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Saif Farhat, Diogo Bolster, and Guillem Sole-Mari

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1 **Linking Mixing Interface Deformation to Concentration**
2 **Gradients in Porous Media**

3 Saif Farhat and Diogo Bolster

4 *Civil and Environmental Engineering and Earth Sciences,*
5 *University of Notre Dame, Notre Dame, IN, US*

6 Guillem Sole-Mari

7 *Geosciences Rennes, University of Rennes, Rennes, FR*

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Abstract

We study the pore-scale transport of a conservative scalar forming an advancing mixing front, which can be re-interpreted to predict instantaneous mixing-limited bimolecular reactions. We investigate this using a set of two-dimensional, high-resolution numerical simulations within a poly-disperse granular porous medium, covering a wide range of Péclet numbers. The aim is to show and exploit the direct link between pore-scale concentration gradients and mixing interface (midpoint concentration isocontour). We believe that such a perspective provides a complementary new lens for better understanding mixing and spreading in porous media. We develop and validate a theoretical model that quantifies the temporal elongation of the mixing interface and the upscaled reaction kinetics in mixing-limited systems accounting for pore-scale concentration fluctuations. Contrary to the classical belief that, given sufficient time, pore-scale fluctuations would eventually be washed out, we show that for $Pe > 1$ advection generates pore-scale concentration fluctuations more rapidly than they can be fully dissipated. For such Péclet numbers, once incomplete mixing is established, it will persist indefinitely. We identify critical Péclet thresholds ($Pe = 18$ for Poiseuille flow, $Pe = 48$ for porous media) where reaction efficiency is minimized. Finally, our developed model accurately reproduces the reaction product mass in a 3D porous media column over a wide range of Péclet numbers, demonstrating its applicability to more realistic systems.

9 I. INTRODUCTION

10 Solute transport, mixing, and reactions in porous media are fundamental processes for
11 many natural and industrial applications ([1–4]). Many reactions are driven by mixing and
12 are considered mixing-limited when reaction time scales are shorter than mixing times ([5–
13 7]). This is often the case for many relevant systems and processes, including groundwater
14 contaminant transport and degradation ([8]), mineral dissolution and precipitation ([9, 10]),
15 and CO₂ sequestration ([11]). To date, classical Darcy-scale and Advection-Dispersion reac-
16 tive transport models have been the conventional framework to describe these processes in
17 porous media applications ([1, 3]). However, in their traditional forms, these models do not
18 account for naturally occurring fluctuations at the pore scale (i.e. incomplete mixing) and
19 the influence these have on mixing-limited reactions ([12, 13]). Accounting for pore-scale
20 concentration fluctuations is crucial to predicting large-scale behaviors, and disregarding

21 them is a significant cause for discrepancies between observations and model predictions
 22 in reactive transport scenarios ([14–19]). Some studies have attempted to incorporate the
 23 effects of incomplete mixing into the advection-dispersion-reaction equation. For instance,
 24 one approach introduces a continuum-scale representation of the reaction rate, incorporating
 25 an effective first-order kinetic term to account for incomplete mixing [20]. Another approach
 26 assumes that the mixing ratio on the sub-Darcy scales is distributed within a Representative
 27 Elementary Volume (REV) according to a Beta distribution [21].

28 In this context, the deformation of mixing interfaces and the pore-scale concentration fluc-
 29 tuations are widely recognized as key factors in determining global reaction kinetics ([22–26]).
 30 Mixing interfaces within scalar fields are subjected to simultaneous stretching and shrinking
 31 mechanisms ([27]) arising from pore-scale velocity variations and diffusion, respectively, lead-
 32 ing to the formation of elongated lamellar structures. In some cases, stretching is enhanced
 33 by features such as chaotic advection and the presence of stagnation points. While the for-
 34 mer can only occur in systems with sufficient degrees of freedom such as three-dimensional
 35 porous media ([28, 29]), stagnation points are common to both two and three dimensional
 36 ones. Trapping of fluid elements near the stagnation points induces significant folding and
 37 neighboring elements are swept downstream. Also, in flows with spatially heterogeneous
 38 shear rates, the elongation of the material line can follow a range of sub-exponential growth
 39 rates ([30]). Just like mixing interfaces, pore-scale concentration gradients are controlled by
 40 the competing effects of fluid stretching and diffusion, which enhance and dissipate them,
 41 respectively ([22, 31–33]).

42 A mixing process between two solutions may be modeled as essentially governed by *i)*
 43 a mixing front or interface through which the diffusive flux of solutes occurs, and *ii)* a
 44 normal concentration gradient that determines the rate of said diffusive flux ([26]). In
 45 the context of mixing-limited reactions, the diffusive flux rate across the mixing interface
 46 controls the rate at which reactants come into contact with each other, and therefore affects
 47 the effective reaction rate. As expounded earlier, both the mixing interface length/area and
 48 the typical concentration gradient across it are dynamic quantities that can change over
 49 time. Many studies have highlighted the importance of the coupling between the structure
 50 of the velocity field fluctuations and the resulting scalar field gradients ([33–37]). However,
 51 for applications concerned with reactive transport in porous media, the direct link between a
 52 scalar field’s mixing interface deformation and concentration gradients is, to date, less clear.

It has been observed that under Poiseuille flow, or in fully saturated porous media, the mixing interface initially undergoes elongation until an equilibrium between stretching and shrinking is achieved. At this point, the interface neither elongates nor shrinks ([27, 38]). In a way, this observation challenges the classical view of Taylor dispersion, which states that any transverse variation in the concentration field under a fully developed Poiseuille flow ultimately degenerates to a uniform concentration ([39]). This observation is consistent with experimental and theoretical studies showing that transverse dispersion coefficients do not scale linearly with flow velocity, contrary to the prediction by [40], which assumes complete mixing at the pore scale [41–43].

In this paper we aim to demonstrate and exploit the direct link between the temporal evolution of mixing interface deformation and concentration gradients in mixing fronts. By doing so, we seek to (1) offer an alternative view of the Taylor-Aris dispersion process and (2) analytically quantify the product mass of a bimolecular mixing-limited reaction in porous media, while accounting for incomplete mixing.

II. SIMULATIONS

We generate multiple random realizations of two-dimensional porous media, each with identical statistical properties, to ensure representative simulation results. This is achieved by extracting two dimensional slices from a three-dimensional random porous medium. The latter consists of a random close packing of spheres with a mono-disperse diameter $d_0 = 2\text{mm}$, generated using the algorithm developed by [44], as illustrated in Figure 1 (a). The medium is periodic in all directions to prevent boundary effects. Five two-dimensional domains are extracted; each has dimensions of $50d_0 \times 50d_0$ and a porosity (n) of approximately 0.48. The two-dimensional grains resulting from the slicing are poly-disperse with an average diameter of 1.5 mm. Figure 1 (b) shows the first realization (R1) with others taken as slices at other heights.

The simulations are performed using multiple modules from OpenFOAM v10 ([45]). To generate the pore space mesh, a background structured hexahedral mesh is initially created using the `blockMesh` utility. Subsequently, the `castellatedMesh` feature within the `snappyHexMesh` utility is used to remove cells occupied by circular grains. We based the mesh resolution on the convergence test by [46], which used $\Delta = d_0/60$. Using the same

numerical schemes, we opted for a finer resolution of $\Delta = d_0/100$ to better capture the grain-fluid interface on our structured mesh. Figure 1 (c) shows a zoomed-in example region of the mesh.

To obtain the steady-state velocity field, the `simpleFOAM` algorithm was used to numerically solve the single-phase, steady-state, incompressible Navier-Stokes (NS) equations,

$$\nabla \cdot \mathbf{u} = 0, \quad (1)$$

$$\mathbf{u} \cdot \nabla \mathbf{u} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{u} + \frac{1}{\rho} \mathbf{f}, \quad (2)$$

where $\mathbf{u}$ and ∇p are the velocity field and the pressure gradient, respectively; ρ is fluid density and ν is kinematic viscosity. To drive the flow we apply a body force $\mathbf{f} = [f, 0]$ to maintain a specific, volume-averaged, pore flow velocity ($\bar{u}$). In order to achieve conditions representative of water flowing in natural porous media, which is a process typically dominated by viscous effects (i.e stokes flow), we set the value of the longitudinal body force f , as well as those of ρ and ν , to attain a relatively low Reynolds number $Re = \bar{u}d_0/\nu = 0.15$. Periodic boundary conditions are imposed on both the longitudinal and transverse walls as shown in Figure 1 (b). No-slip boundary conditions are enforced at the contact between the fluid and the solid grains.

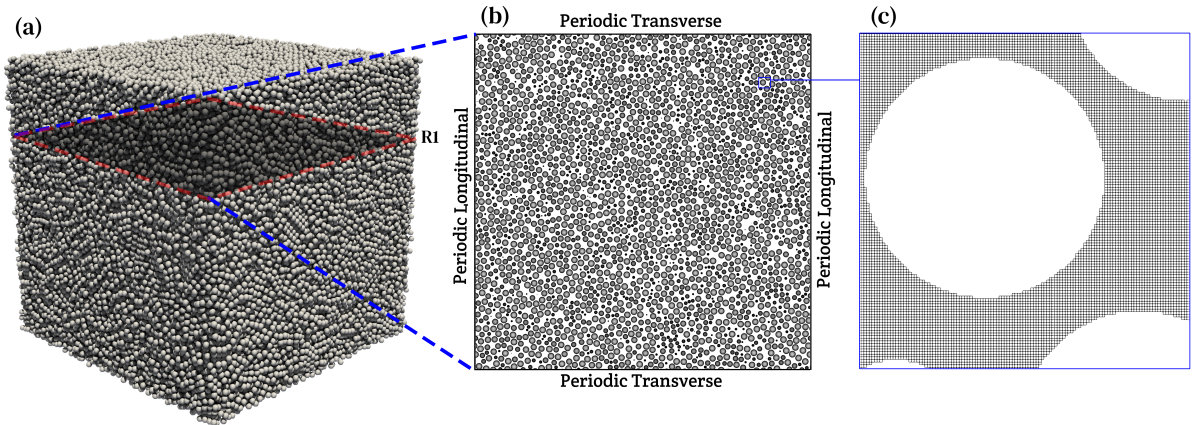


FIG. 1. (a) Periodic cubic random packing of mono-dispersed spherical grains ($50d_0, 50d_0, 50d_0$); (b) Slice taken from the three-dimensional column representing the first realization (R1); (c) Finite volume structured mesh that was used in the simulations ($\Delta=d_0/100$)

