EXIT CONDITION FOR MISCIBLE DISPLACEMENT EXPERIMENTS

J.-Y. PARLANGE[1], J. L. STARR[2], M. TH. VAN GENUCHTEN[3], D. A. BARRY[4], AND
J. C. PARKER[5]

The one-dimensional solute transport is analyzed with the convection-dispersion model, including first and zeroth order irreversible reaction. A simple analytical expression is derived for the residence concentration which depends explicitly on the exit conditions at the end of the soil column or layer. The validity of the flux concentration solution ignoring the finite length of the column is also discussed by relating the exit conditions to the Péclet number.

Consider the standard one-dimensional solute transport equation in a column,

$$\partial c_r/\partial_t = D\partial^2 c_r/\partial x^2 - v\partial c_r/\partial x - f_r \quad (1)$$

where $c_r(x,t)$ is the (resident) solute concentration, D the dispersion coefficient, v the average pore-water velocity, x the distance (measured from the entrance of the column), t the time (corrected for the retardation factor if linear adsorption is taking place) and f_r is a sink/source term for irreversible reactions. Following Kreft and Zuber (1978), it is convenient to introduce the flux concentration (e.g. van Genuchten and Parker 1984) defined as

$$c_f = c_r - (D/v) \, \partial c_r/\partial x \quad (2)$$

Thus c_f obeys the equation,

$$\partial c_f/\partial_t = D\partial^2 c_f/\partial x^2 - v\partial c_f/\partial x \\ - f_r + (D/v)\partial f_r/\partial x \quad (3)$$

Normally f_r is taken as a function of c_r in Eq. (1); if we also require the corresponding term, $f_r - (D/v)\partial f_r/\partial x$, to be a function of c_f in Eq. (3),

[1] Contribution from the Agricultural and Biological Engineering Department, Cornell University, Ithaca, NY 14853.
[2] USDA-ARS, Beltsville, MD 20705.
[3] U.S. Salinity Laboratory, 4500 Glenwood Drive, Riverside, CA 92501.
[4] Centre for Water Research, University of Western Australia, Nedlands, WA, 6009, Australia.
[5] Agronomy Department, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

then it is clear that f_r must represent zeroth or first order kinetics. Interestingly, the corresponding term in Eq. (3) is also the same zeroth or first order term; thus those two cases are quite remarkable. The initial condition is taken as

$$c_f(t = 0, x) = 0 \quad (4)$$

with obviously the same condition for c_r. The boundary condition at $x = 0$ is taken as

$$c_f(t, x = 0) = c_o \quad (5)$$

with the corresponding condition for c_r obtained from Eq. (2). Note that if material is sent for a finite time only, as is often the case in practice, then c_f goes back to zero. As long as the governing equation remains linear, it is elementary to obtain the solution for that case once the solution for the case of Eq. (5) is known by superposition of solution, as done, for instance, by van Genuchten and Alves (1982).

The second boundary condition depends on the conditions at $x = L$, where the solution leaves the column. If the liquid below the column is collected with negligible dispersion taking place in the collector, $c_r = c_f$ in the collector. Since c_f must be continuous at $x = L$, c_r will be continuous at $x = L$ if, and only if,

$$(\partial c_r/\partial x)_{x=L} = 0 \quad (6)$$

Parker (1984) has discussed a mechanism giving rise to a discontinuity in c_r at $x = L$, which "should occur in fractured or aggregated porous media having continuous relatively large pores." The maximum discontinuity occurs when c_r and c_f within the column are unaffected by the outflow boundary" (Parker 1984), i.e., the concentration is that obtained for a semi-infinite column.

We may note that at $x = 0$, condition (5) also leads to a macroscopic discontinuity in c_r. However this discontinuity is physically quite different from the one that may occur at $x = L$. At $x = 0$ the discontinuity results from a boundary layer which becomes infinitely thin as diffusion in the reservoir at $x \leq 0$ is neglected and no other "mechanism" is required. However at $x =$

L, c_r would be continuous, and Eq. (6) would hold if it were not for the presence of cracks or other preferential paths in the column. Thus it seems reasonable to state that, in general, we do not know the appropriate boundary condition at $x = L$ and that the actual value of c_r at $x = L$ will lie in general somewhere below the value predicted by Eq. (6) and above the value obtained for a semi-infinite column.

