Predictions of dynamic changes in reaction rates as a consequence of incomplete mixing using pore scale reactive transport modeling on images of porous media

Z. Alhashmi *, M.J. Blunt, B. Bijeljic

Department of Earth Science and Engineering, Prince Consort Road, Imperial College London, London SW7 2BP, United Kingdom

Abstract

We present a pore scale model capable of simulating fluid/fluid reactive transport on images of porous media from first principles. We use a streamline-based particle tracking method for simulating flow and transport, while for reaction to occur, both reactants must be within a diffusive distance of each other during a time-step. We assign a probability of reaction \( P_r \), as a function of the reaction rate constant \( k_r \) and the diffusion length. Firstly, we validate our model for reaction against analytical solutions for the bimolecular reaction \( A + B \rightarrow C \) in a free fluid. Then, we simulate transport and reaction in a beadpack to validate the model through predicting the fluid/fluid reaction experimental results provided by Gramling et al. (2002). Our model accurately predicts the experimental data, as it takes into account the degree of incomplete mixing present at the sub-pore (image voxel) level, in contrast to advection–dispersion reaction equation (ADRE) model that over-predicts pore scale mixing. Finally, we show how our model can predict dynamic changes in the reaction rate accurately accounting for the local geometry, topology and flow field at the pore scale. We demonstrate the substantial difference between the predicted early-time reaction rate in comparison to the ADRE model.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

Keywords:
Fluid/fluid
Reactive transport
Pore-scale
Micro-CT image
Mixing
Reaction rate

1. Introduction

Fluid/fluid reactive transport is an important field of study in the earth sciences. It is a combination of fluid transport and chemical reactions between migrating fluids and/or organisms in the subsurface. It occurs as natural phenomena as well as in industrial and environmental applications, such as the transport of pollutants in the subsurface, nuclear waste storage, and carbon dioxide \((\text{CO}_2)\) storage (Lichtner et al., 1996). Coupled reaction and transport is traditionally described at the macro-scale by the advection–dispersion reaction equation (ADRE) defined in one-dimensional (1D) form as (Sahimi, 1995):

\[
\frac{\phi}{\partial t} \frac{\partial c}{\partial x} = -q \cdot (qc) + \nabla \cdot (\phi D \nabla c) + R
\]

where \( \phi \) is porosity, \( c \) is the molar concentration (moles/m\(^3\)), \( q \) is the Darcy velocity (m/s), \( D \) is the dispersion coefficient (m\(^2\)/s), and \( R \) is the reaction rate (moles/m\(^3\) s).

However, even without reaction \( (R = 0 \text{ in Eq. (1)}) \), the traditional advection–dispersion equation (ADE) has proven to be inadequate to predict solute transport in the subsurface: several authors have shown poor agreement between predictions using the ADE and laboratory studies (Cortis and Berkowitz, 2004; Levy and Berkowitz, 2003; Moroni et al., 2007; Silliman and Simpson, 1987; Sternberg et al., 1996) and...
We assign a probability of reaction between neighboring reactants that can be related to the batch reaction rate. We first validate the model for reaction in a free fluid against analytical solutions. Next, we test and validate our predictions for reactive transport in porous media by comparing them with the results of experiments by Gramling et al. (2002). We then quantify the degree of incomplete mixing at the pore scale and calculate its impact on the dynamic change in reaction rates. This new pore scale model is capable of handling irregular geometries characterizing the images of pore space, providing predictions of time-dependent dispersion coefficients and reaction rate.

2. Model description

The fluid/fluid reactive transport model consists of four main parts described in this section: pore-space geometry, flow, transport, and chemical reaction.