After solving the flow, we take advantage of the system's periodicity to extend the domain length by duplicating the mesh in Figure 1 (b) along the principal flow direction, thus aiming to obtain column-type scales capable of capturing asymptotic regimes of spreading and mixing processes ([46]). This approach reduces computational costs by simulating flow solely within the elementary domain. Next, the `scalarTransportFoam` algorithm is used for simulating the transport of a conservative scalar by numerically solving the transient advection-diffusion equation,

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = D \nabla^2 C, \quad (3)$$

where C is solute concentration, and D is the molecular diffusion coefficient. As the initial condition we set up a sharp front transitioning from $C = 1$ to $C = 0$ at x -distance $d_0/2$ from the inlet (i.e., $C([x, y], t = 0) = 1 - H(x - d_0/2)$), where $H(x)$ is the Heaviside step function. The left boundary condition is a continuous injection $C(x = 0, t) = 1$. The right boundary has a zero-gradient Neumann boundary condition. The simulations are stopped before the solute leaves the domain. We simulate six grain Péclet number configurations: $Pe = 1, 10, 32, 100, 316$, and 1000 , by varying the molecular diffusion coefficient, where

$$Pe = \bar{u} d_0 / D. \quad (4)$$

This range insures that we are covering transport regimes all the way from where diffusion plays a role to where advection significantly dominates. Figure (2) presents a portion of the domain. It shows the concentration and gradient magnitude fields for $Pe = 32$ and $Pe = 1000$ at different times for one realization.

III. TEMPORAL EVOLUTION OF THE MIXING INTERFACE AND CONCENTRATION GRADIENTS

In this section we present the measurements of time-dependent mixing interface length in 2D saturated random porous media as well as concentration gradient magnitudes. While these measurements are done for the transport of a single-species concentration front as described in the previous section, this setup is relevant to reactive transport as it can be re-interpreted (see Section IV.C) to represent the transport of an instantaneous bimolecular irreversible reaction. In such a setting, assuming a mixing ratio of 1 and equal dispersion

125 coefficients for all species, the 0.5 iso-concentration line of the conservative transport simula-
 126 tions is analogous to the mixing interface between the reactants. This work is not limited to
 127 this specific mixing ratio; while other iso-concentration values could be relevant to different
 128 mixing ratios, the underlying dynamics remain consistent. The mixing interface is subjected
 129 to two main deformation mechanisms: stretching and shrinking. In two-dimensional, ran-
 130 domly packed porous media, the former is caused by gradients in the non-uniform velocity
 131 fields and the impact with stagnation points around grains. The latter is mainly due to dif-
 132 fusion, which allows solute to sample different transverse velocities, thereby limiting mixing
 133 interface growth. Lamella coalescence is another shrinking mechanism, which happens when
 134 adjacent lamellae merge to form a single, thicker layer. This simultaneous stretching and
 135 shrinking leads to lamellae being more elongated at higher Péclet numbers, as can be seen
 136 in Figure (2). We quantify the temporal deformation of the interface, $L^*(t)$, as the relative
 137 increase in its length $L(t)$ with respect to the initial sharp interface length L_0 .

$$L^*(t) = \frac{L(t) - L_0}{L_0}. \quad (5)$$

138 Initially, the mixing interface undergoes rapid deformation, as shown in Figure (3). During
 139 this ballistic regime, lengthening is dominated by differences in advection experienced by
 140 different trajectories ([4]). At later times, stretching and shrinking effects reach an equilib-
 141 rium, resulting in a plateau in the length of the mixing interface. For Péclet number = 1 and

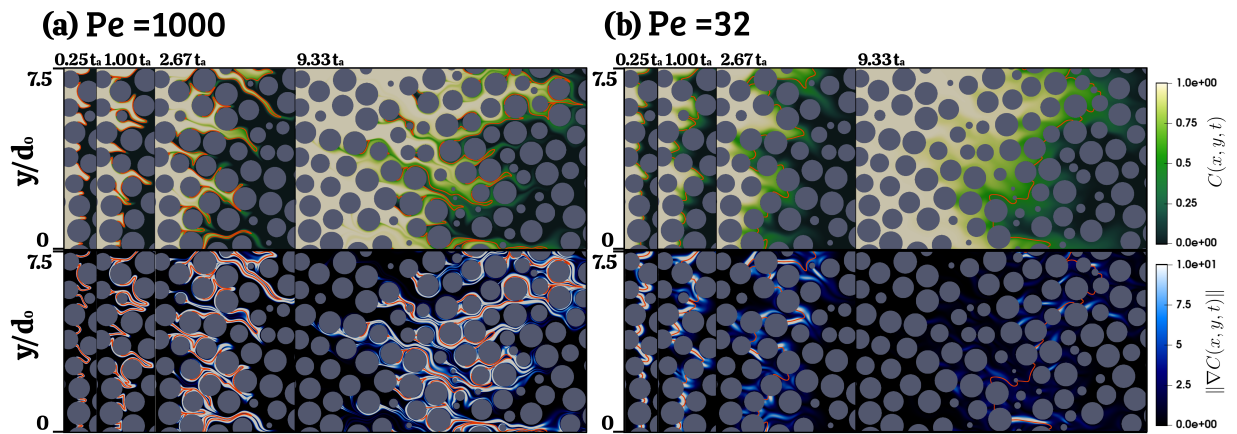


FIG. 2. Portion of the domain of concentration (top) and gradient magnitude (bottom) fields at
 0.25, 1, 2.67, 9.33 advection times for $Pe = 32$ and $Pe = 1000$. In both top and bottom, the
 superposed red line depicts the mixing interface ($C = 0.5$)

below (not shown here), the interface slightly fluctuates (due to the random variability of local pore space geometry) around its initial length, without showing any definitive growth or shrinking.

At early times, a region of significant concentration gradient magnitudes is formed which aligns with, and deforms like the mixing interface, as shown in the $t_a = [0.25, 1]$ samples for $Pe=1000$ in Figure (2), $t_a = d_0/\bar{u}$ being the advection time. However, unlike the mixing interface, the region of significant gradients evolves into a two-dimensional strip-like structure, expanding over time until its connection with the mixing interface becomes less intuitive, as seen in the $t_a = 9.33$ snapshot. Like the mixing interface length, concentration gradients tend to intensify with an increase in the Péclet number. To quantify and study the temporal evolution of concentration gradients, we calculate the change in their integral $G(t)$ over the entire mixing area, relative to the initial value G_0

$$G^*(t) = \frac{G(t) - G_0}{G_0}, \quad G(t) = \iint_{\Omega} \|\nabla C(x, y, t)\| \partial x \partial y. \quad (6)$$

Here, Ω denotes the mixing area defined as $(\Omega = (x, y) | 0 < C(x, y) < 1)$. Note that due to the step initial condition the gradient field in the transverse direction is zero and a Dirac delta in the longitudinal one, meaning that $G_0 = L_0$. At early times, $G^*(t)$ increases because the concentration gradients at the pore-scale decay slower than the rate at which they are created as the plume spreads. Later on, both the decay of concentration gradients and the plume spreading rate converge to an equilibrium, attaining a constant value for $G^*(t)$. Our simulation results reveal that $G^*(t)$ aligns precisely with the growth of the mixing interface $L^*(t)$, as shown in Figure (3), not only initially and at early times but for the full duration. The interface length at any given moment is, in fact, the same as integral of the pore-scale gradient magnitudes over the entire mixing area despite the seeming qualitative divergence at later times discussed in relation to Figure 2. This result further highlights the relevance of measuring and predicting the mixing interface length, as it can be directly linked to concentration gradients and therefore mixing and reaction.

IV. MODELING THE LINK OF CONCENTRATION GRADIENTS AND MIXING INTERFACE LENGTH

Motivated by, and building upon the findings of the previous section, we aim to write a direct mathematical expression for predicting mixing interface length, which can then be used to estimate mixing-limited reactive transport. The model exploits a local link between the orientation (slope) of the mixing interface and transverse concentration gradients. We ultimately show that the identity found numerically in the previous section (Figure 3) can be explained by this analytical model. We start with a classical simple pressure-driven flow in a two-dimensional channel (Poiseuille flow). Although this setting lacks critical defining features of flow in porous media, it can often serve as an idealized representation of flow through individual pores ([47, 48]). We derive an analytical solution for the asymptotic time behavior and then tackle the transient regime. Finally, we combine all of this to propose an analytical solution to estimate the upscaled reaction kinetics in porous media, accounting for incomplete mixing.

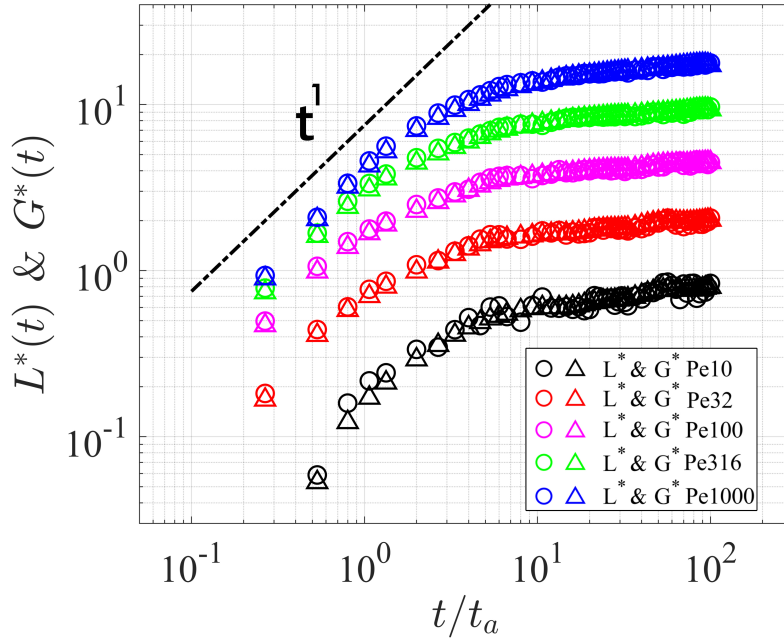


FIG. 3. Ensemble of the temporal growth of the mixing interface length (L^*) (circles) with comparison to the growth of gradient magnitude integral (G^*) (triangles) across Péclet cases.