It might be tempting to state that if there is a significant discontinuity at $x = L$, then Eq. (1) is not necessarily the governing equation, but two or more transport equations for different paths should be considered as considered, for instance, by Gaudet et al. (1977) when water can be divided into mobile and immobile components (as is basically the case in Parker's example, 1984). However, even when Eq. (1) is the appropriate model, there is still no guarantee that Eq. (6) will hold exactly, i.e., the variability in pore sizes could still lead to a value of c_r lower than the prediction of Eq. (6) even if the discontinuity is less than calculated from the semi-infinite solution.

This dilemma in the appropriate boundary condition at $x = L$ is closely linked to the value of the Péclet number

$$P_e = vL/D, \qquad (7)$$

where v is the average fluid velocity, and C is basically obtained by curve fitting. Scheidegger (1957) (see also the illuminating chapter 10 of Bear 1972) on hydrodynamic dispersion points out that D can have two limiting behaviors:

1) The first is when dispersion results primarily from molecular transverse diffusion (e.g., between mobile and immobile water).
2) The other is when mixing takes place at the junction between different paths (e.g., around a sand grain).

In case (1) D is essentially proportional to v^2/D_d (D_d being the molecular diffusion), and in case (2) D is essentially proportional to va, where a is the characteristic grain size. Also, in case (1) P_e will often be smaller than one (it is equal to 2.5×10^{-3} in Parker's experiment) and greater than one in case (2). Of course in many cases a mixture of (1) and (2) will take place. When dispersion follows case (1), upstream dispersion at $x = L$ is irrelevant, and the semi-

infinite column solution holds; whereas in case (2), Eq. (6) will hold. Thus, even though in general we do not know the boundary condition at $x = L$, the value of the Péclet number will provide some information on whether Eq. (6) or the semi-infinite column solution will be more accurate. This is the reason why Barry and Parker (1987) (following Kreft 1981) chose continuity of c_r at the interfaces in a layered medium as the preferred boundary condition rather than take the solution for a semi-infinite medium in each layer, although the latter has also been used (see Kreft 1981).

In conclusion, there is in general a real ambiguity in the boundary condition for c_r at $x = L$. Only in extreme cases can the condition be written with confidence, with the normal situation lying between those two extremes.

BREAKTHROUGH CURVE FOR $P_e \geq 4$

Case of no Irreversible Reaction

Let us consider the solution to Eq. (3) with $f_r = 0$ and a semi-infinite column; when Eqs. (4) and (5) hold, we have

$$2c_f/c_o = \text{erfc}\,\frac{x - tv}{\sqrt{4Dt}} + \exp\frac{vx}{D}\,\text{erfc}\,\frac{x + tv}{\sqrt{4Dt}} \qquad (8)$$

It has been observed (Parlange and Starr 1975) that, if $P_e \geq 4$, the breakthrough curve obtained from Eq. (8), which has been used routinely in the past (Nielsen and Biggar 1962) agrees closely with the solution of Eq. (1) when condition (6) is used; van Genuchten and Parker (1984) reached the same conclusion "provided the column Péclet number is not much less than 5." Still, c_f and c_r differ within the column unless P_e is very large, e.g., $P_e \geq 16$ (Parlange and Starr 1975).

We are now going to probe the reason for Eq. (8) predicting the breakthrough curve accurately when Eq. (6) holds. More generally, we shall argue that Eq. (8) holds whatever the boundary condition at $x = L$ is as long as $P_e \geq 4$. In so doing, we shall obtain a convenient expression for c_r within the column. Finally in the next section we shall generalize the results for zeroth and first order kinetics.