2.1. Pore-space geometry

We use an experimental beadpack image to represent the porous medium, as shown in Fig. 1. This is a random close packing of equally-sized spherical grains whose coordinates are measured (Finney, 1970) and for which the segmentation into an image has been performed by Prodanović and Bryant (2006). The grains have a diameter of $1.3 \times 10^{-3}$ m, as in the experiments by Gramling et al. (2002). The image is represented on a Cartesian grid consisting of $500 \times 500 \times 500$ grid-voxels (corresponding to $x$, $y$, and $z$ dimensions respectively) with a porosity $\phi$ of 36.24%. Each grid-voxel represents either a pore or solid voxel; $\phi$ is defined as the ratio between the number of pore voxels to the total number of voxels. The voxels have a size of $2.6 \times 10^{-5}$ m in all dimensions; $\Delta x = \Delta y = \Delta z$. The image consists of 10 grain sizes in each direction which provides a representative pore structure of a beadpack.

2.2. Flow

The geometry, solid surface properties, and the initial and boundary conditions have to be defined to simulate incompressible Newtonian flow governed by the Navier–Stokes equations:

$$\nabla \cdot \mathbf{u} = 0$$  \hspace{2cm} (2)
\[-\nabla P + \mu \nabla^2 \mathbf{u} = \rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) \quad (3)\]

where \( \rho \) is the density (here we use water with \( \rho = 1000 \text{ kg/m}^3 \)), \( \mu \) is the dynamic viscosity (\( \mu = 0.001 \text{ Pa s} \)), \( \mathbf{u} \) is the velocity vector (m/s), and \( P \) is the pressure. We calculate the single-phase flow field in the voxels of pore space by the method presented in Raeini et al. (2012) and Bijeljic et al. (2013) that is based on an implementation of the finite volume method using OpenFOAM (OpenFOAM, 2011). Both velocity and pressure fields are solved by implementing the pressure implicit with splitting of operators (PISO) algorithm. On solid boundaries, the normal and tangential components of the velocity are zero. A constant pressure drop is assumed across the model, and the velocities in a grid cell are linear without a solid boundary the velocities in a grid cell are linear.

2.3. Transport

We track the motion of particles for every time-step by advection and diffusion,

\[ \mathbf{x}(t + \Delta t) = \mathbf{x}(t) + \mathbf{x}_{\text{Advection}} + \mathbf{x}_{\text{Diffusion}} \quad (4) \]

where the vector \( \mathbf{x} \) labels particle position.

We use a streamline-based method for advective particle tracking through the pore voxels (\( \mathbf{x}_{\text{Advection}} \)) that incorporates a novel formulation accounting for zero flow at the solid wall boundaries (Nuñes-Pereira et al., 2015), which is an extension of Pollock’s algorithm (Pollock, 1988) commonly used for field scale applications (Batycky et al., 1997). For void voxels without a solid boundary the velocities in a grid-cell are linear interpolations of the voxel face velocities as in the Pollock algorithm; however, for the pore voxels bounded by solid walls semi-analytical streamline tracing is more complex. The analytical solutions for velocities in these cases have been provided elsewhere (Nuñes-Pereira et al., 2015). This approach determines particle advective motion within a voxel as well as the exit position. One of the main advantages of this method is that particles can travel several voxels in single time-step without error if advection dominates, and thus reduces the computational cost of the simulation.

The movement of particles by diffusion (\( \mathbf{x}_{\text{Diffusion}} \)) is based on a random walk, which is a series of random spatial displacements based on the mean diffusive displacement (\( \xi \)) that define particle transitions (Bijeljic et al., 2013) such that:

\[ \xi = \sqrt{6D_m \Delta t} \quad (5) \]

\[ x_{\text{Diffusion}} = \xi \sin \varphi \cos \theta \quad (6a) \]

\[ y_{\text{Diffusion}} = \xi \sin \varphi \sin \theta \quad (6b) \]

\[ z_{\text{Diffusion}} = \xi \cos \varphi \quad (6c) \]

where \( \Delta t \) is the time-step size (s), \( D_m \) is the molecular diffusion coefficient (m²/s), and the particle vector position (\( \mathbf{x}_{\text{diffusion}} \)) has components \( x, y, \) and \( z \). \( \varphi \) and \( \theta \) are random numbers in the range from 0 to \( 2\pi \) and 0 to \( \pi \) respectively.