A. Asymptotic Regime in a 2D Poiseuille Flow

The velocity $u(y)$ of a Newtonian-fluid in pressure-driven laminar flow between two parallel plates separated by a distance $2h$, subjected to no-slip boundary conditions, is given by

$$u(y) = \frac{3}{2}\bar{u}\left(1 - \frac{y^2}{h^2}\right) \quad -h \leq y \leq h. \quad (7)$$

A snapshot of the concentration field and the mixing interface after 10 advection times for $Pe = 100$ is presented in Figure 4(a). In Appendix A we derive an analytical solution for the mixing interface plateau length in Poiseuille flow. Starting from the standard two-dimensional advection-diffusion equation for a conservative scalar $C(x, y, t)$, we use Reynolds decomposition to separate $C(x, y, t)$ and $u(y)$ into their respective means ($\bar{C}(x, t)$, $\bar{u}$) and fluctuations ($C'(x, y, t)$, $u'(y)$). At asymptotic times (i.e. after a characteristic diffusive time scale $t_D = \frac{(2h)^2}{D_m}$), we can invoke Taylor dispersion theory ([39]) to derive an analytical expression of the mixing interface slope $m(y)$ at each point along the y -axis. A detailed derivation is outlined in Appendix A. Using this approach, we can explicitly link the local interface slope to concentration gradients as:

$$m(y) = \frac{\partial x}{\partial y} = -\frac{\nabla_y C'(y)}{\nabla_x \bar{C}} \Big|_{x=\mu_1(t)} = \frac{\bar{u}}{2D} \left(y - \frac{y^3}{h^2}\right), \quad (8)$$

where $\nabla_y C'(y)$ is the transverse gradient of concentration fluctuations and $\nabla_x \bar{C}$ is the longitudinal gradient of mean concentrations, both calculated at the location of the longitudinal first spatial moment ($\mu_1(t) = \bar{u}t + x_0$) of the mixing interface (i.e. $\bar{C} = 0.5$) (see Figure 4(b)). Equation 8 directly proves that the transverse variation in the concentration field ($\nabla_y C'(y)$) under Poiseuille flow never converges to a uniform concentration. Although it will decrease over time it persists in a balance with the mean concentration gradient forever and it is important for reactive transport.

With the formulation for the slope given in equation (8), the plateau mixing interface length growth (L_∞^*) relative to the initial length can be calculated using the arc length formula as:

$$L_\infty^*(Pe) = \frac{\int_{-h}^h \sqrt{1 + \left(\frac{\partial x}{\partial y}\right)^2} dy - L_0}{L_0} = \int_0^1 \sqrt{\frac{Pe^2}{16} (y^* - y^{*3})^2 + 1} dy^* - 1, \quad (9)$$

where $y^* = y/h$. In Figure 4(c), we validate our analytical solution by numerically integrating equation (9) and comparing it to the measured L_∞^* for a set of two-dimensional Poiseuille

207 flow simulations. We observe an exact match between the observed L_∞^* and the theoretical
 208 one. Hence, in diffusion dominated systems ($Pe \leq 1$), the interface length experiences no
 209 significant growth ($L_\infty^* \approx 0$). On the other hand, in advection dominated systems, char-
 210 acterized by high Péclet numbers, L_∞^* scales as $Pe/16$. The key thing to highlight here is
 211 that mixing interface deformation directly stems from (i) the gradient of transverse concen-
 212 tration fluctuations (see Figure 4(b)) and (ii) the gradient of the mean concentration in the
 213 longitudinal direction. We will continue to assume this to model the transient behavior.

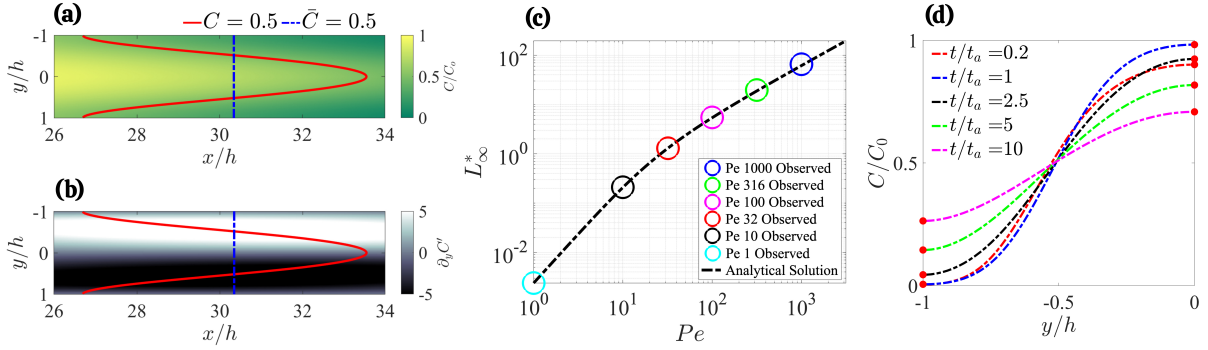


FIG. 4. (a) Scalar field for 2D Poiseuille flow at $Pe=100$ and 10 advection times, showcasing the
 0.5 mixing interface isoline (in red) and 0.5 mean concentration location (in blue) (b) same as (a)
 but showing the transverse gradient of concentration fluctuations (c) quantification of the plateau
 mixing interface growth across various Péclet numbers: comparing observations to equation (9) (d)
 Concentration profile along $\mu_1(t)$ in 2D Poiseuille flow simulation for $Pe=100$ at different times.

B. Transient Regime

217 At time $t = 0$, the initial sharp mixing interface has a zero slope, i.e., $m(y, t = 0) = 0$.
 218 Subsequently, it undergoes simultaneous steepening and flattening. At late times, and under
 219 Poiseuille flow setting, $m(y, t \rightarrow \infty)$ becomes constant and is described by equation (8).
 220 However, for flow in porous media, $m(y, t \rightarrow \infty)$ fluctuates, but its mean along the mixing
 221 interface, $\bar{m}(t)$, eventually converges to a constant value as its length reaches a plateau. To
 222 mathematically describe this, we aim to model the gradients across a single lamella with
 223 a characteristic width $2h_c$ by quantifying the temporal evolution of (i) $\nabla_y C'(y, t)$ and (ii)
 224 $\nabla_x \bar{C}(t)$ at $x = \mu_1(t)$.

225 To begin, we first assume that the mixing isoline has a continuous and differentiable
 226 functional form $x_L = f_L(y, t)$. By definition, the length of this isoline can be expressed
 227 using its first spatial derivative $(\partial_y f_L(y, t))$ and the gradients along it as

$$L(t) = \int_0^H \sqrt{1 + \left[\frac{\partial f_L(y, t)}{\partial y} \right]^2} \partial y = \int_0^H \sqrt{1 + \left[-\frac{\nabla_y C(y, t)}{\nabla_x C(y, t)} \right]_{iso}^2} \partial y. \quad (10)$$

228 To simplify (10), we approximate the concentration gradients along the 0.5 mixing isoline
 229 using those at the first spatial moment ($x = \mu_1(t)$), as supported by the proof in Appendix
 230 A. Although the proof is derived for asymptotic times, we assume that it is a valid approxi-
 231 mation during the transient regime also, as we will demonstrate later. With this in mind, we
 232 take H as the channel width for Poiseuille flow, and the water-filled voids for porous media
 233 (i.e. nH). Within a single lamella, $\nabla_x C(y, t)$ along the 0.5 isoline can be approximated by
 234 its mean value $\nabla_x \bar{C}(t)$. Hence, the interface length calculation can be simplified as

$$L(t) \approx \int_0^H \sqrt{1 + \left[-\frac{\nabla_y C'(y, t)}{\nabla_x \bar{C}(t)} \right]_{\mu_1(t)}^2} \partial y \approx H \sqrt{1 + \left[-\frac{\nabla_y C'(\zeta, t)}{\nabla_x \bar{C}(t)} \right]_{\mu_1(t)}^2} = H \sqrt{1 + \left[-\frac{\overline{\nabla_y C'}(t)}{\nabla_x \bar{C}(t)} \right]_{\mu_1(t)}^2}. \quad (11)$$

235 Here we have used the mean value theorem for integrals to quantify the mixing interface
 236 length in terms of the mean slope $\bar{m}(t) = -\overline{\nabla_y C'}(t)/\nabla_x \bar{C}(t)$. ζ is an unspecified point
 237 along $x = \mu_1(t)$ at which the value of $\nabla_y C'(\zeta, t)$ is equal to the mean value of the function
 238 $\nabla_y C'(y, t)$ over $[0, h_C]$. Thus, $\nabla_y C'(\zeta, t)$ can be replaced by $\overline{\nabla_y C'}(t)$ which is defined as
 239 $\overline{\nabla_y C'}(t) = (1/h_C) \int_0^{h_C} \nabla_y C'(y, t) \partial y$.

