




# Mixing-Limited Reactions in Porous Media

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## Abstract

Mixing-driven reactions in porous media are ubiquitous and span natural and engineered environments, yet predicting where and how quickly reactions occur is immensely challenging due to the complex and nonuniform nature of porous media flows. In particular, in many instances, there is an enormous range of spatial and temporal scales over which reactants can mix. This paper aims to review factors that affect mixing-limited reactions in porous media, and approaches used to predict such processes across scales. We focus primarily on the challenges of mixing-driven reactions in porous media at pore scales to provide a concise, but comprehensive picture. We balance our discussion between state-of-the-art experiments, theory and numerical methods, introducing the reader to factors that affect mixing, focusing on the bracketing cases of transverse and longitudinal mixing. We introduce the governing equations for mixing-limited reactions and then summarize several upscaling methods that aim to account for complex pore-scale flow fields. We conclude with perspectives on where the field is going, along with other insights gleaned from this review.

**Keywords** Mixing · Reactions · Upscaling

## 1 Introduction

Mixing-driven reactions in porous media are ubiquitous and span natural and engineered environments. In geologic systems, examples are abundant including intrinsic and engineered remediation, natural attenuation, mineral formation, hydrothermal ore-deposits, dissolution

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of CO<sub>2</sub> into brackish water during geologic CO<sub>2</sub> sequestration, use of surfactants and CO<sub>2</sub> for enhanced oil recovery, and reactions between methane and sulfate in smoker vents on ocean floors to mention but a few (Alvarez and Illman 2005; Kitanidis and McCarty 2012; Bethke 2007; Wise 2000; Niemi et al. 2017; Sheng 2010). In engineering settings, we can consider microfluidic systems with applications in biotechnology, porous media combustion technology, or fixed-bed reactors, where a solid phase is embedded within a flowing system creating a porous medium (e.g., hollow film membrane bioreactors for wastewater treatment) (Li 2008; Mujeebu et al. 2009; Stephenson et al. 2000). Many biochemical reactions critical to life occur in biological tissues, a large component of which is a porous medium (Vafai 2010). Other, perhaps less conventional systems that can be modeled as a porous medium, in that flow moves through a region densely populated with solid, include flow and transport through wetlands which can process large amounts of nutrients and contaminants (Carleton and Montas 2007), or atmospheric boundary layer exchange flows with open canopies which, through chemical reactions, can control critical fluxes between forests and the atmosphere (Freire et al. 2017). It is important to note that this list of examples is nowhere near comprehensive, and only represents a fraction of applications in porous media where mixing-driven reactions occur. However, this list does display the extremely broad range of spatial and temporal scales that arise in such problems.

Within the context of porous media, predicting where and how quickly chemical reactions occur can be immensely challenging due to the complex and nonuniform nature of flow processes, and the enormous range of spatial (i.e., molecular, pore, continuum scales) and temporal (seconds to geological time) scales over which reactants can mix. At pore scales, factors including pore size distributions, geometry, tortuosity and connectivity all play a role, while at larger scales we must consider heterogeneity, say in the physical or geochemical makeup of an aquifer. These complex features translate into complex flows that ultimately control the detailed manner in which chemicals move through a porous medium, but more importantly how chemical constituents can come into contact with one another, which is key to the occurrence of any chemical reaction. Complex flows can bring reactants into contact or cause them to separate and thus enhance or diminish the interfacial area between them. Mixing is the process then that brings reactants together, enabling them to ultimately react. Thus, it is often argued that if we are ever going to successfully predict mixing-driven reactions, as a first step we must develop models capable of predicting mixing processes. To this end, several useful measures of mixing, including the dilution index (Kitanidis 1994), concentration variance, and scalar dissipation rate (Pope 2000; Le Borgne et al. 2010), have been proposed, each of which aims to quantify how much volume a solute occupies, how uniform a concentration field within a plume is, and how quickly the system is homogenizing. Often the evolution of these indices can be tied back to velocity field characteristics, particularly ones that account for flow-induced deformation such as Lyapunov exponents or the Okubo–Weiss Parameter (de Barros et al. 2012; Engdahl et al. 2014), which for example enables the identification of reaction hotspots, that is, the locations where reactions are most likely to occur (Wright et al. 2017).

When considering the broad range of examples listed in the first paragraph, transport scales can be on the order of anything from millimeters to kilometers. Yet ultimately, mixing is driven by interactions at the smallest molecular scales by diffusion. The multiscale nature of mixing presents a challenge in predicting mixing-driven reactions at scales of practical interest. Real flows also often vary in time, yielding temporal complexity (Dentz et al. 2000). Environmental flows often come with a high degree of uncertainties, where balances between advection-dominated and dispersion-dominated scenarios that must be considered are not always clear. Additionally, chemical reactions have their own characteristic time scales, meaning there is

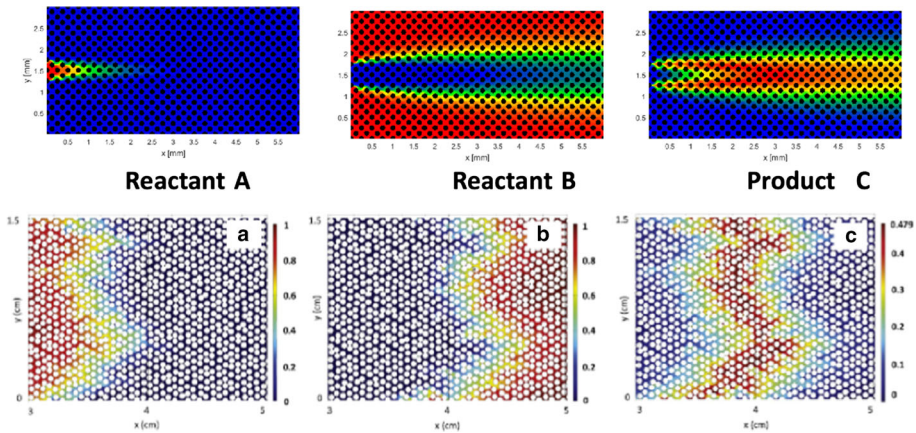
a competition between reaction kinetics and transport phenomena all acting at potentially vastly different time scales. Even in simple settings, models of mixing-driven reactions result in a (tightly) coupled sets of nonlinear partial differential equations. Translating such models across scales is where a truly challenging problem emerges.

The objective of this paper is to critically review the factors that affect mixing-limited reactions in porous media and approaches used for prediction of such processes across scales. So as to maintain focus and not overwhelm the reader, we will focus primarily on the challenges of mixing-driven reactions in porous media at pore scales as well as upscaling of these to continuum scales. We are interested in cases where multiple chemical reactants are initially segregated in different spatial regions of the porous media. We assume that at least two chemical species from different regions are required for the reaction of interest to occur. For simplicity, we limit our scope to single-phase flow with dissolved reactants, although there are interesting and important cases involving multiphase flow, such as geological carbon sequestration where the reactants are mixed when the nonwetting supercritical CO<sub>2</sub> phase is injected into a brine reservoir. Note that multiphase flow introduces a new level of complexity since the fluid displacement patterns are affected by capillary pressure entry effects, not only the pore space geometry (Jiménez-Martínez et al. 2015, 2017). We also do not consider cases where the solid phase itself may act as a separate reactant (e.g., sorption/precipitation/dissolution). To provide a concise but comprehensive picture, we balance our discussion between state-of-the-art experiments, theory and numerical methods. Much of what we discuss holds equally and presents similar challenges in upscaling from continuum scales to larger scales that account for larger-scale heterogeneities, which we discuss only briefly in the concluding section. For more comprehensive reviews of mixing that emphasize larger scales, the reader is referred to several recent articles, e.g., Dentz et al. (2011, 2017).

The paper is structured as follows. Section 2 introduces the reader to the factors affecting mixing. Both transverse and longitudinal mixing are considered, and factors such as pore space geometry, flow velocity, flow direction, and sorption are considered. Section 3 introduces the reader to governing equations for mixing-limited reactions. Equations for flow at the pore and continuum scale are presented, as well as equations for solute transport and reaction at these scales. Upscaling methods are also represented, where approaches to account for more complex heterogeneities are considered. The conclusion comes next, where perspectives on where the field is going are given, along with other insights gleaned from this review.

