EXIT CONDITION FOR MISCELLAE DISPLACEMENT EXPERIMENTS

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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 Peclet number.

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

$$\frac{dc}{dx} = D\frac{dc}{dt} + \omega c - \frac{dc}{dx} - f$$  \hspace{1cm} (1)

where \(c(x,t)\) is the (resident) solute concentration, \(D\) the dispersion coefficient, \(c\) 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 \(f\) is the sink/source term for irreversible reactions. Following Kraft and Zuber (1978), it is convenient to introduce the flux concentration (e.g., van Genuchten and Parker 1984) defined as

$$c = c - \frac{(D/v) dc}{dx}$$  \hspace{1cm} (2)

Thus \(c\) obeys the equation,

$$\frac{dc}{dt} = D\frac{dc}{dx} + \omega c - \frac{dc}{dx} - f + \frac{(D/v) dc}{dx}$$  \hspace{1cm} (3)

Normally, \(f\) is taken as a function of \(c\) in Eq. (1); if we also require the corresponding term, \(f = -\frac{(D/v) dc}{dx}\), to be a function of \(c\) in Eq. (3).

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

$$c(x = 0, t) = 0$$  \hspace{1cm} (4)

with obviously the same condition for \(c\). The boundary condition at \(x = 0\) is taken as

$$c(x = 0, t) = c_0$$  \hspace{1cm} (5)

with the corresponding condition for \(c\), obtained from Eq. (2). Note that if material is sent for a finite time only, as is often the case in practice, then \(c\) 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, \(c = 0\); in the collector. Since \(c\) must be continuous at \(x = L\), \(c\) will be continuous at \(x = L\) if, and only if,

$$\frac{dc}{dx}|_{x=L} = 0$$  \hspace{1cm} (6)

Parker (1984) has discussed a mechanism giving rise to a discontinuity in \(c\) at \(x = L\), which "should occur in fractured or agarred media having continuous relatively large pores."

The maximum discontinuity occurs when \(c\) and \(c_{L}\) 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 the condition (5) also leads to a macroscopic discontinuity in \(c\). 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 \(x = 0\) is neglected and no other "mechanism" is required. However at \(x =
Let us consider the solution to Eq. (3) with $L = 0$ and a semi-infinite column, when Eqs. (4) and (5) hold, we have

$$P_e = 2.4$$

where $P_e$ is the average fluid velocity, and $C$ is the concentration at the inlet.

In case (1) $C_e$ is exponentially proportional to $P_e^2$, $D_C$ being the molecular diffusion, and in case (2) $D_C$ is exponentially proportional to $P_e$, where $D_C$ is the characteristic grain size. Also, in case (1) $P_e$ will often be smaller than one (it is equal to $2.5 \times 10^{-3}$ in Parker's experiment) and greater than one (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. (4) will hold. Thus, even though in general we do not know the boundary condition at $L = 0$, the value of the Péclet number will provide some information about whether Eq. (4) or the semi-infinite column solution will be more accurate. This is the reason why Barry and Parker (1987) followed Kretz (1981) chose continuity of $c$, at the interfaces in a layered medium as the preferred condition rather than take the solution for a semi-infinite medium in each layer, although the latter has also been used (see Kretz 1981).

In conclusion, there is in general a real ambiguity in the boundary condition for $c$ at $x = L$. Only in extreme cases can the condition be written with confidence, with the normal situation lying between those two extremes.
general,  
\[ c = c_0 + \lambda \exp \left( \frac{\beta}{D} \right) \left[ \frac{L}{c} + \frac{iv}{\sqrt{D}} + \frac{iv}{\sqrt{D}} \right] + \exp \left( \frac{\beta}{D} \right) \left[ \frac{L}{c} + \frac{iv}{\sqrt{D}} + \frac{iv}{\sqrt{D}} \right] \]

where \( \lambda \) is a constant of integration, such that, with \( c = c(0, x, \beta) \)  

\[ \lambda = \frac{D_t(0, x, \beta)}{D} \]  

(10)  

which reduces to Eq. (15) of Parlane 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 \( P \) sufficiently large. Obviously \( D = D_w \) for \( \lambda = 0 \) since Eqs. (8) and (9) then are the exact solution for a semi-infinite column.  