Using Eq. (8) for c_f, Eq. (2) yields c_r or, in

general,

$$\frac{c_r}{c_o} = \frac{c_f}{c_o} + \lambda \exp \frac{vx}{D} \left\{ \text{erfc} \frac{L + tv}{\sqrt{4Dt}} - \frac{v}{D} \sqrt{Dt} \right.$$

$$\left. \cdot \left[\frac{1}{\sqrt{\pi}} \exp - \frac{(L+tv)^2}{4Dt} - \frac{L+tv}{\sqrt{4Dt}} \text{erfc} \frac{L+tv}{\sqrt{4Dt}} \right] \right\}$$

$$+ \exp \frac{vx}{D} \left\{ -\text{erfc} \frac{x+tv}{\sqrt{4Dt}} + \frac{v}{D} \sqrt{Dt} \right.$$

$$\left. \cdot \left[\frac{1}{\sqrt{\pi}} \exp - \frac{(x+tv)^2}{4Dt} - \frac{x+tv}{\sqrt{4Dt}} \text{erfc} \frac{x+tv}{\sqrt{4Dt}} \right] \right\} \quad (9)$$

where λ is a constant of integration, such that, with $c_r = c_r(t, x; \lambda)$

$$\frac{\partial c_r(t, L; \lambda)}{\partial x} = (1 - \lambda) \frac{\partial c_r(t, L; 0)}{\partial x} \quad (10)$$

where $\partial c_r/\partial x$ at $x = L$ and $\lambda = 0$ is the minimum value possible for the gradient of c_r when back diffusion at $x = L$ is negligible. Hence, c_r in Eq. (9) appears as a linear interpolation between the two extreme values of c_r when $\lambda = 0$ and 1. Note that λ can be a function of time if desired. The parameter λ varies between 0 and 1: for $\lambda = 1$ we have the limiting case when Eq. (6) holds, and for $\lambda = 0$ the profile within the column is unaffected by upstream diffusion at $x = L$. Fig. 1 illustrates the results for Péclet numbers equal to 4, 8, and 16 and different dimensionless times $T = tv^2/D$. The left side gives the whole profile for c_f and c_r for $\lambda = 0$ and 1 (the extreme cases). The right side gives the details for other values of λ near $x = L$. Away from $x = L$ all c_r profiles merge into one curve, exhibiting the typical boundary layer behavior discussed in Parlange and Starr (1975).

The left side is hardly distinguishable from Fig. 2 in Parlange and Starr (1975). The only difference is that here c_f and c_r for $\lambda = 1$ are strictly equal, whereas they are very slightly different in Fig. 2, because in that case we calculated c_r ($\lambda = 1$) using Eq. (1) (with $f_r = 0$) while here we use Eq. (2) with c_f obtained for a semi-infinite column. Thus when Eq. (6) holds exactly (case considered by Parlange and Starr 1975) Eq. (8) is only approximated true, and if the breakthrough curve is fitted with Eq. (8), then an apparent diffusivity, D_{ap}, is deduced which differs slightly from the diffusivity D of Eq. (1).

In general, if Eq. (10) is used as boundary

condition at $x = L$, and Eq. (1) is solved using boundary layer techniques for $P_e \geq 4$ as in Parlange and Starr (1975), c_r thus obtained will differ slightly from c_r in Eq. (9), and at $x = L$ it will differ slightly from c_f ($x = L$) given in Eq. (8). Then curve fitting to this c_r with c_f at $x = L$ will again yield a D_{ap} different from D in Eq. (1), with, in general,

$$D \simeq D_{ap}/[1 - \lambda D_{ap}/Lv] \quad (11)$$

which reduces to Eq. (15) of Parlange and Starr (1975), correcting an obvious misprint in the latter. (See also Eq. (22) of Barry and Parker (1984), which agrees with the equation above for $\lambda = 1$ and P_e sufficiently large. Obviously $D = D_{ap}$ for $\lambda = 0$ since Eqs. (8) and (9) are then the exact solution for a semi-infinite column.

Curve fitting breakthrough curves with Eq. (8) to estimate D yields a D_{ap}, which will be reliable if $P_r = vL/D_{ap}$ is greater than 4. Although the corresponding c_r within the column is not exactly known, this has little influence on the breakthrough curve. However, from the discussion above on the hydrodynamic dispersion, we expect that λ is close, if not exactly equal to, 1, especially if P_r is largely independent of v.