## 2 Factors Affecting Mixing-Limited Reactions

We generally distinguish two different mixing scenarios—transverse and longitudinal. Both cases are for the “model” mixing-controlled reaction:  $A + B \rightarrow C$ , where both reactants and the product are solutes. The first is illustrated schematically in Fig. 1(i), and the second in Fig. 1(ii). In Fig. 1(i), uniform steady flow is from the left with fluid containing mostly reactant B, and there is a small source zone of reactant A that is input continuously. Diffusion transverse to flow mixes the two reactants, and the product C is formed. Transverse mixing-limited reaction scenarios eventually reach steady state because the mass input rate of A is balanced by mass consumption rate of A by the reaction. At steady state, there is a “plume” region with high reactant A and negligible reactant B; product C is generated along the plume fringe. There is ample evidence that this mixing scenario is widely applicable in practice based on several studies reporting the length and stability of groundwater plumes at underground

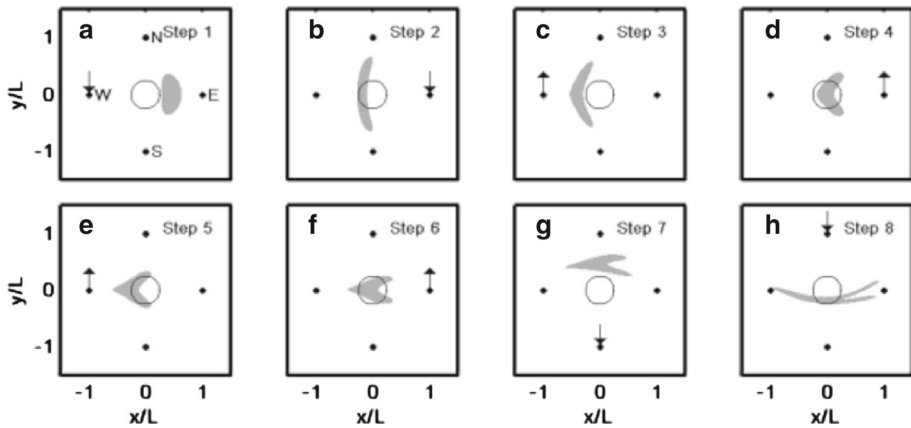


**Fig. 1** The two mixing scenarios considered in this paper (i) transverse mixing and (ii) longitudinal mixing. Both cases show results of pore-scale numerical simulations for mean uniform flow from left to right and with the bi-molecular reaction  $A + B \rightarrow C$ . The transverse scenario is at steady state for Peclet number = 10 and Damkohler number = 100. The longitudinal scenario is from Hochstetler and Kitanidis (2013) and shows a time snapshot for Peclet number = 14.4 and Damkohler number = 25. See Sect. 3 for the definitions of the Peclet and Damkohler number

storage tank sites (Connor et al. 2015), as well as from controlled field experiments of natural attenuation (Rasa et al. 2013).

In Fig. 1(ii), the domain initially is occupied by reactant B. Fluid containing reactant A is continuously input into the domain through the left boundary. The porous medium structure imposes heterogeneity upon the flow resulting in an irregular penetration of reactant A into reactant B. As A and B diffuse across this irregular interface the reaction proceeds to form the product C. We call this the longitudinal mixing case, since the two fluid regions mix predominantly in the flow direction; unlike the transverse mixing case, this case is an inherently transient system, as the mixing region changes over time and the amount of product mass increases with time. Practical examples for this scenario include cases of active groundwater remediation where reagents are injected into contaminated zones (Semprini et al. 1990). While we organize our review recognizing this dichotomy of mixing cases (like most studies in the literature), it should be noted that longitudinal mixing processes will be important near the leading boundary of the plume during the transient phase, while transverse mixing will be important along the plume fringes.

In the two cases presented above, the background flow is considered to be steady, which is an idealization. Note that externally imposed flow variability can have significant impacts on longitudinal and transverse mixing. For example, temporal oscillations in the mean flow direction will enhance mixing (Cirpka et al. 2015; Lester et al. 2010). Such fluctuations can occur in undeveloped groundwater aquifers, since there are often variations in flow direction driven by seasonal hydrologic events (e.g., rainfall, snow) (Rehfeldt and Gelhar 1992; Goode and Konikow 1990; Pool and Dentz 2018; Di Dato et al. 2018). From an engineering and remediation perspective, complex spatial and temporal variations in flow can be imposed by fluid injection/extraction (e.g., through pumping wells in a groundwater system), thereby dramatically enhancing mixing among reactants initially segregated in different fluid regions (Piscopo et al. 2015; Libera et al. 2017). Under some conditions, chaotic advection can occur which further enhances mixing and reaction (Neupauer et al. 2014; Sposito 2006; Trefry et al. 2012). An example is shown in Fig. 2, where different groundwater pumping rates at



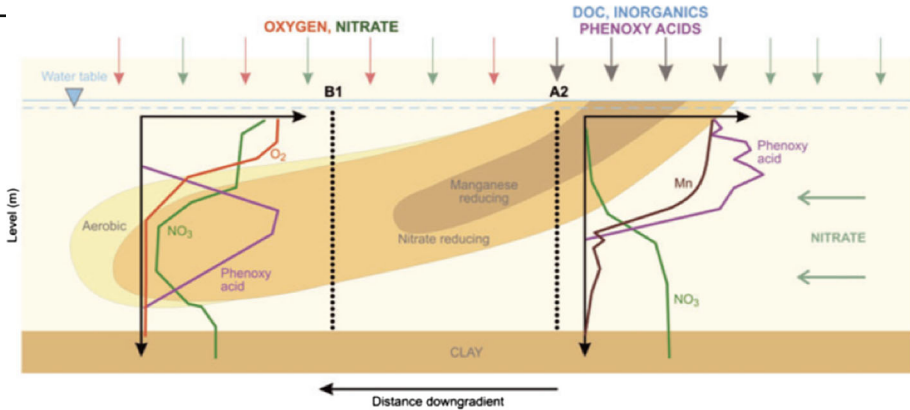
**Fig. 2** Chaotic Advection: Position of the treatment solution plume (gray) after each step of a designed injection-extraction strategy in a homogeneous aquifer. The open black circles show the initial position of the treatment solution plume. Small filled black circles show well locations. The arrow denotes the active well, with injection indicated by a downward pointing arrow and extraction indicated by an upward pointing arrow.. Adapted from Mays and Neupauer (2012)

four wells are applied to enhance plume stretching and mixing. In Step one, injection occurs at the W well, and the plume moves to the east. In Step two, injection occurs at the E well, and the plume moves to the west. In each subsequent step, water is injected or extracted at a single well and the plume becomes increasingly distorted from its initial shape. In some remediation systems, multiple chemical reagents must be injected and various strategies such as alternating pulsed injection are used to control mixing and promote reaction over large spatial zones (e.g., McCarty and Semprini 1993; Semprini et al. 1990; Gandhi et al. 2002; Phillips et al. 2013; Bagtzoglou and Oates 2007)

We next present an overview of some porous medium properties that affect mixing-controlled reactions for the transverse and longitudinal scenarios. Although the underlying pore-scale physics and processes are similar in both scenarios, different experimental and modeling investigations have been used for each scenario (e.g., the steady-state nature of the transverse mixing case allows for simplified laboratory experimentation) and therefore we discuss each separately.

## 2.1 Transverse Mixing-Limited Reactions

Cases involving transverse mixing-limited reactions have important practical relevance for assessing natural attenuation of groundwater contamination at hazardous waste sites where there is a long-term persistent source of dissolved pollutant. Often, naturally occurring microorganisms utilize the pollutant as, for example, an electron donor in a degradation reaction, provided there are dissolved electron acceptors (e.g., oxygen or nitrate) in the upgradient groundwater. As in Fig. 1, a steady-state dissolved contaminant plume results. The resulting steady-state length of the plume is an important quantity for assessing the overall contamination risk and degree of natural attenuation. A conceptual model of a steady-state plume at a field site in Denmark is shown in Fig. 3, along with measured profiles of phenoxy acid (pollutant and electron donor), and the electron acceptors oxygen and nitrate. Soluble Mn is also shown, due to reduction of insoluble manganese oxide as an electron acceptor. The



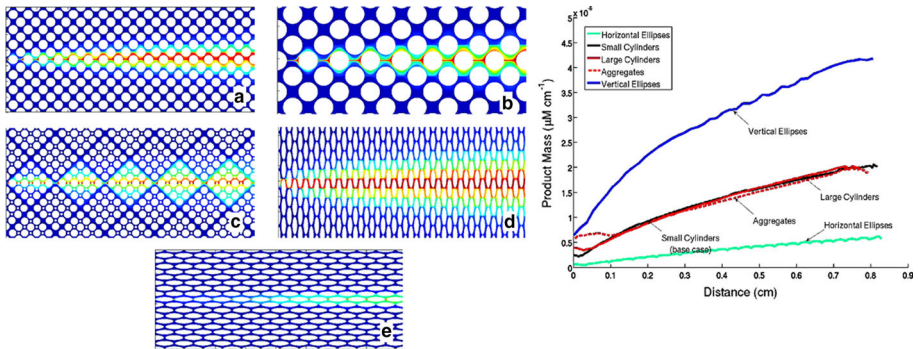
**Fig. 3** Conceptual model for the landfill leachate plume at the Sjoelund Landfill site [from Bjerg et al. (2011)]

conceptual model is based on the assertion that transverse mixing of oxygen and nitrate limit the distance that phenoxy acid can migrate downgradient before reacting.