240 A sample of the temporal evolution of the concentration profile along $x = \mu_1(t)$ for
 241 the Pe=100 Poiseuille flow simulation at different times is presented in Figure 4(d). From
 242 equation (11), one only needs to quantify the temporal change of concentrations fluctuations
 243 at the maximum mean longitudinal velocity $C'(t, y_t = 0)_{\mu_1(t)}$ and the minimum one $C'(t, y_t =$
 244 $h_C)_{\mu_1(t)}$ over a half lamella width (h_C) to estimate $\overline{\nabla_y C'}(t)$. In other words, we need to find
 245 the difference between the red dots shown in Figure 4(d) along each line. Hence, the mean
 246 transverse gradient can be quantified as:

$$\overline{\nabla_y C'}(t)_{\mu_1(t)} = \left[\frac{C'(t, y_t = 0) - C'(t, y_t = h_C)}{h_C} \right]_{\mu_1(t)}. \quad (12)$$

247 Here, we define the lamella width as the characteristic distance between the peak and trough
 248 concentrations along $x = \mu_1(t)$. A useful analogy here is to think of the concentration profile

along $x = \mu_1(t)$ as a wave, with the lamella width representing the wavelength, where $C'(t, y_t = 0)_{\mu_1(t)}$ and $C'(t, y_t = h_c)_{\mu_1(t)}$ are the peak and trough values. In Poiseuille flow, the lamella width ($2h_c$) is independent of the Péclet number, equal to the channel width ($2h$), and remains constant over time.

To quantify lamella width in randomly packed porous media, we assume that the mixing interface consists of a bundle of lamellae. Initially, the lamella width is determined by the characteristic pore size and is independent of the Péclet number. Over time, processes such as folding, stirring, and coalescence cause the lamellae to interact, and their width asymptotically approaches a constant value dependent on the Péclet number. We define a representative lamella as the one whose elongation matches the average elongation of the interacting bundle. The mixing interface can then be modeled as a bundle of non-interacting representative lamellae, each with a $2h_c$ width, where measuring the elongation of one lamella is sufficient to estimate the deformation of the entire interface.

In Appendix B, we derive an analytical formula for the representative lamella width ($2h_c$):

$$2h_c = \frac{\gamma D}{u} \sqrt{205 \left(\frac{D_l^\infty}{D} - 1 \right)}, \quad (13)$$

where γ represents the advective tortuosity, and D_l^∞ is the asymptotic longitudinal dispersion coefficient. Alternatively, $2h_c$ can be estimated by redefining the Péclet number in equation (9) as $Pe_c = \frac{u(2h_c)}{D_m}$ and fitting $L_\infty^*(Pe_c)$ to the observed plateau length growth:

$$2h_c \approx \frac{4}{3} Pe^{-0.45}. \quad (14)$$

As the Péclet number increases, the lamella width decreases, driven by stronger stretching and weaker coalescence. Both equations are in reasonable agreement when $D_l^\infty/D > 1$, as will be demonstrated shortly.

We cross-checked this width by measuring the characteristic lamella width directly from the simulations. In Figure 5 (a), we show an example of the concentration field for $Pe = 100$ at 20 advection times, highlighting the 0.5 mixing interface isoline in red and the 0.5 mean concentration location in blue. From this, $2h_c$ can be quantified by dividing the water-filled pore width by the number of intersections (N) between the continuous 0.5 isoline and the 0.5 mean concentration location (i.e., $2h_c \approx nH/N$). We did this for the simulated Péclet range at late times ($t/t_a > 20$) across all five realizations. In Figure 5 (b), we show a boxplot for the acquired length scales, which are consistent with the values defined in equations (13) and

(14). As an approximation, we assume that the asymptotic-time lamella width is also valid

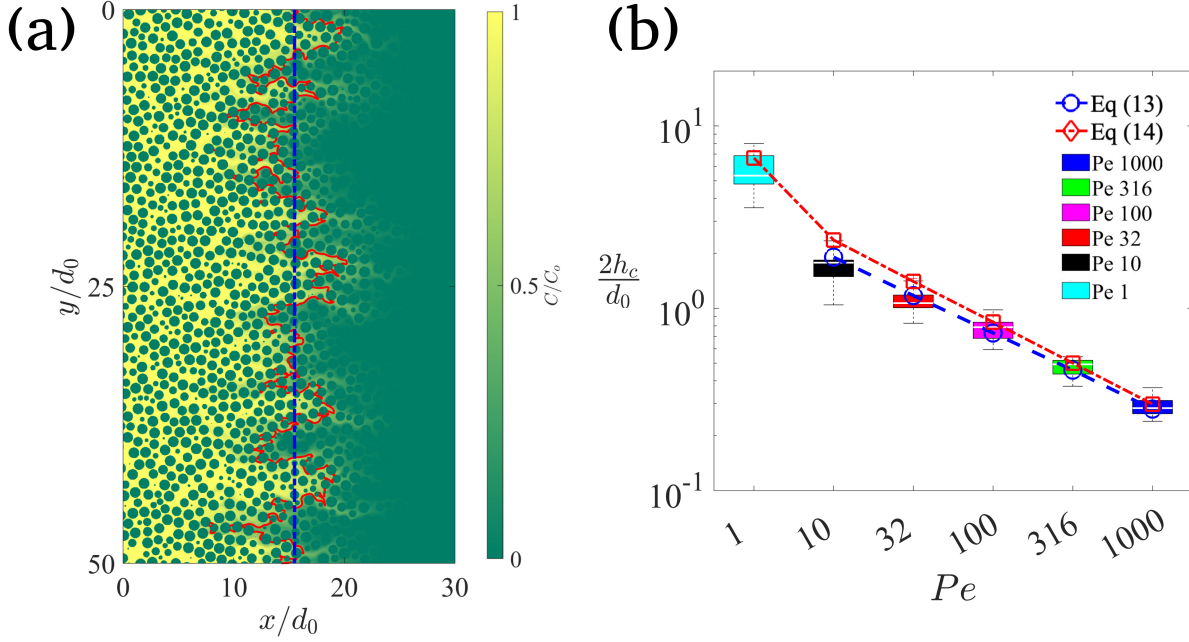


FIG. 5. (a) Scalar field for 2D porous media flow with $Pe = 100$ at 20 advection times, highlighting the 0.5 mixing interface isoline in red and the 0.5 mean concentration location in blue. (b) Box plot of the normalized lamella width, $2h_c$, at late times, quantified by the number of intersections, N , between the continuous 0.5 isoline and the 0.5 mean concentration location (i.e., $2h_c \approx nH/N$). Results are shown for different Péclet numbers over all five realizations, and compared to the width described in equations (13) and (14).

at earlier times. This has negligible effects after one advection time, as we will demonstrate later. It is interesting to note that the width of the concentration fluctuations ($2h_c$) scales with the Péclet number in a manner similar to the Batchelor scale for exponential stretching ($S_B \propto Pe^{-1/2}$), rather than the scaling observed for power-law stretching ($S_B \propto Pe^{-1/3}$) ([7, 49]). This suggests that the stretching rate in a two-dimensional randomly packed porous medium is stronger than that of a simple shear flow. However, further investigation of this will be the focus of a future work.

To quantify $\bar{m}(t)$, we propose two analytical approaches and give the reader the liberty to choose between them

(1) by separately calculating the transverse concentration gradient $\overline{\nabla_y C'}(t)$ and the longitudinal concentration gradient $\nabla_x \bar{C}(t)$, where their ratio yields $\bar{m}(t)$. The concentration

profile at a given location y_t is modeled using a complementary error function, assuming an apparent velocity $u_a(t)$ and longitudinal dispersion $D_l(t)$. The apparent velocity is computed by convolving the position distribution $P(y, t)$, obtained from the Green's function, with the longitudinal velocity $u(y)$. The transverse gradient is then calculated from the difference in concentration fluctuations at two transverse positions ($y_t = 0$ and $y_t = h_c$). For the longitudinal gradient, it can be estimated using the maximum gradient of the classical advection-diffusion equation with a continuous injection. For full details, we direct the reader to Appendix C.

(2) using the closure solution for $C'(x, y, t)$ proposed by ([50]). They applied volume averaging to estimate the concentration field of a conservative solute in a stratified flow from early to late times by relaxing several of the assumptions required for Taylor dispersion, only valid at late times. Their proposed closure is

$$C'(x, y, t) = b_0(x, y, t) + b_1(y, t) \nabla_x \bar{C}(x, t), \quad (15)$$

where $b_0(x, y, t)$ and $b_1(y, t)$ represent the influence of the initial condition and convective source, respectively. For the considered Heaviside initial condition, the former is zero (see [50] for full details), while the latter is given by

$$b_1(y, t) = - \int_0^t \int_0^{h_c} u'(\eta) Gr(y, \eta, t - \tau) \partial \eta \partial \tau, \quad (16)$$

where $Gr(y, \eta, t - \tau)$ is the Green's function for transverse diffusion across the domain, given by ([51])

$$Gr(y, \eta, t - \tau) = \frac{1}{h_c} + \frac{2}{h_c} \sum_{\alpha=1}^{\infty} \cos\left(\frac{\alpha\pi y}{h_c}\right) \cos\left(\frac{\alpha\pi \eta}{h_c}\right) e^{-\frac{D\alpha^2\pi^2(t-\tau)}{h_c^2}} \quad 0 \leq y \leq h_c. \quad (17)$$

The velocity fluctuation $u'(\eta)$ can be found by subtracting the mean longitudinal velocity ($\bar{u}$) from equation (7). Thus, executing the integrals in (16) we can quantify the concentration fluctuations at $C'(t, y_t = 0)_{\mu_1(t)}$ and $C'(t, y_t = h_c)_{\mu_1(t)}$ and we get the following analytical solution for the mixing isoline mean slope:

$$\bar{m}(t) = - \left[\frac{\nabla_y C'(t)}{\nabla_x \bar{C}(t)} \right]_{\mu_1(t)} = \frac{6\bar{u}h_c}{\pi^4 D} \sum_{\alpha=1}^{\infty} \frac{(1 - (-1)^\alpha)(1 - e^{-4\alpha^2\pi^2 \frac{t}{t_D}})}{\alpha^4}. \quad (18)$$

When $t/t_D \gg 1$, diffusion has had sufficient time to significantly spread the scalar over the characteristic distance $2h_c$ and the mean slope of the interface becomes constant. At late

times ($t \rightarrow \infty$), equation (18) matches the mean of the slope described earlier in equation (8).