On the other hand if curve fitting Eq. (8) yields $P_r = vL/D_{ap}$ which is less than 1, then the result for D_{ap} is reliable only if λ is close to zero, i.e., when there is no back diffusion at $x = L$. Since there is no way to know a priori whether this is true, use of Eq. (8) is unreliable for low P_r. However, if in addition P_r is inversely proportional to v, suggesting that the flow through cracks is dominant, then the result might be meaningful.

To understand the limitations of Eqs. (8) and (9) as a solution to the problem when P_e is not too large, e.g., less than 4, it must be emphasized that even though Eq. (9) is consistent with Eq. (2) it does not satisfy Eq. (1) (with $f_r = 0$) unless $\lambda = 0$. The following analysis reconfirms all above results from a different point of view. In addition it is especially well adapted to the study of irreversible effects, which we now consider.

Case of Irreversible Reactions

As shown earlier, if f_r in Eq. (1) is a function of c_r only, the corresponding form in Eq. (3), $f_r - D/v \, \partial f_r/\partial x$, will be a function of c_f only, if and only if, $f_r = kc_0$ or $f_r = kc_r$ (k being constant),
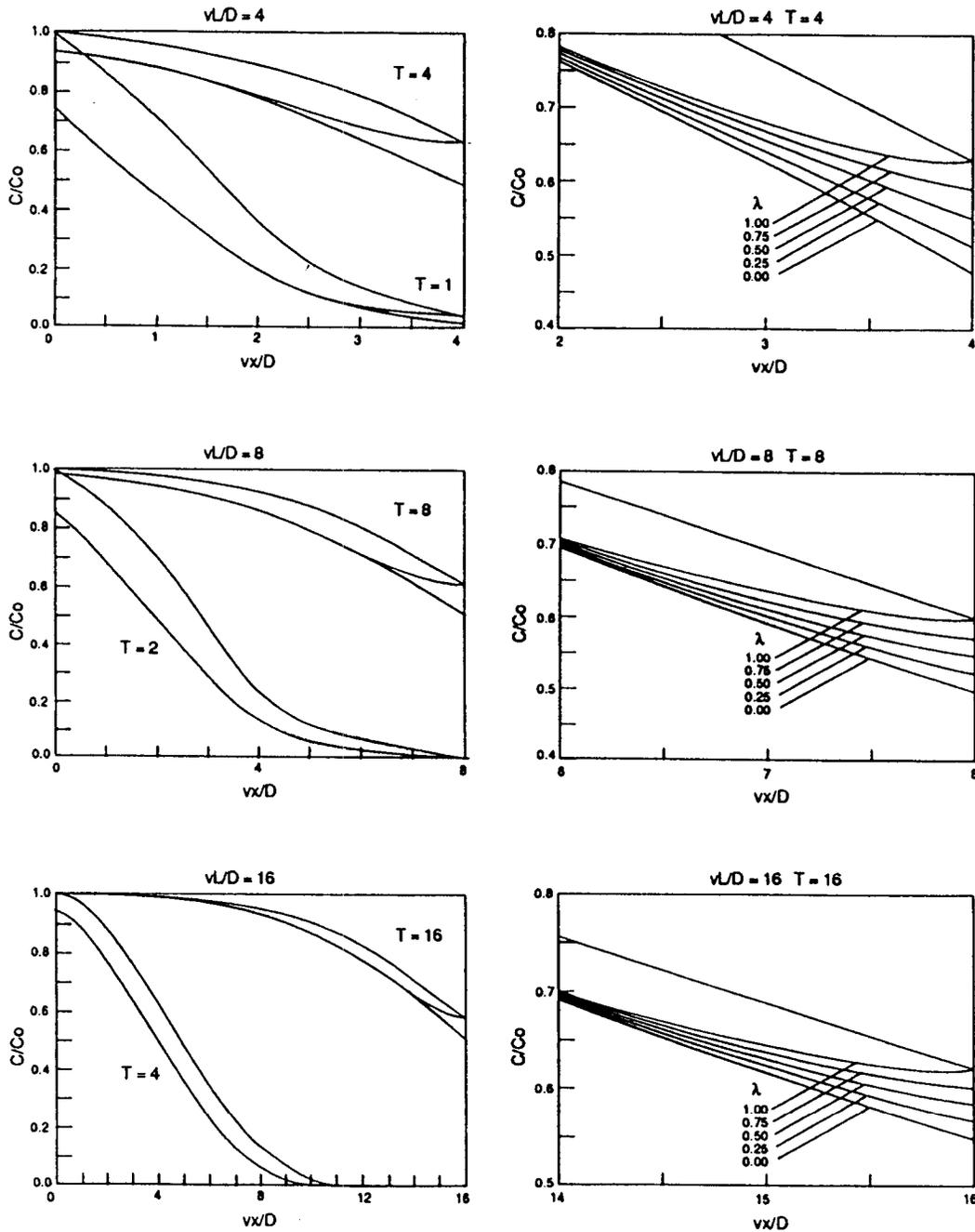
FIG. 1. Profiles in a column for Péclet numbers,