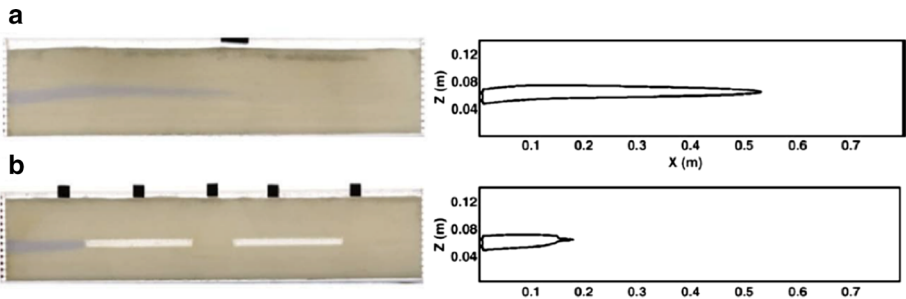
### 2.1.1 Effect of porous media structure heterogeneity

Porous media structure is relevant at the pore scale, and at larger scales where variations in permeability give rise to streamline compression and expansion. At the pore scale, heterogeneity arises from variations in grain size, grain orientation, and grain geometry, all of which can influence transverse-limited reactions. Examples are shown in Fig. 4, where microfluidic experiments and matching pore-scale modeling studies were performed to capture these effects (Willingham et al. 2008). Transverse mixing-limited reaction was evaluated using two different cylindrical grain sizes, two different orientations of an ellipse, and three different grain geometries. Flow was constant from the left; species 'A' and 'B' were input along the bottom and top half, respectively, of the inlet boundary; the reaction that produces the product 'C' is assumed to occur instantaneously as soon as the two species mix. Visually it is apparent that the largest amount of C is produced for the vertical ellipse, and the least amount for the horizontal ellipse. This is due to greater tortuosity, contact time, and streamline compression in the former, where streamline compression enhances mixing because the time scale of diffusion depends on the squared distance between adjacent streamlines ( $t \sim L^2/D$ ). There is no apparent difference in amount of C produced for the two different cylinder sizes; the same pore throat sizes were used for both, and this may dominate differences in mixing for different sized grains. The amount of C produced in the aggregate pore structure also matched the cylinders, indicating similar reactant contact times and streamline compression. Although only simulation results are shown in Fig. 4, companion microfluidics experiments are in close agreement. Acharya et al. (2007) conducted similar simulations for random grain geometries and configurations, and found that more complex grain geometries and configurations generally give rise to greater transverse dispersion and reaction.

The effects of larger-scale spatial heterogeneity in pore structure can also affect mixing and reaction by causing convergence and divergence of streamlines. Microfluidic and larger flow cell experiments using reactive solutes have been performed with high permeability inclusions (or lenses) surrounded by lower permeability material (Willingham et al. 2010; Rolle et al. 2009). Complementary numerical studies are also available (Werth et al. 2006). An example of a flow cell experiment is shown in Fig. 5. A solution of 0.004 mol/L NaOH (pH = 11.49)



**Fig. 4** (left) Simulation results showing production of C from A (top half) and B (bottom half) being introduced from the left boundary of each porous media. (right) Cumulative amount of C produced in each porous media with distance along the pore structures [from Willingham et al. (2008)]

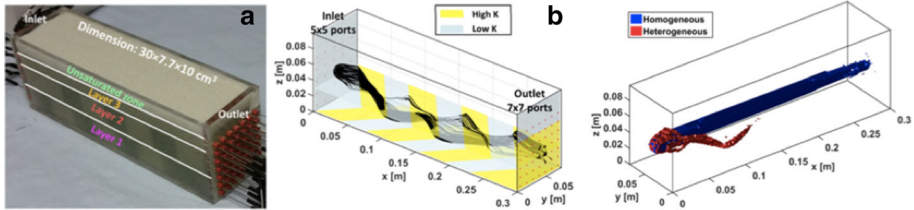


**Fig. 5** Flow cell experiment showing how high permeability inclusions can shorten the length of a reactive solute plume. Flow is from left to right. The reactive solute in the plume is NaOH, and it reacts with HCl in the surrounding pore water [from Rolle et al. (2009)]

was used for the reactive plume, and an ambient solution of 0.01 mol/L HCl ( $\text{pH} = 2.03$ ) was used for the surrounding groundwater. Flow was left to right, and all solutions were amended with the pH indicator bromophenol blue, which changed its color from yellow to blue in the pH interval of 3–4.6. The top panel is for a homogeneous porous medium, while the bottom has two rectangular high permeability inclusions. As shown, the blue color disappears in approximately 1/3 the travel distance when the higher permeability inclusions are present, and this is due to compression of the streamlines in the high permeability inclusions and subsequent enhanced diffusive mixing.

More complex arrangements of two-dimensional heterogeneity have been explored numerically; e.g., Werth et al. (2006) considered a system where irregularly shaped high permeability inclusions were placed into a lower permeability domain. This resulted in substantial mixing enhancement relative to a homogeneous domain, again as a result of streamline compression and enhanced mixing.

The effects of three-dimensional arrangements of heterogeneity have also been explored numerically. Three-dimensional spatial variability in permeability and anisotropy can introduce additional transverse mixing mechanisms that enhance reaction. In particular, there can be helical flow with twisting streamlines which causes intermixing of the inlet fluid stream tubes containing different chemical reactants. Helical mixing of a conservative tracer was studied experimentally in a flow cell, and then matched through numerical modeling (Ye



**Fig. 6** Helical flow cell with corresponding flow paths and reactive plume length [from Ye et al. (2016)]

et al. 2016). The calibrated model was then used to simulate reactive plume lengths under homogeneous and helical flow conditions. The flow cell, helical flow paths, and reactive plume length are shown in Fig. 6. The reactive plume length under helical flow conditions is approximately one-third of that under homogeneous flow.

## 2.2 Longitudinal Mixing-Limited Reactions

Again, we assume that the bulk flow is one-dimensional and steady in order to focus on the role of porous medium structure and reaction rate. Within the context of longitudinal mixing, there are two particularly well-known experimental papers that highlight some of the key challenges of translating pore-scale reactions to continuum scales (Raje and Kapoor 2000; Gramling et al. 2002). Prior to these experiments, the traditional thinking was that one could measure transport parameters (advection, dispersion) for a porous medium and estimate reaction parameters from a traditional batch experiment, lump these parameters together in an advection–dispersion reaction equation and predict reactive transport. Raje and Kapoor (2000) constructed a glass bead-filled column and displaced 1,2-naphthoquinone-4-sulfonic acid with aniline, a known bimolecular reaction that produces 1,2-naphthoquinone-4-aminobenzene. They measured transport parameters from a column experiment with no reactions, and measured the reaction rate in a beaker where they mixed the two reactants together and measured the rate of production of the product. In all cases, the fitted parameters matched experimental observations next to perfectly. With these parameters, they parameterized the advection–dispersion reaction equation and predicted breakthrough curves of the product that would be produced in a displacement experiment. Actual measured values were about 40% less than those predicted by their model. In an analogous setup, Gramling studied the reaction between  $\text{CuSO}_4$  and  $\text{EDTA}^{4-}$ , a colorimetric bimolecular reaction where the light intensity of the product  $\text{CuEDTA}$  was used to construct spatial distributions of concentrations. The rate of this reaction is sufficiently fast that it can be considered instantaneous (Hering and Morel 1988). Again, mismatches between predictions from a parameterized ADRE were on the order of 40% with lower concentrations of product observed than predicted. The experiments of Raje and Kapoor and Gramling, which are for one of the simplest imaginable porous media, a homogeneous one-dimensional column packed uniformly with sand, highlight that simply taking known dispersion parameters and known chemical kinetic parameters and lumping them together is not sufficient to predict reactive transport in a porous medium. The main reason for this is that a traditional continuum level parameterized ADRE is implicitly assuming perfect mixing of chemical reactants over the pore scale, while in reality the complex and tortuous nature of the pore-scale flow means that this is not true and that mixing is not perfect. Incomplete mixing at pore scales can significantly reduce large scale reaction rates, although much like Taylor dispersion (e.g., Bolster et al. 2011) in certain instances at asymptotic times, mixing may be sufficient to overcome this (Jose and Cirpka 2004).