2.4. Reaction

We simulate the irreversible reaction \( A + B \rightarrow C \). Since the reaction is a second order irreversible reaction, the general formula for reaction rate \( r \) (mol/m² s) is given by (Petrucci et al., 2002):

\[ r = \frac{dc_c}{dt} = -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = k_r c_A c_B \quad (7) \]

where \( k_r \) is the reaction rate constant (m³/mol s). The subscripts \( A \), \( B \), and \( C \) denote the chemical species \( A \), \( B \), and \( C \) respectively, and \( c \) is the molar concentration per unit pore volume (mol/m³).

We move both particles \( A \) and \( B \) by advection and diffusion as described in the previous section. In each time-step, we allow reaction. We allow particles \( A \) and \( B \) to react if they are less than a distance \( \xi \) (Eq. (5)) apart. If there is more than one possible reaction within a distance \( \xi \), the closest reactant pair is considered first. After reaction, the product \( C \) replaces particles \( A \) and \( B \) and is placed in the position equidistant between \( A \) and \( B \).

The reaction between two particles only occurs with a randomly assigned probability, \( P_r \), which is related to the reaction rate constant \( k_r \). The reaction zone (or sphere) in which reactions may occur has a radius \( \xi \). The number of reactions (\( M_r \)) in each time-step \( \Delta t \) is given by:

\[ M_r = N_A N_B P_r = C_A C_B V_z^2 P_r \quad (8) \]

where \( N_A \) and \( N_B \) are the number of particles \( A \) and \( B \) that can react (they lie within the sphere), \( C_A \) and \( C_B \) are the concentrations of \( A \) and \( B \) (number of particles per unit volume) and \( V_z \) is the volume of the reaction zone = \( \pi \xi^3 \).

Let \( n \) represent the number of moles that each particle in the simulation represents. Then \( c = nC \), where \( c \) is the particle concentration in moles per unit volume. Then the number of moles (\( n_r \)) that react is:

\[ n_r = \frac{n C c A c B}{N_A N_B} V_z^2 P_r \quad (9) \]

The reaction rate \( r \) with units of moles per unit volume per unit time (mol/m³ s) is:

\[ r = \frac{n C c A c B}{N_A N_B} \frac{V_z^2 P_r}{\Delta t} \quad (10) \]

In our simulations we have \( n = n_A = n_B = n_C \); every particle represents the same number of moles, regardless of chemical species. Then \( r \) in Eq. (10) can be written as:

\[ r = \frac{c A c B V_z^2 P_r}{n} \quad (11) \]
Hence from Eq. (7), we can find a relationship between \( P_r \) and \( k_r \):

\[
P_r = \frac{n \Delta t}{V} k_r. \tag{12}
\]

Then using Eq. (5) \( P_r \) is:

\[
P_r = \frac{n}{8n D_m S} k_r. \tag{13}
\]

This approach is conceptually similar to the work of Hansen et al. (2014) in a CTRW framework in which a rigorous relationship between reaction radius and rate of reaction was derived. In that work \( P_r \) was defined to be 1; here it can take any value \( \leq 1 \). It is worth mentioning that in this work both reactants have the same \( D_m \) therefore the reaction zone is fixed for both reactants. However in the case that the value of \( D_m \) differs between reactants, the \( D_m \) for the limiting reactant is chosen.

All the model simulations were carried out on a single Linux cluster with 12 CPUs in parallel provided by Imperial College High Performance Computing (HPC) Service.

3. Results and discussion

In this section we first validate the model by comparing the results of our simulations for reaction in a free fluid against analytical solutions. Then we test and validate our predictions for reactive transport in porous media by comparing our predictions with the experimental results of Gramling et al. (2002). Finally, we demonstrate how our model can predict dynamic changes in the reaction rate.