In Figure 6 (a), we show the close alignment between the mixing interface elongation quantified using our analytical solution to that from the set of Poiseuille flow simulations for different Péclet numbers. Next, we apply this approach to estimate $L^*(t)$ in porous media, only this time using the characteristic length scale $2h_C$ as prescribed in equation

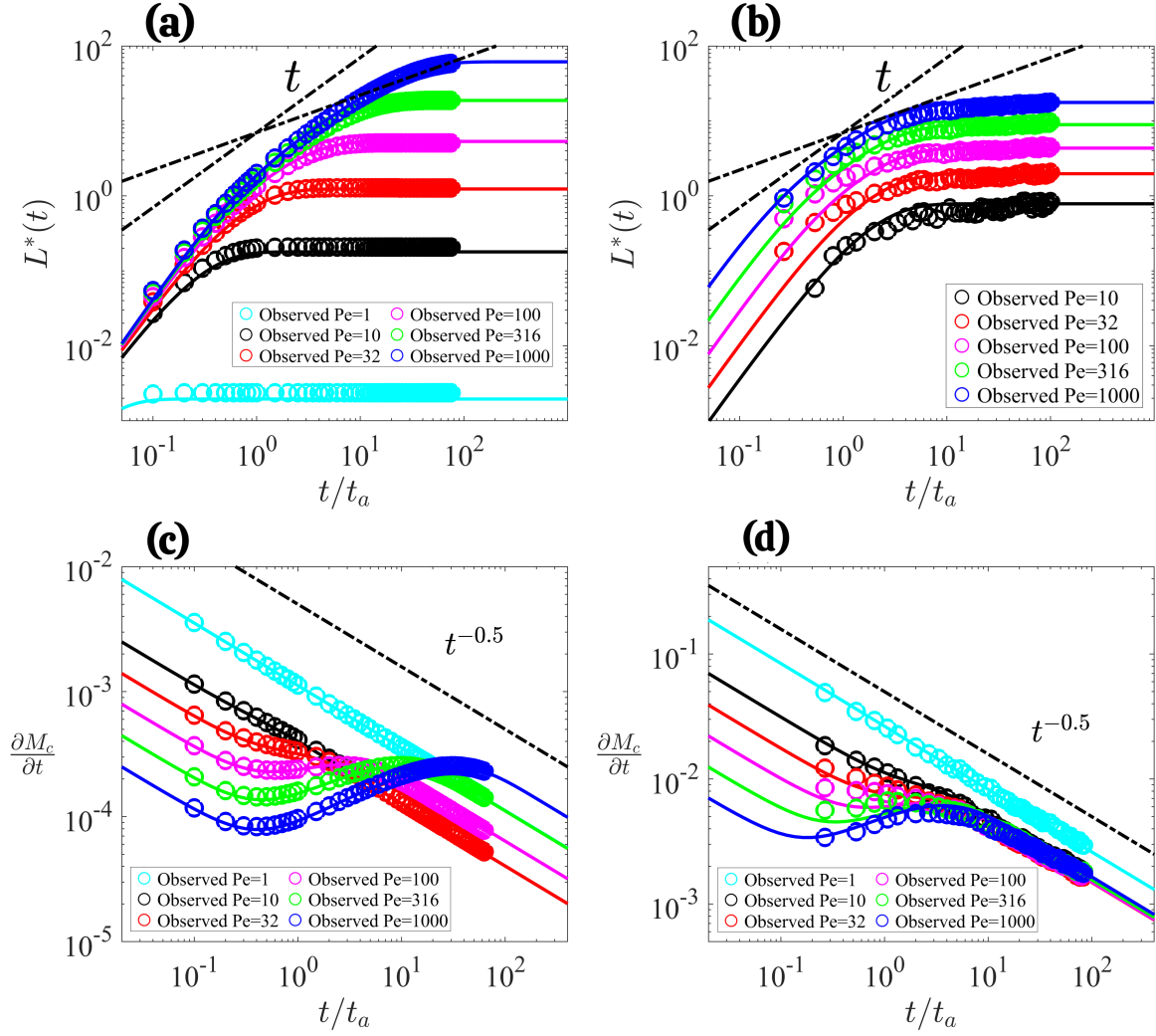


FIG. 6. Comparing the growth of the mixing interface length between simulations (circles) and the analytical solution (solid lines) across different Péclet numbers in (A) Poiseuille flow and (B) porous media. This also present a comparison for the rate of C production in (C) Poiseuille flow and (D) porous media setting.

(14). Figure 6 (b), show the comparison for the porous media, and it matches nicely with the observation. The early time mismatch is unsurprising prior to one advection time, mainly because the characteristic length scale of concentrations fluctuations at such early times is not well represented by the one prescribed in equation (14) (or the characteristic lamella width has not had time to evolve yet). This is also why the curves do not converge as time approaches zero ($t \rightarrow 0$), in a manner similar to Figure 6 (a). However, we find it interesting that after as little as one advection time (the characteristic time to traverse one grain), the difference between a complex porous media flow and a simple Poiseuille flow can all be encapsulated within the characteristic width scale ($2h_C$).

Lastly, we make use of the theory developed in this section to link back to the data presented in Section III. In Appendix D, we show that the model predicts the equality between the mixing interface length, $L(t)$, and the integral of pore-scale concentration gradients, $G(t)$, supporting our observations in Figure (3).

C. Temporal Evolution of Mixing-Limited Reactive Transport

The conservative transport simulations can be re-interpreted to study an instantaneous, bimolecular, irreversible reaction ($C_A + C_B \rightarrow C_C$). The subscripts, A, B, and C refer to the invading solution, the displaced one, and the reaction product. To do so, one can define two reaction independent, conservative species u_A and u_B , as

$$u_A = C_A + C_C \quad , \quad u_B = C_B + C_C . \quad (19)$$

Assuming an instantaneous, irreversible reaction, C_A and C_B cannot coexist at the same point in space and time; thus the concentration of C_C can be defined as:

$$C_C(x, y, t) = \min(u_A(x, y, t), u_B(x, y, t)) . \quad (20)$$

This assumes that all chemical species have the same molecular diffusion coefficient. We now aim to propose a solution for the production rate of C_C in both Poiseuille flow and porous media flow. In mixing limited reactive transport, the production of C_C is limited by the flux of either C_A or C_B across the interface between the two solutions. For a spatially homogeneous system, the product concentration C_C is symmetric around the mixing interface ([13]). Hence, the rate of C_C production can be represented by integrating Fick's law

346 along the mixing interface as:

$$\frac{dM_c(t)}{dt} = 2 \int_{L(t)} D |\nabla C_A(\xi, t)| dl \approx 2DL(t) \overline{|\nabla C_A(t)|}. \quad (21)$$

347 Here, ξ represents the coordinate normal to the mixing interface. The average gradient
 348 magnitude along the 0.5 isoline ($\overline{|\nabla C_A(t)|}$) can be estimated in terms of the averages of the
 349 pore-scale longitudinal ($\overline{|\nabla_x C_A(t)|_{iso}}$) and transverse ($\overline{|\nabla_y C_A(t)|_{iso}}$) concentration gradients
 350 along the mixing interface. The average longitudinal gradient along the 0.5 isoline decay as
 351 $1/\sqrt{4\pi D_e(t)t}$, in which $D_e(t)$ is the effective dispersion coefficient. The effective dispersion
 352 coefficient $D_e(t)$ measures the mean width of a point injection within the channel's cross
 353 section, essentially representing the Green's function of the transport problem. In appendix
 354 E, we show that the effective dispersion coefficient can be directly quantified using the mixing
 355 interface mean slope $\bar{m}(t)$ as:

$$D_e(t) = D(1 + 1.25\bar{m}^2(t)). \quad (22)$$

356 This means that the effective dispersion could be directly approximated from the length
 357 of the mixing interface as $D_e(t)/D \approx 1.25(L(t)/L_0)^2$. Lastly, the average transverse
 358 concentration gradients can be quantified using the longitudinal one as $\overline{|\nabla_y C_A(t)|_{iso}} =$
 359 $\bar{m}(t) \overline{|\nabla_x C_A(t)|_{iso}}$. Hence, we can re-write equation (21) as

$$\frac{dM_c(t)}{dt} = L_0 \sqrt{\frac{D}{\pi t}} \frac{1 + \bar{m}^2(t)}{\sqrt{1 + 1.25\bar{m}^2(t)}}. \quad (23)$$

360 Here, L_0 represents the initial length of the mixing interface. For Poiseuille flow, L_0 is equal
 361 to H , while in porous media, it is nH . If one normalizes the reaction production rate in
 362 equation (23) by the plume spreading length, we get:

$$\frac{C_C \text{ Production rate}}{\text{Spreading length}} : \frac{1}{\sqrt{2D_e(t)t}} \frac{dM_c(t)}{dt} \approx L_0 \frac{1}{\sqrt{2\pi t}}. \quad (24)$$

363 This implies that the temporal production rate of C_C per unit mixing area is independent
 364 of the Péclet number and is approximately $(\sqrt{2\pi t})^{-1}$.

365 In Figure 6 (c), we present a comparison between the observed rate of mass production
 366 from the simulations and the analytical solution outlined in this paper, showing an exact
 367 alignment between the two. For $t/t_D \gg 1$, both $D_e(t)$ and $\bar{m}(t)$ converge to constant
 368 values and equation (23) scales as $\propto t^{-1/2}$. We use equation (23) to specify the following
 369 two limiting regimes approximations:

370 1. For diffusion-dominated systems, $\frac{dM_c(t)}{dt} \approx L_0 \sqrt{D/(\pi t)}$.

371 2. For advection-dominated systems, $\frac{dM_c(t)}{dt} \approx L_0 \sqrt{D/(4t)} \bar{m}(t)$.

372 Our diffusion-dominated, limiting regime approximation is equivalent to the well-mixed
373 assumption solution proposed by [13].

$$\left. \frac{dM_c(t)}{dt} \right|_{wm} = L_0 \sqrt{D^*/(\pi t)}, \quad (25)$$

374 where D^* is the sum of the diffusion and hydrodynamic dispersion coefficients which for
375 $\sim Pe \leq 1$ is approximately equal to the molecular diffusion ([52]). However, for $Pe > 1$, it
376 is no longer a valid assumption and our model demonstrates how to account for incomplete
377 mixing. In Figure 6 (d), we demonstrate how our model closely captures the observed data
378 under porous media flow.