$P_e = vL/D$, equal to 4, 8, and 16. The left side gives the results for dimensionless times $T = v^2t/D$ equal to P_e and $P_e/4$. At each time the top curve is c_f from Eq. (8), the bottom curve is c_r for $\lambda = 0$, and the intermediary one corresponds to $\lambda = 1$. (For $P_e = 8$ and 16 and $T = P_e/4$, c_r is independent of λ.) The right side gives the details of the profiles near the end of the column for $T = P_e$, and c_r for $\lambda = 0.25, 0.50, 0.75$ in addition to $\lambda = 0$ and 1. The top curve is still c_f.

or a linear combination of the two. Then, the irreversible reaction in Eq. (3) follows the same zeroth and first order kinetics. To simplify the analysis we shall call c_f, as before, the flux concentration for the semi-infinite column with c_r obeying Eqs. (2) and (10). Since c_r depends on the choice of λ, we shall call c_{r1} and c_{r0} the solutions when $\lambda = 1$ and 0, respectively. Again, by letting f_r be zero, the following results apply to the case of no irreversible reaction as well. From Eq. (2) we have,

$$c_{r0} = c_f + \exp\left(\frac{vx}{D}\right) \int_x^\infty \frac{\partial c_f}{\partial \tilde{x}} \exp\left(-\frac{v\tilde{x}}{D}\right) d\tilde{x} \tag{12}$$

$$c_{r1} = c_f + \exp\frac{vx}{D} \int_x^L \frac{\partial c_f}{\partial \tilde{x}} \exp -\frac{v\tilde{x}}{D} d\tilde{x} \tag{13}$$

Thus

$$c_{r1} - c_{r0} = -\frac{D}{v} \exp\frac{v(x - L)}{D} \left(\frac{\partial c_{r0}}{\partial x}\right)_{x=L} \tag{14}$$

and in general to satisfy condition (10)

$$c_r = (1 - \lambda)c_{r0} + \lambda c_{r1} \tag{15}$$

which can also be written,

$$c_r = c_{r0} + \lambda \exp\frac{v(x - L)}{D}$$
$$\cdot [c_f(x = L) - c_{r0}(x = L)] \tag{16}$$

which is especially convenient since c_f and c_{r0} are known exactly for zeroth and first order kinetics (see Appendix). Note that for $P_e = vL/D \geq 4$, c_r approaches a single curve independently of λ when x is sufficiently less than L, as observed in Fig. 1. Again this boundary layer behavior was the basis for the approach of Parlange and Starr (1975, 1978) Parlange et al. (1982), although Eq. (16) is obtained more directly.

To probe more deeply the reasons for the validity of Eq. (16), let us use c_r to calculate the left hand side of Eq. (1). We find at once that for both zeroth and first order kinetics,

$$\frac{\partial c_r}{\partial t} + v\frac{\partial c_r}{\partial x} - D\frac{\partial^2 c_r}{\partial x^2}$$
$$= -f_r(c_r) + \lambda \exp\frac{v(x - L)}{D} D\left(\frac{\partial^2 c_f}{\partial x^2}\right)_{x=L} \tag{17}$$