3.1. Analytical solutions

We consider a batch system with no porous medium and no flow. From Eq. (7), the analytical solution for second order irreversible reaction is given by:

\[
\Delta C_{AB} = \frac{C_{A0}}{C_{B0}} \cdot \frac{e^{-k_r t \Delta x}}{e^{-k_r \Delta x} - 1}. \tag{14a}
\]

\[
\frac{C_A}{C_{A0}} = \frac{C_{A0}}{C_{B0}} \cdot \frac{e^{-k_r t \Delta x}}{e^{-k_r \Delta x} - 1}, \quad C_{A0} \neq C_{B0}
\]

\[
\frac{C_B}{C_{B0}} = \frac{\Delta C_{AB}}{\frac{C_{A0}}{C_{B0}} \cdot \frac{e^{-k_r t \Delta x}}{e^{-k_r \Delta x} - 1}}, \quad C_{A0} \neq C_{B0}
\]

(14b)

where \( C_0 \) represents the initial concentration (mol/m³). The model system size is \( 70 \times 70 \times 70 \) cubic grid-voxels of length \( \Delta x = 2.6 \times 10^{-5} \) m. In this exercise, we place 12,912 particles of A in the domain; this number is chosen so that the average number of particles per grid-block (= \( 3.76 \times 10^{-2} \) particles/grid-voxel) is the same as used to predict the Gramling et al. (2002) experiment in the next section. For simplicity, in this example, one particle in the model represents one molecule in a real system and therefore \( n = \frac{1}{A_N} \), where \( A_N \) is Avogadro’s number. Reactants are placed randomly inside the batch system with the initial concentration of B being half of A. This represents \( C_{A0} = 3.56 \times 10^{-12} \) mol/m³ and \( C_{B0} = 1.78 \times 10^{-12} \) mol/m³. \( D_m \) is set to be \( 7.02 \times 10^{-11} \) m²/s (Gramling et al., 2002). We take the maximum \( \Delta t \), such that \( \xi = \Delta x \). Hence, in this example, this yields \( \Delta t = 1.6 \) s. We take \( P_r = 0.01 \); from Eq. (13) this means \( k_r = 2.76 \times 10^8 \) m³/mol s. Choosing a smaller \( \Delta t \) does not affect the results; later when we predict the Gramling et al. (2002) experiment we choose a \( \Delta t \) such that \( \xi = \Delta x \).

The model is compared against the analytical solution (Eq. (14)). We define a dimensionless time \( t_\theta = k_r \Delta C_{AB} \), where \( \Delta C_{AB} = C_A - C_B \) is constant (mol/m³) and a dimensionless concentration, \( C_\theta = \frac{C}{C_{A0}} \). Fig. 2 shows the change in \( C_\theta \) for both reactants A and B and the product C as a function of \( t_\theta \). The model predicts the change in concentration with a high degree of accuracy.

Fig. 3 shows the reaction rate \( r \) for both the model and the analytical solution. As expected, the model closely agrees with the analytical solution; in particular we have a sufficient number of particles to model accurately at least a ten-fold variation in reaction rates. These results, with the time-step and density of particles used, suggest that we can apply the reaction algorithm to obtain accurate results for reaction in porous media that will be shown in Section 3.2.

3.2. Comparison with the fluid/fluid reactive transport experiment by Gramling et al. (2002)

3.2.1. Gramling model

Gramling et al. (2002) conducted an experiment of bimolecular reactive transport (A + B → C) in a beadpack. The beads were packed in a rectangular cross section chamber that had a length 0.36 m, height 0.055 m, and width 0.018 m. The beads had an average diameter of \( 1.3 \times 10^{-3} \) m. The reactants were aqueous solutions of sodium EDTA (Na₂EDTA\(^{2-}\)), which is reactant A, and copper sulfate (CuSO₄), which is reactant B, while the product C is copper EDTA (CuEDTA\(^{2+}\)). They measured the relative concentration of product C to the initial concentration of reactant A (\( C/C_{A0} \)) as a function of distance. They compared the measurement results with the solution to an analytical model using a 1D ADRE, Eq. (1), for which the analytical solution for instantaneous local reaction is (Marshall et al., 1996):

\[
\frac{C}{C_{A0}} = \frac{1}{2} \text{erfc} \left( \frac{-x + \frac{q}{\phi} t}{2 \sqrt{D_l t}} \right), \quad x < \frac{q}{\phi} t \tag{15a}
\]

