results, the layer Peclet number should each be > 16 .

At lower Peclet numbers, differences between the more accurate Crank-Nicolson scheme and the mixing cell results are generally less than the experimental errors (Villermux, 1981). Since mixing cell models are simple to code and fast to compute, they are, hence, very attractive tools for simulating reactive transport of solutes. However, since the spatial step size should be close to $2D_s/V$, the method fails when V is very small or D_s is very large.

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NOTATION

C_r	Courant number, $V\Delta t/\Delta z$.
C	normalised liquid phase concentration.
C^*	boundary layer corrected normalized liquid phase concentration.
C_0	normalised influent liquid concentration.
d_i	D_i/V_i^2
D_s	dispersion coefficient, L^2T^{-1} .
$f(C)$	function of C (adsorption isotherm).
h_f	equivalent leachate thickness in the landfill, L .
k_i	isotherm fitting parameter used in (39) and (40) ($i = 1, 2, 3, 4$).
l_i	L_i/V_i for layer $i = 1, 2$.
n_a	porosity of the landfill liner.
P_i	column Peclet number for layer $i = 1, 2$, $V_i L_i/D_i$.
R	retardation factor.
S	normalised solid phase concentration (equivalent liquid phase).
S^*	corrected normalised solid phase concentration (equivalent liquid phase).
t	time, T .
V	mean pore water velocity, LT^{-1} .
z	distance below soil surface, L .
α	rate constant, T^{-1} .
β	constant given by eqn. (16c), L^{-1} .
γ	constant given by eqn. (16d), L^{-1} .
β'	constant given by eqn. (17b), L^{-1} .
γ'	constant given by eqn. (17c), T^{-1} .
Δt	time step, T .
Δz	spatial step, L .

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