

## ANALYTICAL METHOD FOR EVALUATING THE EFFECTIVE MOLECULAR DIFFUSION COEFFICIENT WITHIN POROUS MEDIA

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**Abstract**—This paper presents an original analytical method for calculating the value of the effective molecular diffusion coefficient of an inert tracer transported within a saturated porous medium,  $D_m$ , in terms of the bulk diffusion constant,  $D_0$ . A simple three-step sequence in the tracer core or packed-bed flood is proposed involving (i) a (convection-dominated) tracer slug injection, (ii) a shut in to allow the slug to spread by diffusion and, finally, (iii) a postflush of the tracer slug by tracer-free solvent. The effluent profile from this sequence can be compared with a profile where no diffusive step [stage (ii)] was present. The difference in the effluents—the diffusive case will be more spread out in time—is purely due to the effects of molecular diffusion within the porous medium. The flood sequence is described by the convection–dispersion equation in stages (i) and (iii) and by the diffusion equation for stage (ii). Green's function propagator and analytical solutions for each step in the above process are well known for certain boundary conditions. We apply Green's function method to propagate the solution through each stage of the process using the final solution to the previous stage as the initial conditions for the next. The final expression for the effluent profile is complex but can easily be evaluated in closed form, and we have confirmed this by comparison with numerical results. The method is applied to sample experimental tracer effluent results in order to evaluate  $D_m$  of chloride within a sand pack. This comparison showed that a reasonable match to the effluent was found for  $D_m \approx 0.75D_0$ .

### INTRODUCTION

Because of the influence of both diffusion and dispersion on miscible displacement processes in porous rocks, these phenomena are of interest in the oil industry (Blackwell *et al.*, 1959; Brigham *et al.*, 1961; Perkins and Johnson, 1963; Gunn and Pryce, 1969; Fried and Combarous, 1971; Dullien, 1979). Molecular diffusion within porous media may be important in a variety of displacement mechanisms in enhanced oil recovery. This may be either through its indirect influence on the mixing zone behaviour or through its direct control of the oil recovery mechanism as is observed in the gas flooding of fractured reservoirs.

The relative importance of dispersion and molecular diffusion in flow through porous media has been discussed by several authors (Blackwell *et al.*, 1959; Perkins and Johnson, 1963; Gunn and Pryce, 1969; Fried and Combarous, 1971) although the two phenomena are closely coupled together at the pore scale [see Sorbie and Clifford (1991)]. Generally speaking, at flow rates of  $\geq 0.3$  m/day, the spreading in a core will primarily be due to dispersion. However, at very low flow rates, or when the fluids are not convecting, molecular diffusion may dominate and, if two miscible fluids are in contact with an initially sharp interface, they will slowly diffuse into one another. As time passes, the sharp interface between the two fluids will become a diffused mixed zone grading from one pure fluid to the other. This diffusion arises because of the random motion of the molecules. However, unlike in

a bulk fluid, the diffusion of the tracer species is affected by the presence of the porous medium. It is possible to represent diffusive behaviour approximately by selecting an effective molecular diffusion constant,  $D_m$ , which is often based on the average cross-sectional area open for diffusion and the overall length or tortuosity of the medium. Because of this hindered diffusion due to the presence of the porous medium,  $D_m$  is less than the molecular diffusion constant,  $D_0$ , as measured in the bulk fluid (Perkins and Johnson, 1963). The differences in the character of the mixing under flow (dispersion) and stagnant (diffusion) conditions may be modelled at the pore scale using network models as has been shown recently by Sorbie and Clifford (1991).

Most investigators studying diffusion or dispersion in porous media analyse the process by measuring the concentration of the tracer at the core or pack outlet,  $C_{eff}$ , as a function of time,  $T$  (as pore volume);  $C_{eff}$  vs  $T$  is the effluent profile. Brigham *et al.* (1961) report an early graphical method for determining the dispersion coefficient from this type of data. However, more recently, investigators have used direct least-squares fits of the experimental data to analytical solutions of the convection–dispersion equation (van Geneuchten, 1981; Sorbie *et al.*, 1987). This approach gives rather more information than the earlier method of Brigham *et al.* (1961) and also gives an estimate of the goodness of fit between the analytical solution and the experimental data. van Geneuchten and Alves (1982) present an extensive compendium of analytical solutions to the convection–dispersion equation. However, they do not present analytical solutions—or expressions in

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closed quadrature form—which can be used to evaluate the molecular diffusion coefficient within the porous medium. In this paper, we present an analytical solution for a simple three-stage experimental tracer flood which may be used to evaluate the effective molecular diffusion coefficient,  $D_m$ , within the porous medium. This is applied to some sample experimental data for a tracer flood in a sand pack where, for this particular case, it is found that  $D_m \approx 0.75D_0$ .