\[
\frac{C}{C_{A0}} = \frac{1}{2} \text{erfc} \left( \frac{x - \frac{q}{\phi} t}{2 \sqrt{D_l t}} \right), \quad x > \frac{q}{\phi} t \tag{15b}
\]

where \( x \) is the distance (m) from the inlet of the chamber and \( D_l \) is longitudinal dispersion coefficient (m²/s), while the reaction rate \( r \) is:

\[
r = \frac{A_c C_{A0}}{V} \sqrt{\frac{D_l}{\pi t}} \tag{16}
\]

where \( A_c \) is the chamber cross sectional area (m²) and \( V \) is the volume of the system (m³). They found that the maximum
concentration of the product C in the experiment was at least 20% lower than the maximum concentration estimated by the ADRE, Eq. (15). The total mass of C produced by the ADRE $m_{C}^{ADRE} (g)$ can be defined by:

$$m_{C}^{ADRE} = 2 \cdot \phi_{C} C_{0} M_{WI} \sqrt{\frac{D_{L} \tau}{\pi}}$$  \hspace{1cm} (17)$$

where $M_{WI}$ is the molecular mass of C which is equal to 351.75 g/mol.

We simulate transport and reaction through a beadpack image with similar properties to the experiment (Table 1).

Initially, reactant A represented by 35 million particles is placed randomly in the pore-space volume consisting of 19 images in series, the dimensions of which are given in Table 1. The model maintains the same initial $C_{0} = 2.34 \times 10^{15}$ particles/m$^{3}$ concentration of the product C in the experiment as a function of dimensionless time $t_{d}$; solid lines are the results from the analytical solution and the dashed lines are from the model.

Fig. 2. Dimensionless concentration $c_0$ as a function of dimensionless time $t_d$; solid lines are the results from the analytical solution and dashed lines are obtained from the model.

We run the model and compare the results with the experiment at four times: $t_1 = 619$ s, $t_2 = 916$ s, $t_3 = 1114$ s, and $t_4 = 1510$ s, as stated in Gramling et al. (2002). The computational time for our model simulation is 67 h and 27 min. Fig. 4 shows 3D coordinates and 2D projections of particle positions in the pore space at these times. In the figure we define particle dimensionless positions in 3D with the coordinates $x_D = \frac{x}{x_{max}}, y_D = \frac{y}{y_{max}}, z_D = \frac{z}{z_{max}}$ where $x, y,$ and $z$ are the $x, y, z, l$ coordinates.

3.2.2. Comparison with experiment

We run the model and compare the results with the experiment at four times: $t_1 = 619$ s, $t_2 = 916$ s, $t_3 = 1114$ s, and $t_4 = 1510$ s, as stated in Gramling et al. (2002). The computational time for our model simulation is 67 h and 27 min. Fig. 4 shows 3D coordinates and 2D projections of particle positions in the pore space at these times. In the figure we define particle dimensionless positions in 3D with the coordinates $x_D = \frac{x}{x_{max}}, y_D = \frac{y}{y_{max}}, z_D = \frac{z}{z_{max}}$ where $x, y,$ and $z$ are the $x, y, z, l$ coordinates.

The reaction rate $r$ as a function of dimensionless time $t_{d}$; solid lines represent the results from the analytical solution and dashed lines are obtained from the model.

Fig. 3. The reaction rate $r$ as a function of dimensionless time $t_{d}$; solid lines represent the results from the analytical solution and dashed lines are obtained from the model.
coordinates of particle displacement (m) from the inlet and \(x_{\text{max}}, y_{\text{max}}, z_{\text{max}}\) is the system size, as defined in Table 1.

As expected, the reaction occurs in the regions where both reactants mix, causing the product C concentration to increase. This is seen in Fig. 5 which shows the profile of the \(C_r/C_{r0}\) ratio (the ratio of product C concentration to the initial concentration of reactant A) at different times. We note that the increase in \(C_r/C_{r0}\) ratio is the most pronounced at early times (e.g. compare the peaks for the ratios at \(t = 100\) s and \(t = 200\) s with the peaks for the ratios for, say, \(t = 400\) s and \(t = 500\) s).