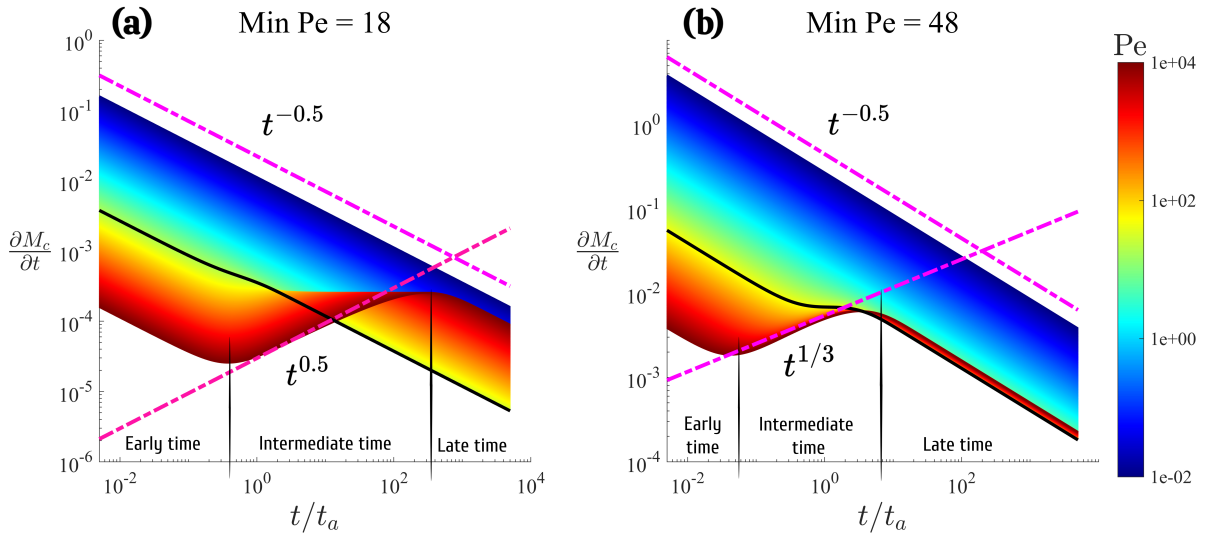


FIG. 7. Temporal production rate of C across a wide range of Péclet numbers: (a) Poiseuille flow, with the black solid line indicating $Pe = 18$; (b) porous media flow, with the black solid line indicating $Pe = 48$.

379 We use the solution developed in this paper to examine the mass production rate over a
380 wide range of Péclet numbers ($Pe = 0.01$ to $Pe = 10,000$), as shown in Figure 7. Under
381 Poiseuille flow (see Figure 7 (a)), the mass production rate, $\frac{dM_c(t)}{dt}$, is initially dominated by
382 molecular diffusion, scaling as $t^{-0.5}$. After some time, the elongation of the mixing interface
383 begins to enhance mass production significantly for advection-dominated cases, leading to

an intermediate temporal scaling of $t^{0.5}$. The duration of this intermediate phase scales with Péclet number ($\Delta t_{int} \propto Pe$). At later times, the system behavior transitions back to the $t^{-0.5}$ scaling.

In porous media flow (see Figure 7 (b)), the initial behavior is similar to that of Poiseuille flow; however, the intermediate and late-time behaviors differ significantly for advection-dominated cases. The intermediate phase begins earlier, scaling with $t^{1/3}$. This phase is also shorter-lived with a weak Péclet number dependence ($\Delta t_{int} \propto Pe^{0.1}$). Although the system eventually reverts to the $t^{-0.5}$ scaling at late times, $\frac{dM_c(t)}{dt}$ displays significantly less variability compared to Poiseuille flow for $Pe > 1$. This weaker Péclet dependence is likely related to the inverse relationship between the representative lamella width and the Péclet number. For $Pe > 1$, using Equations (14), (18), and (23), the late-time scaling is derived as $\propto Pe^{0.05}$, which aligns closely with the observed scaling of $\sim Pe^{0.035}$. We note the Péclet numbers associated to minimum late-time $\frac{dM_c(t)}{dt}$, observed at $Pe = 18$ for Poiseuille flow and $Pe = 48$ for porous media flow. The reduced $\frac{dM_c(t)}{dt}$ at late times around these Péclet numbers is closely related to their associated low longitudinal dispersion.

Lastly, we compare the analytical solution presented in this paper with other works in the literature, specifically the three-dimensional column simulation by [46]. They aimed to numerically replicate the laboratory experiment by [13], which involved a closely packed column under fully saturated conditions. We use equation (13) to estimate the lamella width, and use the initial mixing interface area (A_0) instead of the length (L_0). Also, to quantify the product mass (M_c), we numerically integrate equation (23). In Figure 8, we present a comparison between our model and the well-mixed model for different Péclet numbers. Our model closely estimates the product mass for most cases, except for $Pe = 10$, where it slightly overestimated the observation. Nevertheless, it still outperforms the well-mixed solution. It is worth noting that, although our model was developed using a two-dimensional approach, it can be directly applied to a three-dimensional system.

V. SUMMARY AND CONCLUSION

In this paper, we conducted a set of high-resolution pore-scale flow and transport simulations to study mixing-limited reactive transport under laminar saturated flow conditions. Using OpenFOAM, we solved the Navier-Stokes and advection-diffusion equations for a pe-

414 riodic porous medium generated by a packing algorithm that randomly arranges spherical
 415 grains. Our simulations cover a wide range of Péclet numbers, from diffusion-dominated
 416 to advection-dominated transport regimes. We observed that under Poiseuille flow, and
 417 in fully saturated porous media, the mixing interface length and the integral of pore-scale
 418 concentration gradients undergo an initial growth until an equilibrium between stretching
 419 and shrinking is reached. We observed that the length of the mixing interface at any mo-
 420 ment is equal to the integral of the pore-scale concentration gradient magnitudes over the
 421 entire mixing area/volume. This presents a potential advantage, as experimentally it may
 422 be easier to measure one over the other. Additionally, we find this insight valuable because
 423 understanding the deformation of the mixing interface, a local quantity, provides insight
 424 into the behavior of the overall mixing area or volume, and vice versa.

425 For example, in a two-dimensional plug flow with continuous injection, where all solutes
 426 have identical velocities, the mixing interface length $L(t)$ remains constant. Consequently,
 427 one could also infer that the integral of the local concentration gradient magnitudes $G(t)$ is
 428 constant as well. Thus, local gradients would decay at the same rate as plume spreading.

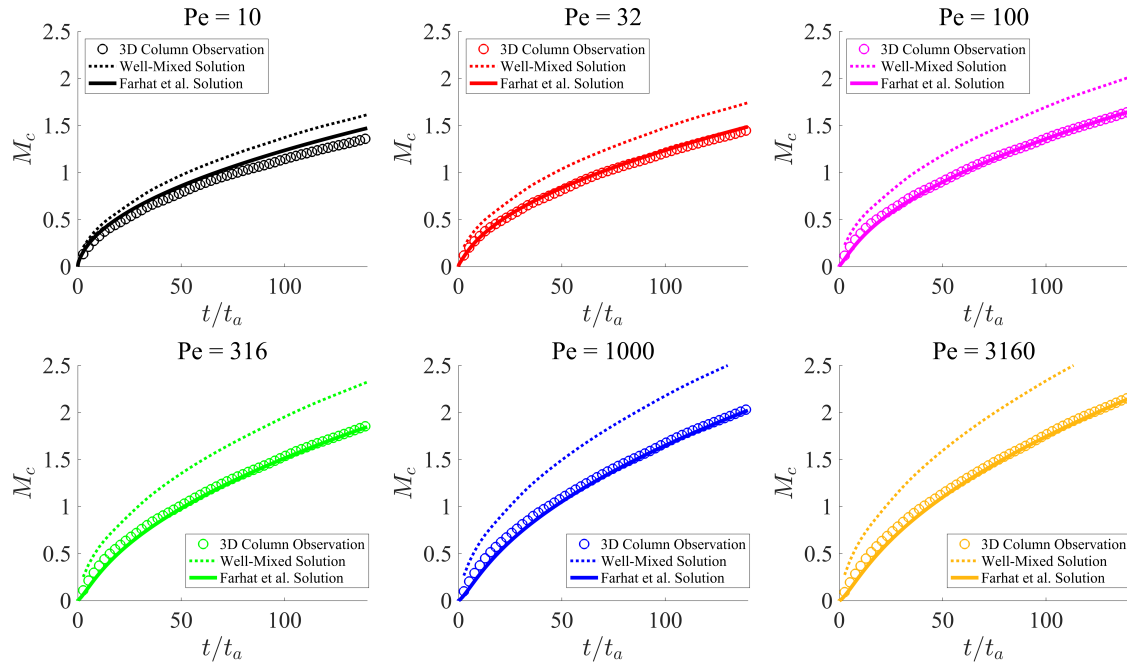


FIG. 8. Comparing the analytical solution developed in this paper (solid lines) and the well-mixed solution (dotted lines) to the 3D column observation of [46] (circles) under different Péclet numbers

429 This can be confirmed by noting that in such a system, where gradients exist only in the
 430 flow direction, the maximum gradient decays as $\propto 1/\sqrt{4\pi Dt}$. Meanwhile, the plume width
 431 spreads as $\propto \sqrt{2Dt}$. Now, consider another endmember case: a purely advective Poiseuille
 432 flow with no diffusion. Here the mixing interface length would grow indefinitely, necessitating
 433 $G(t)$ to grow indefinitely as well. Since the concentration difference across the front must
 434 remain constant, the solute front width would need to compress at a rate of $\propto t^{-1}$, precisely
 435 matching the growth of $L(t) \propto t$. This behavior is due to the incompressibility of the fluid
 436 and is consistent with the findings of [22].