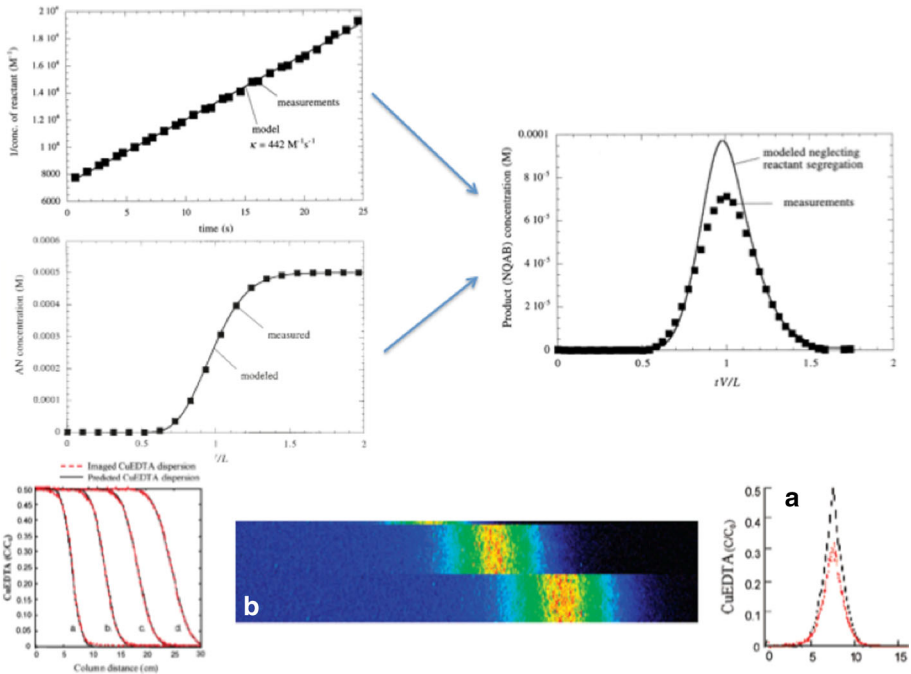


Raje and Kapoor's and Gramling's work clearly highlight these shortcomings and have motivated many studies since their publication, including others to look even closer at the mechanisms that lead to incomplete mixing. These are illustrated in numerical simulations as shown in Fig. 1 (Hochstetler and Kitanidis 2013); this figure shows that the reactive front is not uniform, but has some paths which are faster and some that are slower, giving rise to a very complex concentration distribution. Any upscaled model that is to be effective in predicting reactive transport must account for this in some, preferably efficient, form.

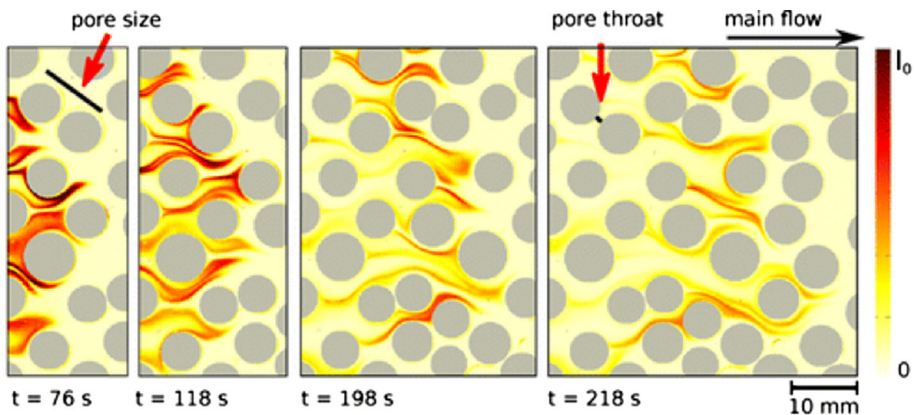
The mechanisms that give rise to incomplete mixing were studied in further detail by de Anna et al. (2014). Like Gramling, they used a colorimetric bimolecular reaction to visualize the reaction front and quantify the amount of product produced (although the specific reaction they used was a different one) but in a two-dimensional microfluidic reactor. The nature of their setup allowed them to clearly visualize transport, mixing and reaction mechanisms with a dynamical measurement of local concentrations with a sensitivity of 3 orders of magnitude, enabling assessment of a wide range of Peclet and Damkohler numbers by varying the flow rate within the cell and the local reaction rate. The resulting images and analysis demonstrate that the underlying transport and reaction are more complex than a simple classical continuum level ADR can describe, reflecting a rich set of incomplete mixing dynamics that must be accounted for. A major conclusion of their work is that while classical continuum-scale Fickian ADR theory would predict a scaling of the cumulative mass of product  $C$  with the square root of time, they identified two other regimes where the produced mass evolves faster than the Fickian behavior. Thus, a major problem with a classical continuum level ADR is not just that it might over-predict the rate of reaction, as suggested by Raje and Kapoor and Gramling, but that it cannot capture the correct temporal scaling of mass production; this means that any constant effective parameter model will likely not be able to capture the full range of true behaviors. Also, de Anna's experiments show that the geometry of the mixing interface between reactants, controlled by the geometry of the medium, determines the rate of mass production. To describe and model this, they demonstrate that the invading solute can be considered as stretched lamellae, whose dynamics they can describe. Mass transfer across lamellar boundaries limits the rate of reaction. At later times, a second regime occurs where these lamellae coalesce. The rate of this coalescence and the associated mixing zone dictate the rate of product formation. In this regime, the mass of product is directly proportional to the volume of the mixing zone, as calculated from conservative species. For further details on this see Sect. 4 (Figs. 7, 8).

### 3 Governing Equations for Flow, Transport and Reaction: Pore Scale

In this section, we present the governing equations that are typically solved for modeling of flow and transport of mixing-driven reactions at the pore scale. For the sake of simplicity, we focus exclusively on the equimolar bi-molecular reaction  $A + B \rightarrow C$ , which it is often argued is the fundamental building block of all more complex mixing-driven reactions (Gillespie 2000). Flow at the pore scale is governed by the Navier–Stokes equation, with no slip boundary conditions imposed at the grain–fluid solid interface boundaries. For many applications of practical interest in porous media, the Reynolds number  $Re = VL\rho/\mu$ , where  $V$  is a characteristic velocity,  $L$  a characteristic length and  $\nu$  the fluid viscosity, is small such that  $Re \ll 1$  (e.g., when pore sizes are small, velocities are slow and the fluid is highly viscous). Under such circumstances, it is not necessary to solve the full Navier–Stokes equations, and it is often reasonable to only solve for Stokes flow, where inertial effects are negligible and pressure forces are balanced by viscous ones, such that



**Fig. 7** (top) Rajc and Kapoor (2000) and (bottom) Gramling et al. (2002) measured (left) transport and reaction parameters to predict (right) reactive column experiments. In both cases, there is a discrepancy of about 40% with larger concentrations of product predicted than measured



**Fig. 8** Concentration of product at various times in a longitudinal mixing-limited reaction experiment of de Anna et al. (2013). Note the clear filamentary lamellar structure of the product, rather than a vertically uniform concentration

$$\hat{\nabla} \hat{p} = \hat{\mu} \hat{\nabla}^2 \hat{\mathbf{v}}, \quad \hat{\nabla} \cdot \hat{\mathbf{v}} = 0 \tag{1}$$

where  $\hat{\mathbf{v}}$  is the fluid velocity,  $\hat{p}$  is the pressure of the fluid, and  $\hat{\mu}$  is the viscosity of the fluid. Hats denote dimensional quantities. Other than for highly idealized geometries (e.g.,

Kitanidis and Dykaar 1997; Bolster et al. 2009), this equation must be solved numerically, which can be done by any number of methods; see below.

Given a solution for the velocity field, the governing equation for transport of the chemical constituents is given by

$$\frac{\partial \hat{C}_i}{\partial \hat{t}} + \hat{\nabla} \cdot (\hat{\mathbf{v}} \hat{C}_i) = \hat{\nabla} \cdot (\hat{D} \hat{\nabla} \hat{C}_i) - \hat{r}_{AB} \quad i = A, B \quad (2)$$

$$\frac{\partial \hat{C}_C}{\partial \hat{t}} + \hat{\nabla} \cdot (\hat{\mathbf{v}} \hat{C}_C) = \hat{\nabla} \cdot (\hat{D} \hat{\nabla} \hat{C}_C) + \hat{r}_{AB}, \quad (3)$$

where  $\hat{C}_i$  is the concentration of reactive species  $i$ ,  $\hat{\mathbf{v}}$  is the pore-scale velocity field, and  $\hat{D}$  is the molecular diffusion coefficient, which is assumed equal and constant for all species. While different formulations can exist for the reaction term, we here focus on it as determined by the law of mass action such that  $\hat{r}_{AB} = \hat{k} \hat{C}_A \hat{C}_B$ , where  $\hat{k}$  is the kinetic reaction rate constant. This reaction term is what couples the transport equations for each of the considered species.