First it is clear from Eq. (17) that the appropriateness of c_r as a solution remains the same

whether irreversible reactions (zeroth and first order) take place or not. Eq. (17) in general differs from Eq. (1) because of the term $\lambda\exp[v(x - L)/D] D(\partial^2 c_f/\partial z^2)$ $x = L$. Thus if $\lambda = 0$, c_{r0} is the exact solution as we already knew, while the maximum discrepancy occurs for $\lambda = 1$. That is for any $\lambda \neq 0$, and especially $\lambda = 1$, c_f obtained for a semi-infinite column cannot be the exact solution for a finite column since it leads to a c_r which does not satisfy Eq. (1). However, as illustrated in Fig. 1b, for x near L, $\partial^2 c_r/\partial x^2$ is much greater than $\lambda\partial^2 c_f/\partial x^2$, and when the two are of the same order for x sufficiently less than L, then $\exp v(x - L)/D$ in Eq. (17) takes over and ensures that the last term in that equation is always negligible as long as $P_e = vL/D \geq 4$. We can estimate $-D\partial^2 c_r/\partial x^2$ in Eq. (17), using Eq. (16), i.e.,

$$-D\frac{\partial^2 c_r}{\partial x^2} = -D\frac{\partial^2 c_{r0}}{\partial x^2}$$
$$+ \lambda v \exp v\frac{(x - L)}{D} \left(\frac{\partial c_{r0}}{\partial x}\right)_{x=L} \tag{18}$$

Again $\partial^2 c_{r0}/\partial x^2$ is the estimate of $\partial^2 c_r/\partial x^2$ when x is sufficiently less than L, whereas, approximately from Eq. (2),

$$\lambda \exp\frac{v(x - L)}{D} D\left(\frac{\partial^2 c_f}{\partial x^2}\right)_{x=L}.$$
$$\sim \lambda v \exp\frac{v(x - L)}{D} \left[\frac{\partial c_{r0}}{\partial x} - \frac{\partial c_f}{\partial x}\right]_{x=L}. \tag{19}$$

However, since

$$\left|\frac{\partial c_{r0}}{\partial x} - \frac{\partial c_f}{\partial x}\right|_{x=L} \lll \left|\frac{\partial c_{r0}}{\partial x}\right|_{x=L} \tag{20}$$

the last term in Eq. (17) is always negligible compared to the $\partial^2 c_r/\partial x^2$ term, as long as P_e is not too small. On the other hand if P_e is small, then Eq. (17) reduces to Eq. (1) only if λ is very small, i.e., there is a significant discontinuity in c_r at $x = L$, and the flow in the column is determined by preferential paths.

Finally, to quantify the accuracy of Eq. (16), Table 1 presents some numerical results for c_{r1}. The solution is exact for $\lambda = 0$ and is most inaccurate for $\lambda = 1$, especially for $P_e = 4$ which is the lowest Péclet number we consider. Thus, in Table 1 we consider only $P_e = 4$ and $\lambda = 1$. The exact solutions to compare with our approximations are obtained using more complex

TABLE 1

Values of c_{r1} for $P_e = 4$ and $v^2t/D = 4$ as a function of vx/D. Second column corresponds to Eq. (9), fourth to Eq. (16) for zeroth order kinetics with $kL/v = 0.2$, sixth to Eq. (16) for first order kinetics with $kL/v = 1$. The third, fifth and seventh columns give the corresponding exact solutions from van Genuchten and Alves (1982)