437 The observation that the mixing interface length reaches a plateau without subsequent
 438 decay somewhat challenges the classical interpretations associated with Taylor dispersion
 439 theory, which state that transverse concentration gradients vanish at late times. To address
 440 this potential discrepancy, we developed and validated a theoretical model that quantifies
 441 the deformation of the mixing interface. This is done by estimating the decay of both lon-
 442 gitudinal and transverse concentration gradients along the 0.5 mean concentration contour.
 443 The model is initially derived for an idealized Poiseuille flow and later extended to apply to
 444 flow in porous media by introducing a characteristic width scale for pore-scale concentration
 445 fluctuations.

446 Our results show that this solution closely aligns with observations in both flow regimes.
 447 We show that transverse concentration gradients persist indefinitely and are crucial for
 448 accurately modeling reactive transport. Specifically, for $Pe > 1$, incomplete mixing, once
 449 established, persists. This provides a new perspective on mixing-limited reactive transport
 450 in both pipe flow and porous media under laminar flow conditions.

451 Finally, based on the theory presented, we propose a model for estimating upscaled
 452 reaction kinetics. For $Pe \leq 1$, the well-mixed assumption provides a reliable estimate of
 453 mixing-limited reactive transport. However, for $Pe > 1$, this assumption no longer holds,
 454 and our model shows how to account for incomplete mixing. At early times, Poiseuille and
 455 porous media flows exhibit similar dependence of the reaction rate on the Péclet number.
 456 However, for $Pe > 1$, their intermediate and late-time phases differ significantly. Poiseuille
 457 flow shows a strong late-time Péclet dependence with a longer intermediate phase, while
 458 porous media flow has a shorter intermediate phase and weaker late-time scaling with Péclet.
 459 We have identified the values $Pe = 18$, for Poiseuille flow, and $Pe = 48$, for porous media
 460 flow, for which late-time reaction rate is minimized. We compare our analytical solution

with a 3D column simulation of a closely packed column under fully saturated conditions. Our model, developed in 2D, accurately estimates reaction product mass across a wide range of Péclet numbers, highlighting its potential for use in more realistic scenarios.

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Appendix A: Mixing Interface Plateau Length in Poiseuille Flow

In this appendix we derive an analytical solution for the mixing interface plateau length in Poiseuille flow. We derive it for the case of flow between parallel plates, but the same solution could be retrieved if circular pipe flow is used. We start with the standard two-dimensional advection diffusion equation for conservative scalar $C(x, y, t)$, assuming an isotropic molecular diffusion coefficient D , that is independent of C

$$\frac{\partial C(x, y, t)}{\partial t} + u(y) \frac{\partial C(x, y, t)}{\partial x} = D \frac{\partial^2 C(x, y, t)}{\partial x^2} + D \frac{\partial^2 C(x, y, t)}{\partial y^2}. \quad (\text{A1})$$

We apply Reynolds decomposition to separate $C(x, y, t)$ and $u(y)$ into their respective means $\bar{C}(x, t)$ and $\bar{u}$, along with fluctuations $C'(x, y, t)$ and $u'(y)$. Substituting this decomposition into (A1), averaging the equation, and then subtracting the average equation from (A1), we obtain the equation for fluctuations

$$\frac{\partial C'}{\partial t} + (u(y) - \bar{u}) \frac{\partial \bar{C}}{\partial x} + u(y) \frac{\partial C'}{\partial x} - \frac{\partial (\overline{u'(y)C'})}{\partial x} = D \frac{\partial^2 C'}{\partial x^2} + D \frac{\partial^2 C'}{\partial y^2}. \quad (\text{A2})$$

At asymptotic times, when $t \gg \frac{(2h)^2}{D_m}$, we use the assumptions of [39] (a) Gradients of fluctuations in transverse direction are larger than in longitudinal direction (b) Horizontal gradients in the mean are larger than horizontal gradients in fluctuations (c) Fluctuations evolve slowly in time. Thus, (A2) reduces to

$$\frac{\bar{u}}{2D} \left(1 - 3 \frac{y^2}{h^2}\right) \frac{\partial \bar{C}}{\partial x} = \frac{\partial^2 C'}{\partial y^2}. \quad (\text{A3})$$

483 By integrating Equation (A3) with respect to y twice and applying no-flux boundary con-
 484 ditions, we obtain an expression for concentration fluctuations:

$$C'(x, y, t) = \frac{u}{8D} \left(2y^2 - \frac{y^4}{h^2} - \frac{7}{15}h^2 \right) \frac{\partial \bar{C}}{\partial x}. \quad (\text{A4})$$

485 The mean concentration, $\bar{C}(x, t)$, is given by and can be approximated using a Taylor series
 486 expansion as follows:

$$\bar{C}(x, t) = \frac{1}{2} \operatorname{erfc} \left(\frac{x - \bar{u}t}{\sqrt{4D_t t}} \right) \simeq \frac{1}{2} - \frac{x - \bar{u}t}{\sqrt{4\pi D_t t}}. \quad (\text{A5})$$

487 Thus, at the mixing isoline defined by $\bar{C} + C' = 0.5$,

$$\frac{1}{2} - \frac{x - \bar{u}t}{\sqrt{4\pi D_t t}} + \frac{\bar{u}}{8D} \left(2y^2 - \frac{y^4}{h^2} - \frac{7}{15}h^2 \right) \frac{1}{\sqrt{4\pi D_t t}} \left(1 - \frac{(x - \bar{u}t)^2}{4D_t t} \right) = \frac{1}{2}, \quad (\text{A6})$$

488 we can simplify this equation and derive an explicit analytical expression for the slope of
 489 the 0.5 isoline with respect to y :

$$\frac{\partial x}{\partial y} = -\frac{\bar{u}}{2D} \left(y - \frac{y^3}{h^2} \right). \quad (\text{A7})$$

490 Also, by integrating (A3) with respect to y once and applying no-flux boundary conditions,
 491 we show that the mixing interface slope $m(y)$ at asymptotic times, can be expressed as
 492 the ratio of transverse gradient of concentration fluctuations to the longitudinal gradient of
 493 mean concentration as:

$$m(y) = \frac{\partial x}{\partial y} = -\frac{\frac{\partial C'}{\partial y}}{\frac{\partial \bar{C}}{\partial x}} = \frac{\bar{u}}{2D} \left(y - \frac{y^3}{h^2} \right). \quad (\text{A8})$$

494 That is, the slope of the 0.5 isoline $\frac{\partial x}{\partial y}$ equals the ratio of the transverse gradient of concen-
 495 tration fluctuations to the longitudinal gradient of mean concentration at $x = \mu_1(t)$. Lastly,
 496 due to the symmetry of the concentration field around the central line ($y = 0$), the mixing
 497 interface plateau length (L_∞) can be expressed as:

$$L_\infty = 2 \int_0^h \sqrt{1 + \frac{\bar{u}^2}{4D^2} \left(y - \frac{y^3}{h^2} \right)^2} dy. \quad (\text{A9})$$

498 **Appendix B: Quantifying the Lamella Width $2h_c$**

499 In this appendix, we propose an alternative method to quantify the lamella width $2h_c$ at
 500 asymptotic times. This approach does not rely on fitting $L_\infty^*(Pe_c)$ to the observed plateau

length growth. First, we use the asymptotic mixing interface slope in equation (8) to find its mean value ($\bar{m}$) over a half lamella width, $y \in [0, h_c]$, as

$$\bar{m}(t = \infty) = \frac{1}{h_c} \int_0^{h_c} \frac{u}{2D} \left(y - \frac{y^3}{h_c^2} \right) dy = \frac{u}{8D} h_c. \quad (\text{B1})$$

Next, we apply the formula derived in Appendix E for the relationship between the global effective dispersion coefficient $D_e(t)$ and the mean mixing interface slope $\bar{m}(t)$. At asymptotic times, $D_e(t)$ equals the asymptotic longitudinal dispersion coefficient D_l^∞ ,

$$D_l^\infty = D(1 + 1.25(\frac{u}{8D} h_c)^2). \quad (\text{B2})$$

As advective tortuosity (γ) increases in the porous media, the lamella transverse width, which aligns with the transverse gradients $\overline{\nabla_y C'}(t)$, also increases. Therefore, equation B2 can be rewritten to isolate h_c and account for tortuosity as

$$2h_c = 16 \frac{\gamma D}{u} \sqrt{\frac{D_l^\infty/D - 1}{1.25}}. \quad (\text{B3})$$

This is the general formula for the lamella width. As a consistency check for Poiseuille flow, one can substitute the Taylor dispersion coefficient ($D_T = D + \frac{2}{105} \frac{\bar{u} h^2}{D}$) into equation B3 to show that $h_c = h$. When $D_l^\infty/D \gg 1$, the lamella width simplifies to

$$2h_c \approx \frac{\gamma}{u} \sqrt{205 D_l^\infty D}. \quad (\text{B4})$$

This formula yields a consistent scaling with that of equation (14) ($2h_c \propto Pe^{-0.45}$).