Curve fitting breakthrough curves with Eq. (8) to estimate \( D \) yields a \( D_w \), which will be reliable if \( P = \beta D \lambda_Dw \) is greater than 4. Although the corresponding \( c \) 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 \( \lambda = 1 \) if not exactly equal to 1, especially if \( P \) is largely independent of \( x \).  

On the other hand, if curve fitting Eq. (8) yields \( P = \beta D \lambda_Dw \) which is less than 1, then the result for \( D_w \) is reliable only if \( \lambda \) 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 \( P \). However, if in addition \( P \) is inversely proportional to \( \lambda \) 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 \( P \) is not too large, smaller than 4, it must be emphasized that even though Eq. (8) is consistent with Eq. (2) it does not strictly Eq. (1) (with \( f = 0 \)) 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 \( f \) in Eq. (1) is a function of \( c \), only, the corresponding form in Eq. (3),  

\[ f = \frac{D}{Dc} \frac{dc}{dt} \]  

will be a function of \( c \) only, if and only if \( f = k_0 \) or \( f = k_0 \), (4 being constant),
FIG. 1: Profiles in a column for Péclet numbers, $P_e = \frac{v_r D}{k}$, equal to 4, 8, and 16. The left side gives the results for dimensionless times $T = \frac{v_r t}{D}$ equal to $P_e$ and $P_e/4$. At each time the top curve is $c_0$, from Eq. (6), the bottom curve is $c_i$ for $i = 0$, and the intermediary one corresponds to $i = 1$. (For $P_e = 8$ and 16, $T = P_e/4$, $c_i$ is independent of $i$.) The right side gives the details of the profiles near the end of the column for $T = P_e$ and $c_i$ for $i = 0, 0.25, 0.5, 0.75$ in addition to $i = 0$ and 1. The top curve is still $c_0$. 
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 \( c_i \) as before, the flux concentration for the semi-infinite column with \( c_i \) obeying Eqs. (4) and (5). Since \( c_i \) depends on the choice of \( \lambda \), we shall call \( c_{i0} \) and \( c_{i1} \) the solutions when \( \lambda = 1 \) and 0, respectively. Again, by letting \( f \) be zero, the following results apply to the case of no irreversible reaction as well.

From Eq. (2) we have,

\[
\begin{align*}
\frac{dc_i}{dt} &= \frac{c_i}{D} \int \frac{\partial c_i}{\partial x} \exp \left( -\frac{x_s}{D} \right) \, dt \\
\frac{dc_i}{dt} &= \frac{c_i}{D} \int \frac{\partial c_i}{\partial x} \exp \left( -\frac{x_s}{D} \right) \, dt
\end{align*}
\]

(13)

Thus,

\[
\lambda c_t - c_{i1} = -\frac{D}{v} \exp \left( \frac{x - L}{D} \right) \left( \frac{\partial c_i}{\partial x} \right)_{x=L}
\]

(14)

and in general to satisfy condition (10)

\[
c_i = (1 - \lambda)c_{i1} + \lambda c_{i1}
\]

(15)

which can also be written,

\[
c_i = c_{i0} + \lambda \exp \left( \frac{x - L}{D} \right)
\]

(16)

which is especially convenient since \( c_i \) and \( c_{i1} \) are known exactly for zeroth and first order kinetics (see Appendix). Note that for \( P_r = \frac{vL}{D} \neq 4 \), \( c_i \) approaches a single curve independently of \( \lambda \) when \( x \) is sufficiently less than \( L \), as observed in Fig. 1. Again this boundary layer behavior was the basis for the approach of Parlane and Starr (1975, 1978) Parlane 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 \( c_i \) to calculate the left hand side of Eq. (1). We find at once that for both zeroth and first order kinetics,

\[
\frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial x} - D \frac{\partial^2 c_i}{\partial x^2} = -f(x, \lambda) + \lambda \exp \left( \frac{x - L}{D} \right) \left( \frac{\partial c_i}{\partial x} \right)_{x=L}
\]