We predict the results with no adjustable parameters. The model accurately predicts the experimental profiles of the product C at all times recorded in the experiment. The predicted mean displacement for \(t_2\) and \(t_4\) agrees well with the experimental data, while for times \(t_1\) and \(t_3\) there is a slight difference. Based on the velocity \(u_{\text{avg}} = 1.21 \times 10^{-4}\) m/s reported in the experiment and applied in our model, the mean displacement should be \(\tau = u_{\text{avg}}t = 0.0749\) m (for \(t_1\)) = 0.1108 m (for \(t_2\)) = 0.1348 m (for \(t_3\)) and = 0.1827 m (for \(t_4\)) which is what our model predicts accurately. However, the experimental data shows that the measured displacement differs from the mean displacement. For \(t_4\), it is slightly higher and it is slightly lower for \(t_3\). This explains the shift in the concentrations profile for our model whether to the left (for \(t_1\)) or to the right (for \(t_3\)).

We explain the dynamic reactive transport behavior by studying the spreading and mixing of reactants. From the model, the spreading can be described by calculating the longitudinal dispersion coefficient \(D_L\), defined by:

\[
D_L = \frac{1}{2} \frac{d\sigma^2}{dt}
\]  

where \(\sigma^2\) is the variance of the particles displacement (Bijeljic et al., 2004). Fig. 6 indicates that \(D_L\) increases over time reaching the same asymptotic value of 1.53 \times 10^{-7} m^2/s for both particles A and B. However, since A is initially present in the pore space, while B is injected, B reaches the asymptotic value later (\(t = 470\) s) as it takes more time to fully sample the velocity field than for A (\(t = 230\) s). These times correspond to an average distances traveled of approximately 21 grain diameters for A and 43 grain diameters for B.

Fig. 6 demonstrates that the amount of spreading is lower at early times when fluids are in the pre-asymptotic regime, which leads to a lower degree of mixing of reactants. This results in a lower reaction rates than if the fluids are assumed to be perfectly mixed as when using the asymptotic dispersion coefficient. However, the asymptotic dispersion coefficient obtained in the non-reactive tracer experiment in Gramling et al. (2002) was 1.75 \times 10^{-7} m^2/s. This means that their experimentally measured longitudinal dispersion coefficient values at \(t_1, t_2, t_3,\) and \(t_4\) were taken in the asymptotic dispersion regime. Since these values do not describe well the fluid transport at early times, when used in ADRE they do not yield accurate results for the product concentration and the reaction rate. The analytical solution of ADRE (Eq. (15)) using a best-fit value of the longitudinal dispersion coefficient \(D_L = 1.75 \times 10^{-7} m^2/s\) over-estimates the concentration of C due to the assumption of perfect mixing with a fixed value of \(D_L\) (see Fig. 5). This compares well with the work of Sanchez-Vila et al. (2010) in which they state that the best-fit for \(D_L\) between the experimental times to their model results is 1.3 \times 10^{-7} m^2/s. Note, however that in our study we take into account the time departure of \(D_L\) in the pre-asymptotic region, which has major effects on the scale of spreading and amount of mixing and thus the reaction rate. Previous work (e.g. Edery et al., 2010; Sanchez-Vila et al., 2010) has pointed out that incomplete mixing explains the discrepancy between the experiment and the ADRE solution. From our pore scale simulations we are able to show how incomplete spreading characterized by a time-dependent dispersion coefficient leads to prolonged incomplete mixing which is the key determinant for early time reactive behavior. An additional advantage is that our model does not presuppose a dispersion coefficient but predicts its dynamic behavior from simulation that takes into account reaction. This capability is important as dispersion in the case of reactive transport can be different from that observed for conservative solutes (Porta et al., 2012).

We note that our model can predict the early-time transport and reaction behavior that is not readily available by the experiment. This has an advantage to look into the pore scale reaction rate dynamic change induced by incomplete mixing which we study in the next section. Moreover, our model does not need a conceptual picture of porous media—instead it solves for flow, transport and reaction directly in the image voxels of the pore space, which accurately defines the geometry and flow field at the sub-pore level.