**DESCRIPTION OF EXPERIMENTAL PROCEDURE**

In order to evaluate the effective molecular diffusion constant within a porous medium,  $D_m$ , a staged experiment was carried out, as described below, and illustrated schematically in Fig. 1:

- (i) A specified volume of tracer slug was injected into an effectively one-dimensional (1D) homogeneous sand pack at a constant relatively high flow rate. At the end of this stage, the concentration profile along the core is denoted as  $c_1(x, t)$ .
- (ii) The resident *in situ* tracer slug—which has initial distribution given by  $c_1(x, t)$ —was then allowed to spread out solely by molecular diffusion for a certain period of time, giving a concentration profile denoted as  $c_2(x, t)$ .
- (iii) The slug was then flowed out of the end of the sand pack at the original flow rate giving a concentration profile which, during its transport through the porous medium, is denoted as  $c_3(x, t)$ . Samples of the tracer are assayed at the core exit in order to build up the effluent profile,  $C_{eff}$  vs  $T$ .

The same experiment was then performed without stage (ii), which allowed the dispersion coefficient for

the convection-dominated parts of the flood [stages (i) and (iii)] to be determined. On comparing the effluent concentration profiles from the floods with and without stage (ii), the effective molecular diffusion constant,  $D_m$ , was determined. Analytical results are developed in the next section which allow us to model the results from the experimental procedure described above in order to find  $D_m$ .

**EQUATIONS FOR FLOW IN POROUS MEDIA**

To analyse the above experimental sequence, it is necessary to produce a mathematical model for each stage of the experiment leading to an expression for the effluent profile. The analytical form of the effluent profile can then be matched with the experimental data by selecting the appropriate value for  $D_m$ . The analytical solutions for the second and third stages of the experiment are obtained using propagating functions derived from the Fourier transforms of the convection–dispersion and the molecular diffusion equations, as described below.

The transport of an inert solute through a one-dimensional saturated porous medium is described by the convection–dispersion equation,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \tag{1}$$

where  $c$  is the solute concentration ( $\text{g}/\text{cm}^3$ ),  $D$  is the dispersion coefficient ( $\text{cm}^2/\text{s}$ ) and  $v$  is the fluid superficial velocity ( $\text{cm}/\text{s}$ ). Equation (1) may be solved analytically for a wide range of boundary conditions (van Geneuchten and Alves, 1982).

In linear flow, the dispersion coefficient,  $D$ , is constant at a given flow rate, and is thought to be of the form (Perkins and Johnson, 1963)

$$D = D_m + D' \tag{2}$$

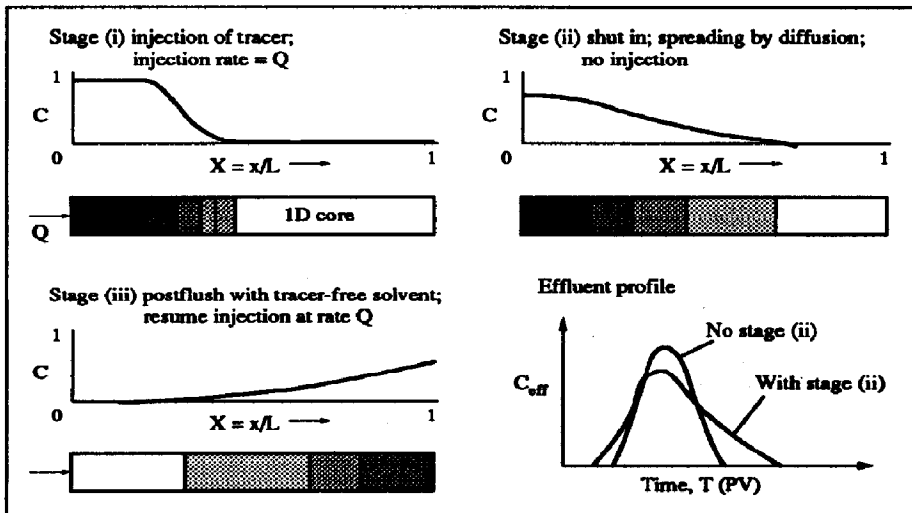


Fig. 1. Schematic sequence of tracer floods used to determine the effective molecular diffusion constant in stage (ii).

where  $D_m$  is the effective molecular diffusion constant and  $D'$  is the dispersive term which depends on the superficial velocity.

