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Comparative assessment of continuum-scale models of bimolecular reactive transport in porous media under pre-asymptotic conditions

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ARTICLE INFO

ABSTRACT

We compare the ability of various continuum-scale models to reproduce the key features of a transport setting associated with a bimolecular reaction taking place in the fluid phase and numerically simulated at the pore-scale level in a disordered porous medium. We start by considering a continuum-scale formulation which results from formal upscaling of this reactive transport process by means of volume averaging. The resulting (upscaled) continuum-scale system of equations includes nonlocal integro-differential terms and the effective parameters embedded in the model are quantified directly through computed pore-scale fluid velocity and pore space geometry attributes. The results obtained through this predictive model formulation are then compared against those provided by available effective continuum models which require calibration through parameter estimation. Our analysis considers two models recently proposed in the literature which are designed to embed incomplete mixing arising from the presence of fast reactions under advection-dominated transport conditions. We show that best estimates of the parameters of these two models heavily depend on the type of data employed for model calibration. Our upscaled nonlocal formulation enables us to reproduce most of the critical features observed through pore-scale simulation without any model calibration. As such, our results clearly show that embedding into a continuum-scale model the information content associated with pore-scale geometrical features and fluid velocity yields improved interpretation of typically available continuum-scale transport observations.

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1. Introduction

Recent developments in pore-scale numerical modeling and imaging technologies are providing remarkable added value to our knowledge of dynamics of reactive transport processes in complex pore spaces (e.g., Molins et al., 2014; Menke et al., 2015). These techniques and approaches allow characterizing and comparing the relative importance of the dynamics associated with advective transport, diffusive mixing and reactive processes at the (micron) scale of individual pores.

Reactive transport applications in hydrogeology typically involve large spatial scales. It would then be desirable to explore the extent at which our knowledge on pore-scale dynamics could be transferred into models that can be applied at a continuum- (or Darcy-) scale. In this work we consider solute transport in porous media in the presence of a homogeneous bimolecular irreversible reaction of the kind A + B → C, which is typically classified as a fluid–fluid reaction. Upscaling this reactive transport problem from the pore- to a continuum-scale is especially challenging under conditions of advection dominated transport and fast reaction, respectively associated with large values of the Péclet, Pe, and Damköhler, Da, numbers (e.g. Gramling et al., 2002; Tartakovsky et al., 2009; Porta et al.,

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2012a). Available column experiments at the laboratory scale document the space–time dynamics of the reaction product C (Gramling et al., 2002; Raje and Kapoor, 2000). These works show that the assumption of complete mixing of the reactants at the pore-scale can lead to considerable discrepancies between measured concentrations of the reaction product C and predictions based on continuum-scale approximations. This result is consistent with theoretical upscaling by Battiato and Tartakovsky (2011). Experimental observations documenting the evolution of the pore-scale reaction rate in a Hele–Shaw cell are illustrated by de Anna et al. (2013, 2014). These authors show that the spatial distribution of the reaction rates within the pore space is highly non-uniform in space and is characterized by a filamentary structure. The pore-scale dynamics of the process of mixing of the reactants, which is inherently linked to the reaction product, has also been investigated through detailed numerical simulations in various settings (e.g., Tartakovsky et al., 2009; Willingham et al., 2010; Porta et al., 2012b, 2013; Hochstetler and Kitanidis, 2013; Rolle and Kitanidis, 2014; Alhashmi et al., 2015). These studies emphasize the critical importance of a proper model of local mixing for the interpretation of reactive transport processes. Similar conclusions are drawn from column scale experiments where pH-controlled reactions take place (e.g., Jose and Cirpka, 2004; Loyaux-Lawniczak et al., 2012; Edery et al., 2015).