Position vx/D	No kinetics		Zeroth order		First order	
	c_{r1} (Eq. 9)	c_{r1} (exact)	c_{r1} (Eq. 16)	c_{r1} (exact)	c_{r1} (Eq. 16)	c_{r1} (exact)
0.00	0.9459	0.9439	0.9035	0.9012	0.8173	0.8158
0.20	0.9345	0.9321	0.8837	0.8809	0.7813	0.7795
0.40	0.9220	0.9190	0.8620	0.8596	0.7466	0.7444
0.60	0.9082	0.9047	0.8412	0.8372	0.7129	0.7103
0.80	0.8933	0.8892	0.8185	0.8137	0.6804	0.6772
1.00	0.8772	0.8724	0.7949	0.7893	0.6489	0.6452
1.20	0.8600	0.8544	0.7705	0.7640	0.6185	0.6141
1.40	0.8418	0.8353	0.7454	0.7378	0.5893	0.5840
1.60	0.8227	0.8153	0.7197	0.7109	0.5611	0.5550
1.80	0.8029	0.7944	0.6935	0.6835	0.5341	0.5270
2.00	0.7825	0.7729	0.6672	0.6558	0.5083	0.5000
2.20	0.7618	0.7510	0.6409	0.6280	0.4838	0.4743
2.40	0.7411	0.7291	0.6149	0.6005	0.4608	0.4499
2.60	0.7206	0.7073	0.5896	0.5736	0.4393	0.4269
2.80	0.7007	0.6863	0.5654	0.5478	0.4196	0.4056
3.00	0.6820	0.6664	0.5429	0.5237	0.4018	0.3862
3.20	0.6649	0.6483	0.5225	0.5018	0.3863	0.3691
3.40	0.6501	0.6327	0.5050	0.4831	0.3734	0.3547
3.60	0.6384	0.6203	0.4912	0.4683	0.3635	0.3435
3.80	0.6306	0.6121	0.4821	0.4585	0.3572	0.3361
4.00	0.6277	0.6091	0.4788	0.4549	0.3549	0.3335

series solutions, which are tabulated by van Genuchten and Alves (1982). Because of the exponential term in Eq. (16), the error is the greatest at $x = L$; thus we give the results for $T = 4$ which is the time when c_{r0} and c_f are very different at $x = L$, so that again we look at the most critical case when the error is greatest.

In the case of $f_r = 0$, i.e., when Eq. (16) reduces to Eq. (9), the approximation for c_{r1} is remarkably close to the exact result, justifying its use for P_e as small as 4. The maximum absolute error at $x = L$ is only about 0.02.

For zeroth order kinetics we taken $kL/v = 0.2$ and $kL/v = 1$ for first order kinetics, which both reduce the concentration at $x = L$ significantly. Not surprisingly this illustration shows a comparable error to the previous case when $f_r = 0$, i.e., the maximum absolute error remains about 0.02 and is not affected by the presence of irreversible effects.

The use of c_r and c_f gave a convenient and far better insight into the structure of solutions of the transport equation. We conclude that as long as the Péclet number is not too small, at least 4

or more, there is no ambiguity about the breakthrough curve as it is, essentially, independent of the boundary condition at the end of the column. Thus calculation of c_f for a semi infinite column yields the appropriate breakthrough curve. There is, however, some ambiguity about c_r within the column, especially near the exit (up to a distance l such that $vL/D \simeq 1$). For $x \leq L - l$ the boundary condition at the exit does not affect c_r. For $x \geq L - l$, the presence of preferential paths might indeed cause a discontinuity of c_r at the exit. The discontinuity, if it exists, has a maximum value resulting from calculating c_r for a semi-infinite column.

If the Péclet number is less than 4 it is necessary to know the boundary condition at $x = L$ to predict the breakthrough curve, and c_f or c_r, within the column. However if curve fitting the solution for a semi-infinite column produces a low Péclet number, say much less than 1, then the solution obtained for a semi-infinite column is again probably reliable because the back diffusion becomes negligible.

Thus we have shown that the flux of material, and the breakthrough curve, are well defined in

most cases, but the residence concentration can be less well defined near the exit of the column. We have provided simple and accurate approximations yielding the flux and the residence concentration which can be used in most practical cases.

APPENDIX

Values of c_f and c_{ro} for zeroth and first order kinetics (e.g., see Parlange and Starr, 1978; and Parlange et al. 1982)