For stage (i) of the flood, the initial conditions, inlet boundary condition and semi-infinite boundary condition are given by eqs (3a), (3b) and (3c), respectively,

$$c_1(x, 0) = 0, \quad x > 0 \quad (3a)$$

$$c_1(0, t) = c_0, \quad t > 0 \quad (3b)$$

$$c_1(x, t) \rightarrow 0, \quad x \rightarrow \infty. \quad (3c)$$

This outlet boundary condition, eq. (3c), is not strictly appropriate for a finite system, but, as long as the Peclet number is fairly large, the effect of the actual boundary conditions of zero diffusion flow at the outlet is negligible (Brigham, 1974). The solution to eq. (1) for the above initial and boundary conditions is well known and is given by (van Geneuchten and Alves, 1982)

$$c_1(x, t) = \frac{c_0}{2} \left[ \operatorname{erfc} \left( \frac{x - vt}{2\sqrt{Dt}} \right) + \exp \left( \frac{vx}{D} \right) \operatorname{erfc} \left( \frac{x + vt}{2\sqrt{Dt}} \right) \right] \quad (4)$$

which is the appropriate solution for stage (i) of the proposed experimental sequence in Fig. 1 [see Appendix A for the derivation of eq. (4)]. The initial slug is injected up to time  $t_a$ , at which point the core is shut in ( $v = 0$ ) and stage (ii) begins.

In dimensionless variables, eq. (1) takes the following form:

$$\frac{\partial C}{\partial T} = \frac{1}{N_{Pe}} \frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} \quad (5)$$

where the various dimensionless quantities are given by

concentration:

$$C = \frac{c}{c_0} \quad (6a)$$

fractional system length:

$$X = \frac{x}{L} \quad (6b)$$

time in pore volumes:

$$T = \frac{vt}{L} \quad (6c)$$

Peclet number:

$$N_{Pe} = \frac{vL}{D} \quad (6d)$$

and the analytical solution in dimensionless variables corresponding to eq. (4) is

$$C(X, T) = \frac{1}{2} \left\{ \operatorname{erfc} \left[ \sqrt{N_{Pe}} \left( \frac{X - T}{2\sqrt{T}} \right) \right] + \exp(N_{Pe}X) \operatorname{erfc} \left[ \sqrt{N_{Pe}} \left( \frac{X + T}{2\sqrt{T}} \right) \right] \right\} \quad (7)$$

Under diffusion alone, as occurs in stage (ii), the movement of the effluent is governed by the molecular diffusion equation where the effective molecular diffusion coefficient is used:

$$\frac{\partial c}{\partial t} = D_m \frac{\partial^2 c}{\partial x^2}. \quad (8)$$

The initial condition for this stage is  $c_2(x, 0) = c_1(x, t_a)$ .

The formal solution for the *in situ* concentration profile as it has evolved at the end of stage (ii),  $c_2(x, 0)$ , is then given in Green's function notation as

$$c_2(x, t) = \int_0^\infty c_1(s, t_a) G_2(x, s, t) ds \quad (9)$$

where  $G_2(x, s, t)$  is Green's function which propagates the initial slug after tracer injection during the diffusive stage and is given by

$$G_2(x, s, t) = \frac{1}{2\sqrt{\pi D_m t}} \left\{ \exp \left[ \frac{-(x-s)^2}{4D_m t} \right] + \exp \left[ \frac{-(x+s)^2}{4D_m t} \right] \right\} \quad (10)$$

Note that the second term in eq. (10) accounts for the reflection boundary condition at the inlet (see Appendix B for this derivation).