Appendix C: Alternative Solution to Gradients at $x = \mu_1(t)$

In this appendix, we propose an alternative solution to quantify the mixing interface line mean slope $\bar{m}(t)$ by separately quantifying (1) $\overline{\nabla_y C'}(t)$, and (2) $\nabla_x \bar{C}(t)$, whose ratio is $\bar{m}(t)$

$$\bar{m}(t) = - \left[\frac{\overline{\nabla_y C'}(t)}{\nabla_x \bar{C}(t)} \right]_{\mu_1(t)}. \quad (\text{C1})$$

(1) Assuming that the concentration profile along any transverse level/location (y_t) follows a complementary error function with its center moving at an apparent velocity $u_a(t)|_{y_t}$

$$C(x, t)_{y_t} = \frac{1}{2} \text{erfc} \left[\frac{x - u_a(t)|_{y_t} t}{\sqrt{4D_l t}} \right]. \quad (\text{C2})$$

where $D_l(t)$ is the longitudinal dispersion coefficient. Hence, the concentration fluctuations at $x = \mu_1(t)$ and $y = y_t$ can be expressed as

$$C'(t)_{y_t, \mu_1(t)} = \frac{1}{2} \operatorname{erfc} \left[\frac{\mu_1(t) - u_a(t)|_{y_t} t}{\sqrt{4D_l t}} \right] - 0.5 = -\frac{1}{2} \operatorname{erf} \left[\frac{\bar{u} - u_a(t)|_{y_t}}{2} \sqrt{\frac{t}{D_l}} \right]. \quad (\text{C3})$$

$u_a(t)|_{y_t}$ is quantified using the history of sampled velocities due to molecular diffusion across $y \in [-h_C, h_C]$ of a pulse initial condition at $y = y_t$. For a comprehensive discussion, we refer the reader to [19]. This approach assumes a Darcy-scale longitudinal velocity profile that remains constant in x . The position history distribution $P(y, t)|_{y_t}$ can be obtained by integrating the Green's function over time and assuming a Fickian transverse diffusion. This reads:

$$P(y, t)|_{y_t} = \sum_{\psi=-\infty}^{\infty} \frac{|y - y_t - 2\psi h_C|}{4\sqrt{\pi}Dt} \Gamma \left[-0.5, \frac{(y - y_t - 2\psi h_C)^2}{4Dt} \right], \quad (\text{C4})$$

where $\Gamma[\psi, z]$ is the upper incomplete gamma function. While (C4) includes summation over an infinite range of ψ virtual sources, in practical applications, ψ is chosen to be large enough to ensure that the integral of $P(y, t)|_{y_t}$ over $y \in [-h_C, h_C]$ equals one. Lastly, the apparent velocity is quantified as the convolution of (a) $P(y, t)|_{y_t}$ and (b) the mean longitudinal velocity $u(y)$ as:

$$u_a(t)|_{y_t} = \int_{-h_C}^{h_C} P(y, t)|_{y_t} u(y) dy. \quad (\text{C5})$$

Lastly, the mean transverse gradient can be quantified using equation (12).

(2) The gradient of the mean concentration in the longitudinal direction $\nabla_x \bar{C}(t)$ at $\mu_1(t)$ can be quantified by the maximum gradient of the one-dimensional [53] solution for the advection diffusion equation with a continuous injection and a Heaviside initial condition.

$$\nabla_x \bar{C}(t) = \frac{1}{2\sqrt{\pi D_l(t)t}}. \quad (\text{C6})$$

For transport in Poiseuille flow, one could get a closed analytical solution by replacing the longitudinal dispersion coefficient in equations (C2), (C3), and (C6) with the effective dispersion coefficient proposed in Appendix D. For porous media, the longitudinal dispersion coefficient $D_l(t)$ could be measured using the temporal change of the plume spreading $\mu_2(t)$ as

$$D_l(t) = \frac{1}{2} \frac{\partial \mu_2(t)}{\partial t}. \quad (\text{C7})$$

540 **Appendix D: Equality Between the Mixing Interface Length $L(t)$ and the Integral**
 541 **of Pore-Scale Concentration Gradients $G(t)$**

542 In this appendix, we demonstrate that the Poiseuille-based model predicts an equality be-
 543 tween the mixing interface length $L(t)$ and the integral of pore-scale concentration gradients
 544 $G(t)$. Specifically, we show that:

$$L(t) = G(t) = \iint_{\Omega} \|\nabla C(x, y, t)\| \partial A, \quad (\text{D1})$$

545 where $C(x, y, t)$ is the concentration field, and Ω represents the spatial domain. To proceed,
 546 we express the magnitude of the concentration gradient in terms of its x - and y -components.
 547 This allows us to rewrite $G(t)$ in terms of the slope $m(x, y, t)$ as:

$$G(t) = \int_{-h_c}^{h_c} \int_{-\infty}^{\infty} \sqrt{(\nabla_y C)^2 + (\nabla_x C)^2} \partial x \partial y = \int_{-h_c}^{h_c} \int_{-\infty}^{\infty} |\nabla_x C| \sqrt{m^2 + 1} \partial x \partial y, \quad (\text{D2})$$

548 where $m(x, y, t)$ is defined as the slope of the concentration isolines. To obtain an expression
 549 for $m(x, y, t)$, we refer to the approach detailed in Section 4.2. Solving the governing equation
 550 for the concentration fluctuation, we find that the leading-order approximation of $C'(x, y, t)$
 551 is:

$$C'(x, y, t) = -\frac{6\bar{u}h_c^2}{\pi^4 D} \cos\left(\frac{\pi y}{h_c}\right) \left(1 - e^{-\frac{\pi^2 D t}{h_c^2}}\right) \frac{\partial \bar{C}}{\partial x}. \quad (\text{D3})$$

552 Taking the derivative of $C'(x, y, t)$ with respect to y , we obtain an expression for $m(x, y, t)$:

$$m(y, t) = \frac{\frac{\partial C'(x, y, t)}{\partial y}}{\frac{\partial \bar{C}}{\partial x}} = \frac{6\bar{u}h_c}{\pi^3 D} \sin\left(\frac{\pi y}{h_c}\right) \left(1 - e^{-\frac{\pi^2 D t}{h_c^2}}\right). \quad (\text{D4})$$

553 This shows that $m(y, t)$ is independent of x , meaning that all concentration isolines in the
 554 domain have the same slope function (constant-length isocontours). Using the expression
 555 for $m(y, t)$, we can now approximate $G(t)$ in equation (D2) as:

$$G(t) \approx 2 \int_0^{h_c} \int_{-\infty}^{\infty} |\nabla_x C| m(y, t) \partial x \partial y \approx 2 \int_0^{h_c} \int_{-\infty}^{\infty} \frac{e^{-\frac{(x-\bar{u}t)^2}{4Dt}}}{\sqrt{4\pi Dt}} m(y, t) \partial x \partial y. \quad (\text{D5})$$

556 Solving this integral yields an explicit expression for $G(t)$:

$$G(t) \approx \frac{24\bar{u}h_c^2}{\pi^4 D} \left(1 - e^{-\frac{\pi^2 D t}{h_c^2}}\right). \quad (\text{D6})$$

557 Finally, approximating the expression for $L(t)$ (as outlined in equation (11)) and using the
 558 leading-order approximation from equation (18), we find:

$$L(t) \approx 2h_c \bar{m}(t) \approx \frac{24\bar{u}h_c^2}{\pi^4 D} \left(1 - e^{-\frac{\pi^2 D t}{h_c^2}}\right). \quad (\text{D7})$$

Thus, we conclude that $L(t) = G(t)$, demonstrating that the proposed Poiseuille-based model for $L(t)$ is consistent with the equality observed in Figure (3) for a porous medium.

Appendix E: Quantifying the Effective Dispersion Coefficient $D_e(t)$ Using the Mixing Interface Mean Slope $\bar{m}(t)$

In this appendix, we demonstrate how to directly calculate the effective dispersion coefficient $D_e(t)$ for a line source using the mixing interface mean slope, $\bar{m}(t)$. To begin, we introduce the following dimensionless quantities:

$$\hat{x} = \frac{x}{h}, \quad \hat{y} = \frac{y}{h}, \quad \hat{C} = \frac{C}{C_{ref}}, \quad \hat{t} = \frac{t}{t_D}, \quad \hat{u} = \frac{\bar{u}h}{D}, \quad (\text{E1})$$

Using Reynolds decomposition, as discussed in Appendix A, the governing equation for the average concentration can be expressed as:

$$\frac{\partial \hat{C}}{\partial \hat{t}} + Pe \frac{\partial \hat{C}}{\partial \hat{x}} = \frac{\partial^2 \hat{C}}{\partial \hat{x}^2} - \frac{\partial \left(\overline{\hat{u}'(\hat{y}) \hat{C}'} \right)}{\partial \hat{x}}. \quad (\text{E2})$$

Using the closure approximation from equation (15), [50] showed that the average model can be closed as follows:

$$\frac{\partial \hat{C}}{\partial \hat{t}} + Pe \frac{\partial \hat{C}}{\partial \hat{x}} = \hat{D}_a(t) \frac{\partial^2 \hat{C}}{\partial \hat{x}^2} + \phi(\hat{x}, \hat{t}), \quad (\text{E3})$$

where $\phi(\hat{x}, \hat{t})$ is a memory function accounting for the initial condition's effects, and $\hat{D}_a(t) = \frac{D_a(t)}{D}$ is the normalized, time-dependent, apparent Taylor-dispersion coefficient:

$$D_a(t) = D - D \int_0^1 \hat{u}'(\hat{y}) b_1(\hat{y}, \hat{t}) d\hat{y}. \quad (\text{E4})$$

An analogous approach to that in Section IV.B yields:

$$b_1(\hat{y}, \hat{t}) = \sum_{\alpha=1}^{\infty} \frac{12Pe(1 + (-1)^\alpha) \left(1 - e^{-\alpha^2 \pi^2 \hat{t}}\right) \cos(\alpha \pi \hat{y})}{\alpha^4 \pi^4}. \quad (\text{E5})$$

Approximating (E5) using the leading-order term ($\alpha = 2$), we solve for the apparent dispersion coefficient:

$$D_a(t) = D + D \left[\frac{9}{2\pi^6} Pe^2 \left(1 - e^{-4\pi^2 \hat{t}}\right) \right]. \quad (\text{E6})$$

[54] showed that the global effective dispersion coefficient for a line source can be calculated using the apparent dispersion as:

$$D_e(t) = 2D_a(t) - D_a(2t) . \quad (\text{E7})$$

Substituting (E6) into (E7) and rearranging, we obtain the explicit solution for the effective dispersion coefficient:

$$D_e(t) = D \left[1 + \frac{9}{2\pi^6} P e^2 \left(1 - e^{-4\pi^2 \hat{t}} \right)^2 \right]. \quad (\text{E8})$$

Finally, by recalling the expression for the transient mixing interface mean slope, as given in equation (18), we show that the global effective dispersion coefficient can be directly quantified using the mean slope $\bar{m}(t)$ as:

$$D_e(t) = D(1 + 1.25\bar{m}^2(t)). \quad (\text{E9})$$

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