From a theoretical perspective, particularly with upscaling in mind, it is often useful to present these equations in dimensionless form as this more clearly elucidates the competition among transport, mixing and reaction processes. To do so we must define the following quantities:

$$C_i = \frac{\hat{C}_i}{\hat{C}_0}, \quad \mathbf{v} = \frac{\hat{\mathbf{v}}}{\langle \hat{v} \rangle}, \quad t = \hat{t} \frac{\langle \hat{u} \rangle}{\hat{l}}, \quad \mathbf{x} = \frac{\hat{\mathbf{x}}}{\hat{l}},$$

$$Pe = \frac{\langle \hat{v} \rangle \hat{l}}{\hat{D}}, \quad Da = \frac{\hat{k} \hat{C}_0 \hat{l}^2}{\hat{D}} \quad (4)$$

where  $\hat{C}_0$  is a characteristic concentration,  $\hat{l}$  is a characteristic length scale,  $\langle \hat{v} \rangle$  is a characteristic/average velocity. Particularly important are the two dimensionless numbers  $Pe$  and  $Da$ , which, respectively, are the Peclet and (diffusive) Damkohler numbers.  $Pe$  quantifies the relative balance between advective and diffusive effects, while  $Da$  the balance between reaction to diffusive effects. Given these definitions, we can recast the transport equations as

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (\mathbf{v} C_i) = \frac{1}{Pe} \nabla^2 C_i - \frac{Da}{Pe} C_A C_B \quad i = A, B$$

$$\frac{\partial C_C}{\partial t} + \nabla \cdot (\mathbf{v} C_C) = \frac{1}{Pe} \nabla^2 C_C + \frac{Da}{Pe} C_A C_B \quad (5)$$

One interesting feature of these equations, which can facilitate their solution in certain circumstance, is that we can define invariants  $C_D = C_A - C_B$ ,  $C_E = C_A + C_C$  and  $C_F = C_B + C_C$ , the evolution each of which can be described by the conservative advection diffusion equation

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (\mathbf{v} C_i) = \frac{1}{Pe} \nabla^2 C_i \quad i = D, E, F \quad (6)$$

A variety of numerical methods have been applied to solve the pore-scale fluid flow and reactive transport equations. Examples include finite element techniques (Hochstetler and Kitanidis 2013); finite volume methods coupled with streamline-based particle tracking methods (Nunes et al. 2015; Alhashmi et al. 2015); lattice Boltzmann methods (LBM) (Acharya et al. 2007); smoothed particle hydrodynamics (SPH) (Tartakovsky et al. 2009), among many more. Due to computational challenges, many studies assume two-dimensional porous media with idealized geometry, although recent advances have enabled extension

to three dimensions. For example, Alhashmi et al. (2016) use a realistic three-dimensional geometry derived from micro-CT images of sandstone rock core. Since diffusion is a key driver of mixing effects, it is important to avoid numerical artifacts such as numerical diffusion when solving advection–diffusion equations, and some investigators use special particle tracking methods adapted for mixing-controlled reaction (Alhashmi et al. 2015; Porta et al. 2013; Sund et al. 2017a). Such particle-based methods can come with their own limitations due to noise associated with finite size effects, although some have argued that this can be exploited to simulate noise that is ubiquitous in real systems (e.g., Benson and Meerschaert 2008; Paster et al. 2014a; Bolster et al. 2016).

The governing equations above can be simplified for idealized transverse mixing cases, when the system is at steady state to

$$\nabla \cdot (\mathbf{v}C_i) = \frac{1}{Pe} \nabla^2 C_i - \frac{Da}{Pe} C_A C_B \quad i = A, B \quad (7)$$

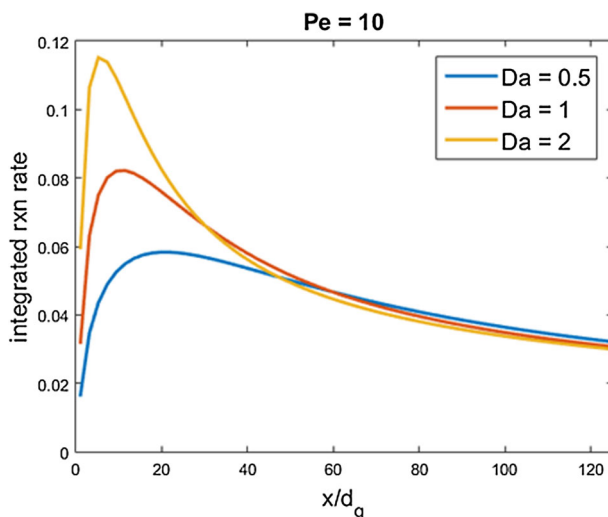
$$\nabla \cdot (\mathbf{v}C_C) = \frac{1}{Pe} \nabla^2 C_C + \frac{Da}{Pe} C_A C_B \quad (8)$$

### 3.1 Example Pore-Scale Solution and Limiting Behavior

As noted, the governing pore-scale equations can be solved numerically given an assumed pore geometry. This has been done in several studies, with the aim to gain deeper understanding of the interactions among mixing and reaction processes for the purposes of upscaling to the continuum scale. This has been done by Porta et al. (2013, 2016) and Hochstetler and Kitanidis (2013) for the longitudinal mixing scenario, and by Knutson et al. (2007) for the transverse mixing scenario. In both cases, the system evolves from a reaction-limited to a transport-limited regime. In the former, the rate of mixing of the two reactants is faster than the intrinsic rate of reaction, while in the latter the reaction rate is fast relative to the rate of mixing. Since the steady transverse mixing scenario is more convenient for illustration, this case is presented. We consider a simple scenario where solutes A and B are input continuously along the bottom and top half on the inlet boundary and a steady-state plume of product C is produced by the bi-molecular reaction (see Fig. 4). The transverse gradients are very large near the inlet zone, so the species are rapidly mixed by transverse diffusion and the overall reaction is limited by the intrinsic reaction kinetics. Further downstream from the inlet, the transverse gradients decrease so that the overall reaction is limited by the mixing rate of the individual species. This can be more clearly shown by using the numerically simulated results for the reactants A and B to compute the vertically integrated reaction rate at a given downstream location. This is computed in dimensionless form as

$$\bar{r}(x) = \frac{Da}{Pe} \int_{-\infty}^{\infty} C_A C_B dy \quad (9)$$

where the overline indicates vertical averaging across the  $y$  direction. Some example results for an idealized 2D domain with a spatially periodic porous medium are shown in Fig. 9. The vertically integrated dimensionless reaction rate computed by (9) is shown as a function of dimensionless distance from the inlet (where the grain diameter is used as the length scale). The figure shows that in the downstream zone all three curves converge so the reaction rate is independent of  $Da$ . The peak of the curve corresponds approximately to the location where the system transitions from reaction limited to mixing limited, and the transition occurs closer to the inlet for a larger reaction rate ( $Da$ ). As demonstrated by several studies (Acharya et al. 2007; Willingham et al. 2008), in the mixing-controlled regime the overall reaction rate



**Fig. 9** Results for the transverse mixing scenario shown in Fig. 4 for periodic porous medium. Vertically integrated dimensionless reaction rate defined by (9) as a function of longitudinal distance divided by grain diameter

scales with  $x^{-1/2}$ , a behavior that is consistent with the figure above. Note that this has an analog for the longitudinal mixing-controlled scenario, where studies of the total mass of product C formed scales with the  $t^{1/2}$ , which is equivalent to the total reaction rate scaling with  $t^{-1/2}$  (Porta et al. 2013; Hochstetler and Kitanidis 2013). The impact of increasing  $Pe$  (not shown) is that the location for transition to mixing-controlled reaction moves further downstream; this is because steep transverse gradients of the reactants will persist over a longer downstream zone with high  $Pe$ , and hence the reactants in this zone are mixing faster than they can be consumed by reaction.

## 4 Upscaling Pore Scale to Continuum Scale

Pore-scale studies yield detailed physical insights and understanding. However, practical applications typically require governing equations at the continuum scale. Development and application of various upscaling methods are at the center of the entire field of porous media modeling; here, we emphasize some special issues for mixing-controlled reactions.

### 4.1 Volume Averaging

A common approach to upscaling in porous media is using the method of volume averaging, which shares many similarities with other methods such as the method of moments and homogenization. One starts by writing the governing equations at the pore scale, identifying a representative elementary volume and then applying an averaging filter to the governing equations. Typically the equation for the average will have terms in it that depend on sub-scale quantities, necessitating a mathematical closure. By invoking a series of assumptions, typically related to strong separation of spatial and/or temporal scales, it is possible to rigorously derive such closures, resulting in an effective continuum or large scale equation. A

common example includes the use of mechanical dispersion, which averages out subscale velocity fluctuations, but effectively captures the spreading that they induce. Note though that because of the assumptions required to produce the closure, this large scale equation may only be valid under very specific conditions (e.g., at late times when the solute has had sufficient time to sample the full range of velocities, although this could be an issue, since if incomplete mixing is missed at early times, it can result in late time overestimation).