Since the solution of eq. (8) will be used in conjunction with the solution of the convection-dispersion equation, it is necessary to apply the same variable transformation giving the pseudo-dimensionless molecular diffusion equation

$$\frac{\partial C}{\partial T} = \frac{1}{N_{Pem}} \frac{\partial^2 C}{\partial X^2} \quad (11)$$

where the quantity

$$N_{Pem} = \frac{vL}{D_m} \quad (12)$$

is denoted as the "molecular" Peclet number. In fact,  $v = 0$  during stage (ii) but the value of  $v$  taken in eq. (12) is that during the convection-dominated stages (i) and (iii).

Finally, during stage (iii) of the sequence, the governing equation is again the convection-dispersion equation, but the initial condition is now  $c_3(x, 0) = c_2(x, t_b)$ , where  $t_b$  was the time allowed for the tracer slug to diffuse. This is written as follows:

$$c_3(x, t) = \int_0^\infty c_2(s', t_b) G_3(x, s', t) ds' \quad (13)$$

where

$$G_3(x, s', t) = \frac{1}{2\sqrt{\pi Dt}} \exp\left[-\frac{(s' - x + vt)^2}{4Dt}\right] \tag{14}$$

$G_3(x, s', t)$  is the propagating function for the convection–dispersion equation (see Appendix A for this derivation). However, the integral with respect to  $s'$  can be evaluated giving the following expression:

$$\begin{aligned} c_3(x, t) = & \frac{c_0}{8\sqrt{\pi(D_m t_b + Dt)}} \exp\left[-\frac{(vt - x)^2}{4Dt}\right] \\ & \times \int_0^\infty \left[ \operatorname{erfc}\left(\frac{s - vt_a}{2\sqrt{Dt_a}}\right) + \exp\left(\frac{vs}{D}\right) \operatorname{erfc}\left(\frac{s + vt_a}{2\sqrt{Dt_a}}\right) \right] \\ & \times \exp\left(\frac{-s^2}{4D_m t_b}\right) \left( \exp\left[\frac{(sDt + (vt - x)D_m t_b)^2}{4(D_m t_b Dt)(Dt + D_m t_b)}\right] \right. \\ & \times \operatorname{erfc}\left\{ \frac{1}{2} \left[ \frac{sDt + (vt - x)D_m t_b}{(D_m t_b Dt)^{1/2}(D_m t_b + Dt)^{1/2}} \right] \right\} \\ & + \exp\left[\frac{(sDt - (vt - x)D_m t_b)^2}{4(D_m t_b Dt)(Dt + D_m t_b)}\right] \\ & \left. \times \operatorname{erfc}\left\{ -\frac{1}{2} \left[ \frac{sDt - (vt - x)D_m t_b}{(D_m t_b Dt)^{1/2}(D_m t_b + Dt)^{1/2}} \right] \right\} \right) ds. \end{aligned} \tag{15}$$

In order to compare this analytical solution with the experimental data,  $c_3(x, t)$  is evaluated at the end of the core ( $x = L$ ), where the effluent concentration is measured as a function of time (pore volume through-put).

**NUMERICAL CONFIRMATION OF ANALYTICAL SOLUTIONS**

In order to check the analytical solutions used in this work, they were compared with the equivalent finite difference solutions to the convection–dispersion equation and the molecular diffusion equation. There is, of course, little doubt about the solutions to the convection–dispersion equation or the diffusion equation, it is mainly eq. (15) which we wish to check. The Crank–Nicolson finite difference method was used with the appropriate initial and boundary conditions. All numerical calculations were carried out with sufficiently fine spatial grids and small time steps to ensure that convergence had been achieved.

A tracer flood in a sand pack was used both as a basis for the analytical/numerical comparison and the evaluation of  $D_m$ . The rectangular sandpack used in the experiments had the following dimensions: length  $L = 30$  cm; cross-sectional area  $A = 11.25$  cm<sup>2</sup>; and porosity  $\phi = 0.44$ . In this experiment, 0.33 pore volumes of chlorine-36 labelled brine were injected into a brine-saturated sand pack at a rate of 60 cm<sup>3</sup>/h ( $v = 3.367 \times 10^{-3}$  cm/s). It was left to diffuse for 887 h, before being flushed out at the original rate of 60 cm<sup>3</sup>/h. The Peclet number for the convection-dominated part of the flood [stages (i) and (iii)] was found to be 78 using the approach described elsewhere (van

Geneuchten, 1981; Sorbie *et al.*, 1987). The bulk molecular diffusion constant,  $D_0$ , of chloride was taken to be  $2.0 \times 10^{-5}$  cm<sup>2</sup>/s. For the purpose of verifying the accuracy of the analytical solutions, the above values were used in both the analytical equations and in the finite difference equations. The analytical solutions were evaluated using *Mathematica*<sup>TM</sup>, a mathematics package capable of accurate numerical integrations which runs on a number of computer systems (Wolfram, 1988).