First order

$$c_{ro}/c_0 = [1 + (1 + 4kD/v^2)^{1/2}]^{-1}$$

$$\cdot [\exp\{1/2\,xvD^{-1}[1 - (1 + 4kD/v^2)^{1/2}]\}$$

$$\cdot erfc\{[x - tv(1 + 4kD/v^2)^{1/2}]/(4Dt)^{1/2}\}]$$

$$+ [1 - (1 + 4kD/v^2)^{1/2}]^{-1}[\exp\{1/2xvD^{-1}$$

$$\cdot [1 + (1 + 4kD/v^2)^{1/2}]\}erfc\{[x +$$

$$\cdot tv(1 + 4kD/v^2)^{1/2}]/(4Dt)^{1/2}\}]$$

$$+ 1/2\,(v^2/kD)\exp[(vx/D)$$

$$- kt]erfc[(x + vt)/(4Dt)^{1/2}] \quad\quad\quad (A1)$$

$$c_f/c_0 = 1/2\,\exp\{1/2xvD^{-1}[1 - (1 + 4kD/v^2)^{1/2}]\}$$

$$\cdot erfc[x - tv(1 + 4kD/v^2)^{1/2}]/(4Dt)^{1/2}\}$$

$$+ 1/2\exp\{1/2\,xvD^{-1}[1 + (1$$

$$+ 4kD/v^2)^{1/2}]\} \quad\quad\quad (A2)$$

$$\cdot erfc\{[x + tv(1 + 4kD/v^2)^{1/2}]/(4Dt)^{1/2}\}$$

Zeroth order

$$c_{ro}/c_0 = P - [1 + v(x + tv)/D]\exp(vx/D)Q$$

$$+ v(t/D\pi)^{1/2}\exp[-(x - tv)^2/(4Dt)]$$

$$- kt + k(t - x/v)P - (kD/v^2)P - k$$

$$\cdot \exp(vx/D)Q[-D/v^2 + t + (x + vt)^2/2D]$$

$$+ k(Dt/\pi)^{1/2}[1/v + (x + vt)/2D]$$

$$\cdot \exp[-(x - vt)^2/(4Dt)]. \quad\quad\quad (A3)$$

$$c_f/c_0 = P + exp(vx/D)Q - kt$$

$$+ k(t - x/v)P + k(t + x/v)\exp(vx/D)Q, \quad\quad (A4)$$

with

$$P = \frac{1}{2}\,erfc[(x - tv)/\sqrt{4Dt}] \quad\quad\quad (A5)$$

and

$$Q = \frac{1}{2}\,erfc[(x + tv)/\sqrt{4Dt}] \quad\quad\quad (A6)$$

It is elementary to check that the above equations satisfy Eq. (2).

REFERENCES

Barry, D. A., and J. C. Parker. 1987. Approximation for solute transport through porous media with flow transverse to layering. Transp. Porous Media. 2:65–82.

Bear, J. 1972. Dynamics of fluids in porous media. Elsevier, New York.

Gaudet, J. P., H. Jégat, G. Vachaud, and P. J. Wierenga. 1977. Solute transfer with exchange between mobile and stagnant water through unsaturated sand. Soil Sci. Soc. Am. J. 41:665–671.

Kreft, A. 1981. On the boundary conditions of flow through porous media and conversion of chemical flow reactors. Bull. Acad. Pol. Sci. 29:25–53.

Kreft, A., and A. Zuber. 1978. On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions. Chem. Eng. Sci. 33:1471–1480.

Nielsen, D. R., and J. W. Biggar. 1962. Miscible displacement: III. Theoretical considerations. Soil Sci. Soc. Am. Proc. 26:216–221.

Parker, J. C. 1984. Analysis of solute transport in column tracer studies. Soil Sci. Soc. Am. J. 48:719–724.

Parlange, J.-Y. and J. L. Starr. 1975. Linear dispersion in finite columns. Soil Sci. Soc. Am. Proc. 39:817–819.

Parlange, J.-Y., and J. L. Starr. 1978. Dispersion in soil columns: Effect of boundary conditions and irreversible reaction. Soil Sci. Soc. Am. J. 42:15–18.

Parlange, J.-Y., J. L. Starr, D. A. Barry, and R. D. Braddock. 1982. A theoretical study of the inclusion of dispersion in boundary conditions and transport equations for zero-order kinetics. Soil Sci. Soc. Am. J. 46:701–704.

Scheidegger, A. E. 1957. On the theory of flow of miscible phases in porous media. Proc. IUGG General assembly, Toronto. 2:236–242.

van Genuchten, M. Th., and W. J. Alves. 1982. Analytical solutions of the one-dimensional convective-dispersive solute transport equation. USDA Tech. Bull. No. 1661 (151 p.).

van Genuchten, M. Th., and J. C. Parker. 1984. Boundary conditions for displacement experiments through short laboratory soil columns. Soil Sci. Soc. Am. J. 48:703–708.