3.2.3. Effective reaction rate

In this experiment the reaction is so fast that the overall reaction rate is controlled by the extent of pore scale mixing. The ADRE assumes that particles are perfectly mixed and react (in this case there is the limit of a fast reaction with \(t_D >> 1\)). However, at the pore scale, individual particles may not be
within reactive distance, since they are not completely mixed by the complex flow field. Fig. 7a shows the reaction rate \( r \) averaged over the whole beadpack as a function of pore volume for the model in comparison to the predicted \( r \) from the ADRE (Eq. (16)). The reaction rate \( r \) in the model is defined as the change in the product concentration over time or 
\[
    r = \frac{dc}{dt}.
\]
In the beginning the ADRE reaction rate is higher than in our model, as it assumes instantaneous mixing of reactants with the largest—asymptotic—value of \( D_i \). Our model predicts a reaction rate that initially increases as particles B are injected: it takes time for the combined interaction of molecular diffusion and the heterogeneous flow field to disperse the reactants (see Fig. 4).

**Fig. 4.** 3D (left) and 2D projections (right) showing particles of A (blue), B (red), C (green) at four different times; a) \( t_1 = 619 \) s, b) \( t_2 = 916 \) s, c) \( t_3 = 1114 \) s, and d) \( t_4 = 1510 \) s.
The total mass of C created in our model by the ratio of cross-sectional areas. Therefore to account all the volume, we multiply the total mass reported in their Fig. 6 do not agree with Eq. (21). For consistency we have used Eq. (21) for comparison purposes, since this clearly conserves mass.

Fig. 5. The profile of the ratio of product C concentration to the initial concentration of the reactant A. The solid lines are simulation results at 100 s, 200 s, 300 s, 400 s, 500 s, \( t_1 = 619 \) s, \( t_2 = 916 \) s, \( t_3 = 1114 \) s, and \( t_4 = 1510 \) s. The points are experimental data from Gramling et al. (2002) at \( t_1 = 619 \) s, \( t_2 = 916 \) s, \( t_3 = 1114 \) s, and \( t_4 = 1510 \) s. The dashed lines are the solution of the ADRE Eq. (15) at \( t_1 = 619 \) s, \( t_2 = 916 \) s, \( t_3 = 1114 \) s, and \( t_4 = 1510 \) s.

Once mixing and spreading due to dispersion are established, the dispersion coefficient becomes constant and the reaction rate is controlled by the extent of mixing and decreases as \( t^{-1/2} \) as in the ADRE, Eq. (16) (see Fig. 7b). The early-time behavior is captured in our model but not in the ADRE. This explains the persistent over-prediction of the peak in the ratio of concentration of C by the ADRE, which is fixed at 0.5 at all times (Fig. 5). Incomplete mixing is most apparent initially and leads to less reaction. This is seen as a smaller peak concentration evolving in both the experiments and our pore scale model (Fig. 5). The slightly higher reaction rate predicted by our model at the intermediate times (Fig. 7a) is due to more reactants being available when the asymptotic dispersion regime is first established. On the other hand, the slightly lower reaction rate at the late times is due to the limiting number of reactants available at the mixing zone.

The total mass of C created by our model \( \frac{m_{\text{Model}}}{m_{\text{Exp}}} \) (g) can be estimated by:

\[
m_{\text{Model}} = nN_C M_{\text{WT}} \left( \frac{\phi_{\text{Exp}} A_C^{\text{Exp}}}{\phi_{\text{Model}} A_C^{\text{Model}}} \right) \tag{20}
\]

where \( N_C \) is the total number of C particles created by time \( t \), and \( \left( \frac{\phi_{\text{Exp}} A_C^{\text{Exp}}}{\phi_{\text{Model}} A_C^{\text{Model}}} \right) \) is the ratio between the cross-sectional area of the experiment system to the cross-sectional area of our model. As mentioned earlier, the model does not take into consideration the full volume of the system, and therefore to account all the volume, we multiply the total mass of C created in our model by the ratio of cross-sectional areas. We also compare to the data using:

\[
m_{\text{Exp}} = \phi_{\text{Exp}} A_C^{\text{Exp}} M_{\text{WT}} \int_0^L \bar{c}(x) dx \tag{21}
\]

where \( L \) is the length of the system and \( \bar{c}(x) \) is the average concentration along the flow direction \( x \) (Fig. 5). Fig. 8 shows the total mass of C produced by the ADRE (Eq. (17)), our model (Eq. (20)), and the experiment (Eq. (21)). There is good agreement between the experiments and our simulation, while the ADRE over-predicts the mass of C.