For the purpose of initially validating the analytical solutions,  $D_m$  is taken to have the same value as the bulk molecular diffusion constant,  $D_0$ . The concentration profiles were generated using the dimensionless forms of the above equations with

$$T_a = \frac{vt_a}{L} = \frac{1}{3}, \quad T_b = \frac{vt_b}{L} = 358.38$$

$$N_{rem} = \frac{vL}{D_m} = 5050.5.$$

Figure 2 shows that there is an excellent match for stages (i) and (ii), respectively, between the analytical and numerical solutions for the *in situ* concentration

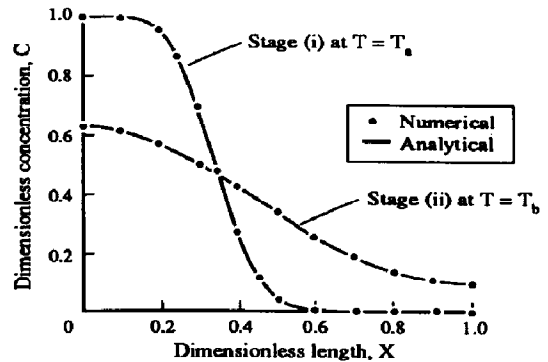


Fig. 2. Analytical and numerical solutions for stages (i) and (ii) in Fig. 1.

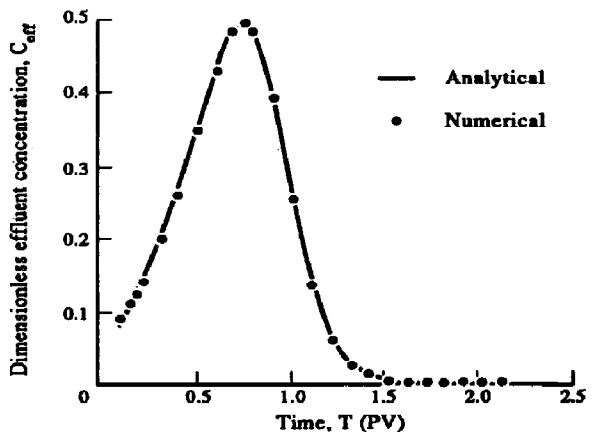


Fig. 3. Analytical and numerical solutions for the effluent profile from stage (iii) in Fig. 1.

distributions within the system. Figure 3 shows the comparison between the analytical and numerical effluent profiles for stage (iii) of the model case. Clearly, these are in excellent agreement, confirming that eq. (15) is the correct analytical solution to this problem.

#### APPLICATION OF THE METHOD TO EXPERIMENTAL DATA

We now wish to apply the analytical solution of eq. (15) to the evaluation of the effective diffusion coefficient for the experimental case, where dispersion  $D$  and  $D_m$  are no longer equal as in the above example. The effective molecular diffusion constant,  $D_m$ , may be established by plotting analytical effluent profiles for a range of values of  $D_m$  and type curve match them with the experimental data. Figure 4 shows the experimental profile, as measured when the effluent left the sand pack, compared with five such evaluations, with the value of  $D_m$  ranging from 0.0 to 1.5 times the bulk molecular diffusion constant ( $D_0 = 2.0 \times 10^{-5} \text{ cm}^2/\text{s}$ ). Note that the time origin for eq. (15) is taken as the start of the postflush period as indicated in Fig. 4. The case where  $D_m = 0$  is equivalent to a flood where there is no stage (ii) and, as expected, this shows the highest peak in the effluent in Fig. 4. Clearly, the timescale of the experiment is such that the effluent profile is sensitive to  $D_m$ . The value of  $D_m$  which appears to give the best fit to experiment for this case is approximately 0.75 of the bulk diffusion constant value,  $D_0$ . We stress that this is not a general result and is presented here as an example application of our analytical method. The relatively high value of the effective molecular diffusion constant in this pack reflects the fact that the sand pack is quite homogeneous and has a well-connected pore space with a tortuosity close to unity.