In the context of reactive transport, many studies have used volume averaging theory to derive continuum-scale advection–dispersion reaction equations starting from the pore-scale; many of these are for heterogeneous reactions on grain surfaces (e.g., Golfier et al. 2009; Guo et al. 2015), but a few have considered the specific case of mixing-controlled bimolecular reactions (e.g., Porta et al. 2012, 2013, 2016; Hochstetler and Kitanidis 2013; Sund et al. 2017a). Here we briefly summarize and present some key features. Quantities can be averaged over the volume of the fluid within an averaging volume unit cell, such that quantity  $*$  averaged in this way is defined as,

$$\langle * \rangle = \frac{1}{V_f} \int_{V_f} * dV, \tag{10}$$

where  $V_f$  is the averaging volume. Then the fluctuation of the quantity  $*$  is defined as,

$$* ' = * - \langle * \rangle. \tag{11}$$

Volume averaging of (5) and (6) leads to

$$\begin{aligned} \frac{\partial \langle C_i \rangle \phi}{\partial t} + \underbrace{\langle \mathbf{v} \rangle \cdot \nabla \langle C_i \rangle}_{\text{advection}} &= \underbrace{\frac{1}{Pe} \left[ \phi \nabla^2 \langle C_i \rangle + \nabla \phi \nabla \langle C_i \rangle \right]}_{\text{diffusion}} \\ &+ \underbrace{\nabla \cdot \left( \frac{\phi}{V_f} \int_{\Gamma_{fs}} C_i' \mathbf{n} dA \right)}_{\text{diffusion}} - \underbrace{\nabla \cdot \langle \mathbf{v}' C_i' \rangle}_{\text{dispersion}} \\ &- \underbrace{\phi \frac{Da}{Pe} r}_{\text{reaction}} \quad i = A, B \end{aligned} \tag{12}$$

$$\begin{aligned} \frac{\partial \langle C_j \rangle \phi}{\partial t} + \underbrace{\langle \mathbf{v} \rangle \cdot \nabla \langle C_j \rangle}_{\text{advection}} &= \underbrace{\frac{1}{Pe} \left[ \phi \nabla^2 \langle C_j \rangle + \nabla \phi \nabla \langle C_j \rangle \right]}_{\text{diffusion}} \\ &+ \underbrace{\nabla \cdot \left( \frac{\phi}{V_f} \int_{\Gamma_{fs}} C_j' \mathbf{n} dA \right)}_{\text{diffusion}} - \underbrace{\nabla \cdot \langle \mathbf{v}' C_j' \rangle}_{\text{dispersion}} \quad j = D, E, F \end{aligned} \tag{13}$$

where  $\phi$  is the porosity of the unit cell. Focusing on reactive component  $B$  and conservative component  $D$ , the reaction term is given by

$$r = \left[ \langle C_B \rangle \langle C_A \rangle + \langle C_B' C_A' \rangle \right] = \langle C_B \rangle (\langle C_B \rangle - \langle C_D \rangle) + \langle C_B' \rangle (\langle C_B' \rangle - \langle C_D' \rangle) \tag{14}$$

Several terms in these volume averaged equations remain to be closed, particularly the dispersion and reaction terms which depend on the product of two fluctuation quantities. Modeling terms like the hydrodynamic dispersive flux,  $J = \langle u' C' \rangle$ , have been thoroughly investigated for many years, and are described in detail in another paper in this issue (Cushman

et al. 2018). Although it can be nonlocal, one can also under certain simplifying assumptions (typically at late times) adopt the widely used Fickian model  $J_i = -\mathbf{D}\nabla\langle C_i \rangle$ , where  $\mathbf{D}$  is the hydrodynamic dispersion tensor, equal to the sum of the effective molecular diffusion coefficient and the mechanical dispersion tensor (Bear 1972) (although this can lead to overmixing at the pore scale and failure to capture the full range of temporal behaviors as discussed in Sect. 2). The simplest approach to describe hydrodynamic dispersion is in terms of its principal components,  $D_L$  and  $D_T$ , oriented parallel and transverse to the mean velocity. In some cases, the dispersion coefficients may depend upon reaction parameters (Shapiro and Brenner 1988; Porta et al. 2012); others have reported that dispersion can be compound specific (Rolle et al. 2012). Multicomponent diffusion in reactive systems must be dealt with carefully (Steeffel et al. 2015; Muniruzzaman and Rolle 2017). We do not consider these complications here and assume that dispersion coefficients are measured for inert solutes.

As explained for the transverse mixing scenario in Sect. 3, the reaction rate-limited region is near the inlet boundary. It is only in this region where an upscaled reaction rate model is required, since in the downstream mixing-limited region the overall reaction rate depends only upon transverse mixing and is independent of the intrinsic reaction kinetic parameters. Moreover, for the case of slow reaction (small  $Da$ ), the different solute species become completely mixed throughout an REV prior to significant reaction, and hence the upscaled reaction expression is identical to the pore-scale kinetic rate law (i.e.,  $\hat{r}_{AB} = \hat{k}\hat{C}_A\hat{C}_B$ ), but with continuum-scale concentration values.

Therefore, the key question is how to upscale the reaction for cases for which the rate is “fast enough” relative to mixing so that there is incomplete mixing within an REV where reaction is occurring, but not so fast that the reaction is mixing limited. For  $Pe \gg 1$  and  $Da \gg Pe$  the following closure relationships can be proposed.

$$C'_B = MC'_D \quad M = \frac{\langle C_B \rangle}{2\langle C_B \rangle - \langle C_D \rangle} \quad C'_D = \mathbf{b} * \frac{\partial}{\partial t} \langle C_D \rangle. \tag{15}$$

where  $*$  denotes convolution in time and  $\mathbf{b}$  is a vector of closure variables that solve the following equations on the small-scale REV

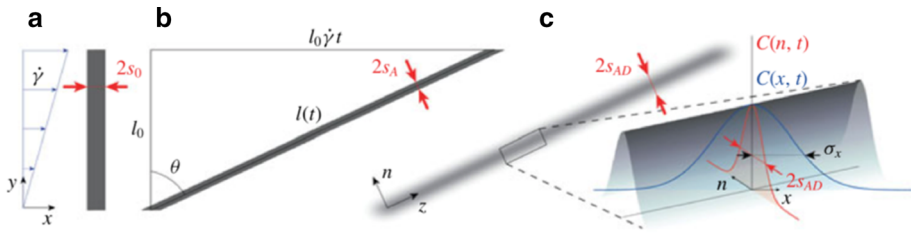
$$\frac{\partial \mathbf{b}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{b} = \frac{1}{Pe} \nabla^2 \mathbf{b} \tag{16}$$

Full details of the volume averaging procedure, as well as a discussion on assumptions and restrictions, are available in Porta et al. (2013). This yields a continuum-scale integro-differential system of equations, which is nonlocal in time:

$$\frac{\partial \langle C_D \rangle \phi}{\partial t} + \phi(\mathbf{v}) \cdot \nabla \langle C_D \rangle = \frac{1}{Pe} \nabla^2 \langle C_D \rangle + \frac{1}{Pe} \nabla \cdot \left[ \mathbf{D}_D * \frac{\partial}{\partial t} \nabla \langle C_D \rangle \right] \tag{17}$$

$$\begin{aligned} \frac{\partial \langle C_B \rangle \phi}{\partial t} + \phi(\mathbf{v}) \cdot \nabla \langle C_B \rangle &= \frac{1}{Pe} \nabla^2 \langle C_B \rangle + \frac{1}{Pe} \nabla \cdot \left[ \mathbf{M} \mathbf{D}_D * \frac{\partial}{\partial t} \nabla \langle C_D \rangle \right] \\ - \frac{Da}{Pe} \langle C_B \rangle &\left[ \left( \langle C_B \rangle - \langle C_D \rangle \right) - M(M-1) \left\langle \left( \mathbf{b}_D * \frac{\partial}{\partial t} \nabla \langle C_D \rangle \right)^2 \right\rangle \right] \end{aligned} \tag{18}$$

where  $\mathbf{D}_D = -Pe(\mathbf{u}'\mathbf{b}')$ . While the theory of volume averaging is rigorous and valid when its assumptions are met, one of the main criticisms of this approach is that the upscaled continuum-scale equations, like those in (18), can sometimes be close to as complicated to solve as the actual pore-scale system. As such alternative approaches may sometimes be more desirable.