Unlike other models published in the literature, our model does not use calibrating parameters to fit empirical data. For instance, Oates (2007) altered the probability density function (pdf) for the concentration to account for incomplete mixing at the pore scale. His approach fits the mean product concentration and the spatial–temporal growth of the variance of a conservative tracer. Rubio et al. (2008) implemented segregation effects to solve the ADRE numerically. They applied different time intervals for transport and reaction. Edery et al. (2009) and Edery et al. (2010) used a CTRW model that involves two calibrating parameters. One is to define the reaction radius and the other is to define the shape of the pdf of concentration. Sanchez-Vila et al. (2010) introduced a continuum scale time-dependent model based on the ADRE. Their model captures the concentration profile in Gramling (2002) with good accuracy. However, their model required three fitting parameters: one to determine the longitudinal dispersion coefficient, and two others to determine the time-dependent reaction rate. Chiogna and Bellin (2013) introduced a continuum Darcy scale model that assumes a mixing ratio distributed within a reference elementary volume (REV). Their model requires the product peak concentration as a calibrating parameter. Hochstetler and Kitanidis (2013) introduced a reactive transport numerical model to upscale a 2D pore scale porous medium into a 1D model. They developed an effective or upscaled reaction rate constant based on an empirical relationship, which is used as a fitting parameter to upscale the ADRE. De Anna et al. (2014) presented a 2D experiment and theoretical model for bimolecular reaction. They showed that the reaction rate is governed by the geometry of the interface where reactants mixed. The advective stretching and molecular diffusion govern the geometry of this mixing zone. Their model uses two fitting parameters to upscale the ADRE.
parameters: the stretching rate and the initial concentration. Also, as stated by the authors, a 3D system is more complex and will result in distinctive reaction front geometries.

4. Conclusions

We have introduced a novel approach to simulate fluid-fluid reactive transport in porous media. It is based on direct simulation on pore scale images. The Navier-Stokes equations are solved to calculate the velocity field and a streamline-based particle tracking method with a random walk is used to simulate advection and molecular diffusion. Reaction can occur when reactants are within a diffusive distance of each other. The probability of reaction is related to the batch-measured reaction rate constant.

We first validated the reaction algorithm by comparing its predictions against an analytical solution for reaction in a free fluid. For coupled transport and reaction, we also predicted the fluid/fluid reactive transport experimental data in a beadpack by Gramling et al. (2002). Our model accurately reproduces the concentration profiles of the experimental data, as it takes into account the degree of incomplete mixing present at the sub-pore (image voxel) level, in contrast to the ADRE that can over-predict pore scale mixing. Crucially, from our pore scale simulations we are able to show how incomplete spreading results in prolonged incomplete mixing which is the key determinant of early time reactive behavior. We demonstrated the nature of dynamic changes in the reaction rate, which are related to the degree of pore scale mixing.

Our model does not use calibrating parameters to fit empirical data. Future work will use this method to simulate reactive transport in different classes of porous media, and for a range of flow and reaction conditions.

Acknowledgment

We would like to thank Emirates Foundation for funding this project. BB and MJB wish to thank the Engineering and Physical Science Research Council for financial support through grant number EP/L012227/1. The authors would also like to thank Imperial College High Performance Computing Service.
for providing the computational resources for the simulator. The image of beadpack is available through: https://www.ims.ull.es/education/departments/earth-science/research/research-groups/perm/research/pore-scale-modelling/micro-ct-images-and-networks/.

References