#### SUMMARY AND CONCLUSIONS

An analytical solution to the combined convection–dispersion and diffusion equations based on

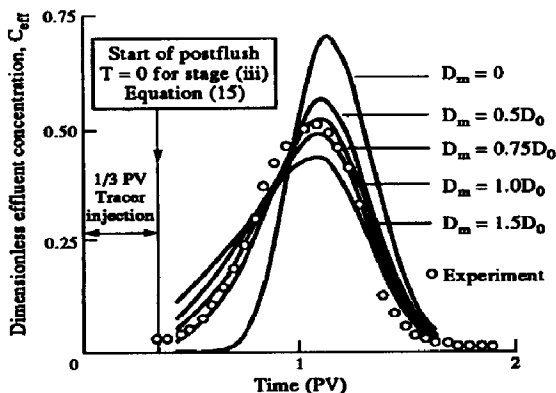


Fig. 4. Evaluation of the effective molecular diffusion coefficient,  $D_m$ , within the porous medium

Green's function formalism is presented in this paper. This gives a novel and convenient way of evaluating the effective molecular diffusion coefficient,  $D_m$ , within a porous medium. The method has been confirmed numerically and has been applied to the analysis of an experimental three-stage tracer flood in order to find  $D_m$ . For the experimental case studied, it was found that  $D_m \approx 0.75D_0$ , but this is not a general finding.

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#### NOTATION

$A$	cross-sectional area of system, $\text{cm}^2$
$c(x, t)$	concentration of tracer, $\text{g}/\text{cm}^3$
$c_0$	input concentration of tracer, $\text{g}/\text{cm}^3$
$C$	dimensionless normalised concentration ( $= c/c_0$ )
$C_{\text{eff}}$	dimensionless effluent concentration [ $= C(X = 1; T)$ ]
$c_1(x, t)$	concentration of tracer in stage (i)
$c_2(x, t)$	concentration of tracer in stage (ii)
$c_3(x, t)$	concentration of tracer in stage (iii)
$\bar{c}(x, p)$	Laplace transform of $c$ w.r.t. $t$
$\hat{c}(s, t)$	Fourier transform of $c$ w.r.t. $x$
$D$	dispersion coefficient ( $= D' + D_m$ ), $\text{cm}^2/\text{s}$
$D'$	velocity dispersion term, $\text{cm}^2/\text{s}$
$D_m$	effective molecular diffusion coefficient, $\text{cm}^2/\text{s}$
$D_0$	bulk molecular diffusion coefficient, $\text{cm}^2/\text{s}$
$G_j$	Green's function propagator for stage $j$
$L$	length of system, $\text{cm}$
$N_{Pe}$	system Peclet number ( $= yL/D$ )
$N_{Pem}$	"molecular" Peclet number defined relative to the convection dominated stages (i) and (iii) ( $= vL/D_m$ )
$PV$	pore volume
$Q$	volumetric injection rate into core, $\text{cm}^3/\text{h}$
$s, s'$	transform variables
$t$	time, $\text{s}$
$t_a$	time taken for tracer slug to be in- jected during stage (i), $\text{s}$
$t_b$	time allowed for tracer slug to diffuse during stage (ii), $\text{s}$
$T$	dimensionless time in pore volumes ( $= vt/L$ )
$T_a$	number of pore volumes of tracer slug in- jected
$T_b$	time allowed for tracer slug to diffuse using same timescale as pore volume dimension- less time
$v$	superficial velocity [ $= Q/(3600A\bar{\phi})$ ], $\text{cm}/\text{s}$
$x$	distance, $\text{cm}$
$X$	dimensionless distance along the system ( $= x/L$ )

#### Greek letter

$\bar{\phi}$  porosity as a fraction

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APPENDIX A: ANALYTICAL SOLUTION AND PROPAGATOR FOR THE CONVECTION-DISPERSION EQUATION

Although the solution to the convection-dispersion equation is quite well known, it is presented here for completeness. Taking the Laplace transforms with respect to time in eq. (1) gives

$$D \frac{d^2 \bar{c}}{dx^2} - v \frac{d\bar{c}}{dx} - p\bar{c} = 0, \tag{A1}$$

On taking the boundary conditions into consideration, the solution to this second-order ordinary differential equation is

$$\bar{c}(x, p) = \frac{c_0}{p} \exp \left[ \frac{x(v - \sqrt{v^2 + 4Dp})}{2D} \right]. \tag{A2}$$

Taking the inverse Laplace transform then yields the solution given in eq. (4) or, in dimensionless variables, eq. (7).