**Fig. 10** **a** Schematic of a lamella of dye of initial length  $l_0$  and advected in a laminar shear flow. **b** Effect of the advection field alone: the strain  $\gamma t$  has stretched the lamella and thinned down its transverse dimension to  $2s_A(t)$ . **c** Effect of both advection and molecular diffusion: at the same strain, the half-width of the lamella is denoted  $s_{AD}(t)$ . Inset: schematic of the Gaussian concentration field of the lamella with its concentration profiles along the flow  $C(x, t)$  and transverse to the lamella  $C(n, t)$  [from Souzy et al. (2018)]

As noted above, upscaling the reaction term is not required in the downstream mixing-controlled region, and hence there is no harm using the pore-scale kinetic rate law and parameters. There may indeed be practical cases for which the reaction-limited zone is small and one is interested in the total amount of product created in a large domain. In these cases, it may be possible to simply neglect the reaction-limited zone and assume fast reaction. Therefore, it is critically important to get the mixing right in order to accurately model the continuum-scale reactive system. For transverse mixing scenarios, there are several studies that show that classical transverse dispersion coefficients for ideal tracers can be used to model fast reactions (e.g., Acharya et al. 2007; Willingham et al. 2008). For example, Acharya et al. (2007) showed that such a continuum-scale model could simulate the microfluidics experiments of Willingham et al. (2008) for a variety of porous media geometries. Modeling longitudinal mixing is more challenging due to the complex dynamics of the mixing interface, as described in Sect. 2. Time-varying models are often needed, as there can be a long pre-asymptotic regime of mixing. These models can be developed using some of the alternative upscaling approaches described next.

### 4.2 Lamellae

A recent model relies on predicting the evolution of the interface between reacting species. At early times it is possible to describe the interface as made up of complex elongated structure which form lamellae, an approach which has had great success in predicting mixing and reactions in a variety of flows ranging from chaotic to turbulent. By predicting the evolution of these lamellar structures (Fig. 10), upscaled models of reactions can be developed. For the case of fast reactions, like in Gramling et al. (2002), the rates of production of mass of product C can be expressed as

$$\frac{dM_C}{dt} = D \int_{\mathcal{E}} |\nabla C_A| d\Sigma \equiv D \Sigma(t) |\overline{\nabla C_A}| \tag{19}$$

where  $\Sigma(t)$  is the length of the interface  $\mathcal{E}(t)$  separating the reactants. This equation basically says that the total amount of reaction is controlled by the diffusive mass transfer of reactant A across the interface into B territory. Then, it is argued that the gradient can be approximated by  $c_0/s(t)$ , where  $s(t)$  is the average interface width. Under purely diffusive conditions  $s(t) \sim \sqrt{Dt}$ , giving rise to the classical result that mass of product grows also as  $M_C(t) \sim \sqrt{Dt}$ . However, in a complex heterogeneous flow, as exists at pore scales within a porous medium,



the interface is trying to grow by diffusion but is also subjected to stretching and compression by advective forces; a balance equation can be written such that

$$\frac{1}{s(t)} \frac{ds(t)}{dt} = \frac{D}{s(t)^2} - \frac{1}{\Sigma(t)} \frac{\Sigma}{t} dt \tag{20}$$

where  $\frac{1}{\Sigma(t)} \frac{\Sigma}{t} dt$  is the interface elongation rate, which is related to flow kinematics (Duplat et al. 2010). At early times the interface length grows linearly in time at some rate  $\gamma$ , and the interface thickness can be predicted to evolve as

$$s(t) = s_0 \sqrt{\frac{3\beta - 2 + 2(1 + \gamma t)^3}{3\beta(1 + \gamma t)^2}} \tag{21}$$

where  $\beta = \frac{s(0)^2 \gamma}{D}$ . Initially lamella width decreases until compression and diffusive growth equilibrate, called the mixing time  $\tau_m$ . After this mixing time, the different elements of the interface can no longer be regarded as independent; they interact via diffusion, and coalescence leads to aggregate lamellae bundles. In this regime, the evolution of the interface length  $\Sigma(t)$  can be estimated as the average length of lamella bundles  $l_b(t)$ , which can be estimated from the overall large scale width of the reaction front, multiplied by the number of bundles  $n_b(t)$ , which should be inversely proportional to the interface width. Thus,  $\Sigma(t) = n_b(t)l_b(t) \sim \frac{\sigma_a(t)}{s(t)}$ . For times bigger than  $\tau_m$ , the interface width grows diffusively and so

$$\frac{dM_C(t)}{dt} \propto \frac{c_0 \sigma_a(t)}{t} \tag{22}$$

When the reactive front width grows as a power law, this means that  $M_c(t) \propto \sigma_a(t)$ , that is the mass produced is directly proportional to the reactive front width. This means that under conditions of non-Fickian width growth, which is common in porous media, particularly at pre-asymptotic times, the mass of reactant will also grow in a non-Fickian manner. Should the width grow in a Fickian manner, as expected at late times, then a classical scaling should emerge. These approaches have been validated both numerically and experimentally by de Anna et al. (2013, 2014), although in both cases the porous media considered do not appear to revert to a late time Fickian scaling, perhaps due to their limited size, meaning that they cannot attain asymptotic times.

### 4.3 Other Approaches

#### 4.3.1 Reactive Random Walks

Many common numerical methods for studying transport and mixing are Eulerian in nature. A paper by Boso et al. (2013) focuses on several popular schemes and states that broadly speaking, because of numerical dispersion, grid-based Eulerian schemes, overestimate dilution/mixing, and thus over-predict mixing-driven reactions. On the other hand, Lagrangian approaches, including among others random walk particle tracking (RWPT) approaches, are free of numerical dispersion, thus presenting a potential advantage. However, concentration fields represented by a finite number of particles produce naturally noisy concentration fields, which can present its own set of problems. Some authors have suggested though that this noise can be used to represent incomplete mixing effects, in particular (e.g., Benson and Meerschaert 2008; Paster et al. 2014b).

Among RWPTs for predicting upscaled mixing-driven reactions, two approaches that have been applied to successfully model the experimental data of Gramling et al. (2002) are from Edery et al. (2009, 2010) and Ding et al. (2013). Ding et al. (2013) also successfully simulate the data of Raje and Kapoor (2000). While the methods both share certain commonalities, being built on random walk theory, there are fundamental differences, particularly in the manner in which the reactive step is modeled. Edery et al. (2009) move particles using a continuous time random walk approach, and then use a 'hard-shell' radius approach to model reactions - that is each A particle and B particle has a fixed radius around it and particles that overlap can react. While the model can clearly reproduce the experimental data and effects of incomplete mixing, open questions remain on how exactly to choose the specific value of the hard-shell radius, and whether it has a clear physical meaning or is an empirical fitting parameter. Some empirical evidence suggests it may be related a characteristic pore size, which may be representative of a scale over which mixing occurs.

Ding et al. (2013) use the reactive RWPT method that was first proposed by Benson and Meerschaert (2008). In this method, particles are moved by a Brownian random walk, and then A and B particles can react probabilistically, where the reaction probability depends on the product of (1) the probability of collocation, which depends on transport, and (2) the probability of reaction given collocation, which depends only on chemistry. This method has been shown to represent incomplete mixing in simple settings and complex flows (Paster et al. 2014a, 2015). In particular, the choice of a finite number of particles can be shown to correspond to a particular initial condition in which incomplete mixing is encoded as noise. Some argue that it is troubling to think that the choice of discretization of a numerical method, i.e., the number of particles chosen, can be used to represent something physical. However, the work of Bolster et al. (2016) demonstrates that this method yields the exact same solution as a finite-difference model with the same initial condition, or a random walk method with 100 times more particles, but whose initial condition is chosen to have the same distribution. This suggests that the equations are being solved consistently.

### 4.3.2 Empirical Closures

Hochstetler and Kitanidis (2013) conducted 2D pore-scale simulations with continuous input of species A into a domain having species B, with the product C created by reaction within the dynamic mixing zone which migrates downgradient. They then fit a continuum-scale model to compute the so-called effectiveness factor EF, defined as  $\hat{\tau} = K_{\text{eff}} \langle c_A \rangle \langle c_B \rangle = E_F k \langle c_A \rangle \langle c_B \rangle$ . Repeating their pore-scale simulations for a variety of reaction rates, they fit the value of  $K_{\text{eff}}$  in the continuum-scale model to match the total product C generated at selected cross sections far enough downstream to achieve a constant  $K_{\text{eff}}$ . Their results were fit to a function of the following form  $E_F = \frac{\gamma\lambda}{Da+\lambda}$  where  $\gamma$  and  $\lambda$  are fitting parameters that would depend upon  $Pe$ .

Sanchez-Vila et al. (2010) used the idea of an effective reaction rate to model the experiments of Gramling et al. (2002). Recall that the reaction Gramling studied is so fast as to typically be considered instantaneous and so an effective kinetic reaction is chosen to capture incomplete mixing effects. Unlike Hochstetler and Kitanidis (2013), Sanchez-Vila et al assume that the effective kinetic rate varies over time. In fact, they assume that it decreases as a power law in time. They justify this choice based on experiments from Haggerty et al. (2004), who show that pore-scale rate-limited mass transfer will lead to this power law. A similar approach can be found in Rubio et al. (2008) using an exponentially decaying segregation factor, while Zhang and Papelis (2011) try different power laws using the approach of Sanchez-Vila et al. (2010).