Several alternative approaches have been proposed with the aim of embedding effects of pore-scale incomplete mixing within Darcy-scale effective reactive transport models (see also the review by Edery et al., 2013). These include particle-based Lagrangian methodologies (e.g., Edery et al., 2009, 2010; Ding et al., 2013) as well as Eulerian approaches (e.g., Sanchez-Vila et al., 2010; Chiogna and Bellin, 2013; Hochstetler and Kitanidis, 2013). Here we focus on the latter set of approaches as applied to bimolecular fluid–fluid reactions. Continuum-scale approaches typically embed effective formulations, which encode incomplete mixing effects into transport and reaction parameters. These effective formulations typically require model calibration against a set of observations, and can be used to interpret available data. In this context, a series of works (e.g., Sanchez-Vila et al., 2010; Chiogna and Bellin, 2013; Rubio et al., 2008) are focused on the interpretation of the experimental dataset of Gramling et al. (2002). These authors document the spatial distribution of the reaction product concentration within a fully saturated column where the host porous medium is a bead pack. Longitudinal (i.e., along the mean flow direction of flow) profiles of solute concentration are reported for diverse time levels and transport conditions. A comparison of the results obtained in the above referenced works shows that very different modeling approaches allow interpreting this particular experimental dataset with comparable levels of accuracy. This suggests that the information content associated with the distribution of the reaction product in the system is insufficient for a unique characterization of incomplete mixing through effective continuum-scale approaches. Alhashmi et al. (2015) perform a three-dimensional pore-scale simulation in an attempt to replicate the reactive experiment scenario of Gramling et al. (2002). They show that spreading of the reactants across the medium can be quantified in terms of a time dependent dispersion coefficient. The temporal evolution of longitudinal spreading is different for

the two reactants A and B. However, to the best of our knowledge, the ability of effective models to characterize the concentration of the two reactants (A and B) within the regions where they mix and the reactive process takes place has not been tested to date.

A mathematical formulation relating pore-scale characteristics and effective reactive transport parameters at a continuum-scale can be derived through formal upscaling methodologies, such as the method of volume averaging (e.g., Whitaker, 1999; Orgogozo et al., 2010; Valdés-Parada et al., 2011; Guo et al., 2015). The latter is applied to bimolecular reactive transport by Porta et al. (2012a). These authors show that it is possible to obtain a closed nonlocal formulation of a reaction term associated with incomplete mixing in the presence of a fast reaction (i.e., large Da values). The assumptions underlying the theoretical analysis of Porta et al. (2012a) have been verified by comparison against direct numerical upscaling of pore-scale simulations performed in simple two-dimensional geometries, i.e., a plane channel (Porta et al., 2012b) and an ordered array of cylinders (Porta et al., 2013). The continuum-scale model proposed by Porta et al. (2012a) is presented in terms of a nonlocal integro-differential formulation, consistent with a recent formulation obtained by Hansen et al. (2014) starting from the generalized master equation. Note that the formulation proposed by Porta et al. (2012a) accounts for the temporal dynamics of the spreading process discussed by Alhashmi et al. (2015) by including a nonlocal in time dispersive transport term.

In this work we start from pore-scale numerical simulations of a bimolecular homogeneous and fast reaction. We consider the latter to take place within a two-dimensional pore space, which is generated by randomly placing in space a set of circular grains of uniform diameter. The key target of the work is to test our ability to interpret the continuum-scale results obtained from direct upscaling of pore-scale simulations in such a disordered system through continuum-scale models. The reactive transport setting we analyze is similar to the one considered, e.g., in Gramling et al. (2002), and we model it in terms of an effective one-dimensional unsteady transport process at the continuum-scale. We distinguish two different approaches, depending on the type of information employed to compute the associated model parameters: (1) an approach based on the use of effective models which require calibration against reactive transport features that are typically observed at the continuum scale, e.g., spatial distribution or breakthrough curves of reactants; and (2) an approach based on upscaled models which only require information on pore-space geometry and on the velocity field to predict reactive transport at the continuum-scale.

A first goal of this work is to provide the numerical approximation of the nonlocal upscaled model of bimolecular reactive transport derived by Porta et al. (2012a). We then consider three additional effective reactive transport models, i.e., the typical advection dispersion reaction equation, which implicitly assumes complete mixing at pore-scale, and the models proposed by Sanchez-Vila et al. (2010) and Hochstetler and Kitanidis (2013). These models differ in terms of the formulation employed to characterize the effective reaction parameters. Consistent with typical applications, we estimate these parameters through results obtained from numerical upscaling of pore-scale calculations.