Taking the Fourier transform of the convection-dispersion equation with respect to the spatial variable,  $x$ , gives

$$\frac{d\hat{c}}{dt} = - (Ds^2\hat{c} - isv\hat{c}). \tag{A3}$$

Integrating eq. (A3) gives

$$\hat{c}(s, t) = \Phi(s) \exp [ - (Ds^2 - isv)t ] \tag{A4}$$

where

$$\Phi(s) = F[\phi(x)]. \tag{A5}$$

The solution of the convection-dispersion equation is the inverse Fourier transform of eq. (A4) and, therefore, by the convolution theorem:

$$c(x, t) = \frac{1}{2\sqrt{\pi Dt}} \int_0^\infty \phi(s) \exp \left[ \frac{-(s-x+vt)^2}{4Dt} \right] ds. \tag{A6}$$

In the same dimensionless units as used above, the solution becomes

$$C(X, T) = \frac{\sqrt{N_{Pe}}}{2\sqrt{\pi T}} \int_0^\infty \varphi(S) \exp \left[ \frac{-(S-X+T)^2 N_{Pe}}{4T} \right] dS \tag{A7}$$

where

$$\varphi(S) = C(S, 0), \tag{A8}$$

APPENDIX B: DERIVATION OF THE PROPAGATOR FOR THE MOLECULAR DIFFUSION EQUATION

Equation (8) may be solved subject to the initial conditions

$$c(x, 0) = \phi(x), \quad -\infty < x < \infty \tag{B1}$$

where

$$\phi(x) = 0, \quad x < 0. \tag{B2}$$

Taking the Fourier transform of the molecular diffusion equation with respect to the spatial variable gives

$$\frac{d\hat{c}}{dt} = -s^2 D_m \hat{c}. \tag{B3}$$

Integrating eq. (B3) gives the solution

$$\hat{c}(s, t) = \Phi(s) \exp (-s^2 D_m t) \tag{B4}$$

where

$$\Phi(s) = F[\phi(x)]. \tag{B5}$$

The solution of the molecular diffusion equation is the inverse Fourier transform of eq. (B4) and, so, by convolution:

$$c(x, t) = \frac{1}{2\sqrt{\pi D_m t}} \int_0^\infty \phi(s) \exp \left[ \frac{-(x-s)^2}{4D_m t} \right] ds. \tag{B6}$$

This is the case when the slug has been flowed into the core sufficiently far from its ends such that it is not affected by the boundaries. However, in the experiment, the tracer was placed in the core such that the rear edge of the slug was against the inlet boundary. Since there is no flow across this boundary, this is equivalent to having an image slug diffusing in the region  $x < 0$ ; that is,  $\phi(-x) = \phi(x)$ . Thus, with this reflection boundary condition the propagating function is

$$\frac{1}{2\sqrt{\pi D_m t}} \left\{ \exp \left[ \frac{-(x-s)^2}{4D_m t} \right] + \exp \left[ \frac{-(x+s)^2}{4D_m t} \right] \right\} \tag{B7}$$

giving a final solution

$$c(x, t) = \frac{1}{2\sqrt{\pi D_m t}} \int_0^\infty \phi(s) \left\{ \exp \left[ \frac{-(x-s)^2}{4D_m t} \right] + \exp \left[ \frac{-(x+s)^2}{4D_m t} \right] \right\} ds. \tag{B8}$$

The corresponding expression in dimensionless form incorporating the "molecular" Peclet number as defined in eq. (12) is as follows:

$$C(X, T) = \frac{\sqrt{N_{Pem}}}{2\sqrt{\pi T}} \int_0^\infty \varphi(S) \left\{ \exp \left[ \frac{-(X-S)^2 N_{Pem}}{4T} \right] + \exp \left[ \frac{-(X+S)^2 N_{Pem}}{4T} \right] \right\} dS \tag{B9}$$

where

$$\varphi(S) = C(S, 0). \tag{B10}$$