In another stochastic approach, Chiogna and Bellin (2013) model Gramling's experiments by assuming a probability density distribution of concentration variations to represent incomplete mixing effects. In particular, based on previous experimental evidence and theory (Oates 2007), they assume that the mixing ratio is distributed within an REV according to a Beta distribution, and then fitting the parameters of this distribution one can successfully model Gramling's results. Such approaches are promising because they allow for links to other explicit pore-scale models which may be used to determine the pdf of concentrations, resulting in a closed-form solution for the case of fast reaction.

### 4.3.3 Mixed and Unmixed Phase Models

Two recent papers model the phenomenon of incomplete mixing in longitudinal reactive transport with a dual continuum approach, where reactants can exist in one of two states: mixed or unmixed (Ginn 2018; Barnard 2017). In both approaches, only the mixed fraction of a solute can actually participate in the reaction, while both fractions can move by advection or dispersion. Mass is progressively exchanged from the unmixed into the mixed fraction following a specified exchange rule. The primary difference in both approaches is the rule for mass exchange between this unmixed and mixed phase. In the words of Ginn "this approach distinguishes self-diffusive mixing from spreading, and in the case of displacement of one solution by another, each containing a participant reactant of an irreversible bimolecular reaction, this results in time-delayed diffusive mixing of reactants". In other words, this approach attempts to capture incomplete mixing effects based on the physical picture consistent with the lamellar picture discussed above. Barnard's model can be thought of as a reaction network (mass transfer from unmixed to mixed and then a mixing-driven bimolecular reaction in the mixed phase). The model has three fitting parameters, which are the order of the mass transfer reaction, the rate of this reaction, and then the rate of bimolecular reaction between the mixed components of the reactants, which is not taken to be instantaneous as in other cases. Ginn's approach is a first-order mass transfer from the unmixed to mixed state, but the rate associated with this mass transfer can vary over time (like Sanchez-Vila and Fernandez discussed above). Unlike Barnard's approach, the reaction rate in the mixed phase is not a free fitting parameter and corresponds to the thermodynamic rate. Both methods can successfully model Gramling's data.

### 4.3.4 Hybrid Approaches

As noted above, while volume averaging is a mathematically rigorous approach to upscaling reactive transport it has two potential limitations, which are that it relies on some strong assumptions that limit its applicability in terms of regimes of Peclet and Damkohler numbers where the upscaled theories hold (Battiato et al. 2009; Battiato and Tartakovsky 2011) and second that the volume averaged equation is often a nonlocal one (in space and/or time) that can be as difficult to solve as the full small-scale equations. In response to this, hybrid approaches try to take advantage of the strengths of volume averaging and use alternative approaches in regions where volume averaging weaknesses are largest. This can often involve a combined upscaling/downscaling approach; e.g., Scheibe et al. (2015) simulate a transverse mixing reaction front in a porous medium where they explicitly resolve the pore scale in the proximity of the front, but not in regions away from where the reaction occurs. Similarly, Siuliukina and Tartakovsky (2018) apply such an approach to model a miscible reaction front in an open fracture. Far from the mixing region between reactants, flow and transport

are described by one-dimensional models, but close to the front small-scale equations (2d Stokes equations and the advection–diffusion reaction equation) model flow and transport. These two sets of equations have to be coupled with one another to enforce continuity of concentrations and fluxes, which is done in an iterative manner. A related hybrid approach is presented by Tang et al. (2015) who considered diffusion-controlled bi-molecular reaction that causes biofilm growth and porous medium clogging; full pore-scale models are needed in the mixing region, while continuum-scale models apply elsewhere. Another recent, but different, hybrid approach is the Lagrangian Transport Eulerian Reaction Spatial (LATERS) Markov Model developed by Sund et al. (2017a,b), which aims to take advantage of a Lagrangian model, the Spatial Markov model (SMM), for certain aspects of the problem and an Eulerian model, built from the volume averaged upscaled equations, for other. The SMM takes care of dispersion and is then stochastically downscaled to a representative elementary volume to compute concentration fluctuations, which in turn are upscaled again to compute the incomplete terms that need to be closed in the Volume Averaged Equations.

## 5 Conclusions

We have provided a brief review of the literature on mixing-limited reaction of two solutes forming a product in porous media, focusing on processes and modeling at pore scales. Both transverse and longitudinal mixing-limited reactions were considered in the context of single-phase flow. Transverse mixing-limited reactions are especially important in groundwater and can limit the extent of mixing and reaction along contaminant plume margins. At the pore scale, transverse mixing is affected by the pore size and geometry, with pores that promote compression of streamlines and greater contact time between solutes, resulting in more reaction.

Longitudinal mixing-limited reactions are inherently transient, as opposed to steady state, and are important in many applications where a reacting front advances with fluid flow. Initially, it was thought that kinetic rate constants from batch experiments could directly be used in reactive transport models to predict longitudinal mixing-limited reactions. However, incomplete mixing at the pore scale revealed that apparent reaction rates were less than expected, and various approaches have been used to scale the reaction rate.

The governing equations for mixing-limited reactions at the pore and continuum scale were presented. At the pore scale, flow is determined with the Navier–Stokes equation. Flow fields are coupled with the advection–dispersion reaction equation to simulate solute transport and reaction. We presented the governing equations in dimensionless form as this naturally highlights the competing processes of diffusion, advection and reaction which can all act at disparate time scales. This is represented by two dimensionless number, the Peclet number (advective vs diffusive processes) and Damkohler number (reactive vs diffusive processes), reducing the number of independent parameters and facilitating comparison of experiments and processes. In particular, the nature of reaction is to couple all of the transport equations together in a tight manner, meaning that uncertainties and errors in one propagate to all, making scaling particularly challenging.

A great deal of effort has been made to upscale results from the pore to the continuum scale. In special cases, e.g., downstream when transverse mixing is slow and reactions are very fast, pore and continuum-scale models can be substituted for one another with no loss in accuracy. However, in many cases, more formal upscaling approaches are needed. One such approach is volume averaging, which uses a filter to average pore-scale results over a

representative elementary volume and determine the governing continuum-scale equations. Using this approach, velocity and concentration fluctuations at the pore scale can be captured in an upscaled model, typically reflected in an upscaled dispersion coefficient and reaction rate. Such formal volume averaging approaches have been developed in the context of mixing-controlled bimolecular reactions. While they provide great value and insight into what processes are most important and at what scales, their application to practical problems can be challenging as the upscaled equations can be almost as complex as the small-scale ones.

Consequently, several more parsimonious upscaling models have been developed. One such approach that has enjoyed great success aims to predict the evolution of the interface between reacting species by conceptualizing it as an ensemble of elongated structures which are continuously diffusing, compressing and stretching. By accurately representing these processes, relatively simple upscaled models can reliably predict mixing-driven reactions. Other approaches include random walk particle methods, where particles representing different chemical species move through random walk and then interact probabilistically to model reaction. Likewise, researchers have developed empirical closures based on simplified volume averaging approaches, mass transfer models have emerged and hybrid approaches, all of which have shown promise in capturing complex incomplete mixing phenomena at pore scales.

Despite all of these advances, many challenges remain in modeling transverse and longitudinal mixing-limited reactions. Pore-scale simulations are computationally very expensive and new methods and faster computers are needed to solve more realistic problems. At the continuum scale typically only simple mixing-limited reaction cases are successfully upscaled. Challenges remain in upscaling more realistic field scale settings, where incomplete mixing at the pore scale limits application of conventional continuum-scale models. Another challenge is integrating pore and continuum-scale models together into so-called hybrid models. Passing information between pore and continuum-scale grid cells, and determining appropriate upscaled parameters is still a big challenge. Accurately simulating mixing-limited reactions in the field requires progress on all of these fronts. Finally, while the experimental data from studies such as Raje and Kapoor (2000) and Gramling et al. (2002) have been invaluable, more sophisticated experiments and data spanning a broader range of parameter space and complexity are needed to push the frontier and develop, refine and truly validate the next generation of state-of-the-art modeling approaches.

While we only touched on it briefly in this review, many of the challenges that arise from predicting and upscaling pore-scale flows exist equally when trying to model and predict mixing-limited reactions at continuum scales that reflect larger-scale heterogeneities within a porous medium (e.g., geologic variability). Many of the upscaling approaches applied to go from pore to continuum scales have also been adapted to these situations (e.g., Werth et al. 2006; Le Borgne et al. 2013; Ding et al. 2017; Oates 2007)

At the continuum scale, mixing and thus mixing-limited reactions are affected by flow field heterogeneity; complex hydraulic conductivity fields lead to flows that include streamline compression and expansion, which enhance mixing and reaction. Moreover, it is generally impossible to fully characterize such small-scale heterogeneity at practical field sites, and hence stochastic approaches are needed that explicitly recognize the uncertainty in predicting mixing-controlled reactions.

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