(17)

The solution is exact from Eq. (17) that the appropriateness of \( c_i \) 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 \( \exp (x - L)/D \) \( \partial c_i/\partial x \) \( x = L \). Thus, if \( \lambda = 0 \), \( c_i \) 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 \( \lambda = 1 \), \( c_i \) obtained for a semi-infinite column cannot be the exact solution for a finite column since it leads to a \( c_i \) which does not satisfy Eq. (1). However, as illustrated in Fig. 1b, for \( x \leq L \), \( \exp (x - L)/D \) is much greater than \( \partial c_i/\partial x \) and when the two are of the same order for \( x \) sufficiently less than \( L \), then \( \exp (x - L)/D \) in Eq. (17) takes over and ensures that the largest term in that equation is always negligible as long as \( P_r = \frac{vL}{D} \neq 4 \). We can estimate \( \partial c_i/\partial x \) in Eq. (17), using Eq. (16), i.e.,

\[
\frac{\partial c_i}{\partial x}_L = -\frac{D}{v} \exp \left( \frac{x - L}{D} \right) \left( \frac{\partial c_i}{\partial x} \right)_{x=L}
\]

(18)

Again \( \partial c_i/\partial x \) is the estimate of \( \partial c_i/\partial x \) when \( x \) is sufficiently less than \( L \), whereas, approximately from Eq. (2),

\[
\lambda \exp \left( \frac{x - L}{D} \right) \left( \frac{\partial c_i}{\partial x} \right)_{x=L} \approx -\lambda \exp \left( \frac{x - L}{D} \right) \left( \frac{\partial c_i}{\partial x} \right)_{x=L}
\]

(19)

However, since

\[
\frac{\partial c_i}{\partial x} \approx \frac{\partial c_i}{\partial x}_L
\]

(20)

the last term in Eq. (17) is always negligible compared to the \( \partial c_i/\partial x \) term, as long as \( P_r \) is not too small. On the other hand if \( P_r \) is small, then Eq. (17) reduces to Eq. (1) only if \( \lambda \) in very small, i.e., there is a significant discontinuity in \( c_i \) 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 \( c_{i1} \). The solution is exact for \( \lambda = 0 \) and is most inaccurate for \( \lambda = 1 \), especially for \( P_r = 4 \) which is the lowest Piclet number we consider. Thus, in Table 1 we consider only \( P_r = 4 \) and \( \lambda = 1 \). The exact solutions to compare with our approximations are obtained using more complex
<table>
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<th>Position (θ)</th>
<th>c₀ (eq. 9)</th>
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<th>c₂ (eq. 16)</th>
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<th>c₄ (eq. 14)</th>
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The zeroth order kinetics in Table 1, fourth to Eq. (10) for zeroth order kinetics with kD/κ = 0.2, sixth to Eq. (16) for first order kinetics with kD/κ = 1. The third, fifth and seventh columns give the corresponding exact solutions from van Genuchten and Alves (1982) and are considered as tabulated by van Genuchten and Alves (1982). The maximum absolute error is only about 0.02 and the present results are remarkably close to the exact results, justifying the use for P₁ as small as 4. The exact solution obtained is therefore suitable for the boundary condition at the end of the column. Thus calculation of c₄ for a semi-infinite column yields the appropriate breakthrough curve. There is, however, some ambiguity about c₄ within the column, especially near the exit (up to a distance l such that c₀/κ = D = 1). For c₄ = L − L the boundary condition at the exit does not affect c₄. For c₄ = L − L, the presence of preferential paths might indeed cause a discontinuity of c₄ at the exit. The discontinuity, if it exists, has a maximum value resulting from calculating c₄ for a semi-infinite column. If the Péclet number is less than 4 it is necessary to know the boundary condition at z = L to predict the breakthrough curve, and c₄ or c₅, 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.

\[
P = \frac{1}{2} \text{erfc} \left( x - x_0 \right) / \sqrt{4Dt} \quad (A5)
\]

and

\[
Q = \frac{1}{2} \text{erfc} \left( x + x_0 \right) / \sqrt{4Dt} \quad (A6)
\]

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

REFERENCES


