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Numerical investigation of pore and continuum scale formulations of bimolecular reactive transport in porous media

Giovanni M. Porta [a,*], Sergey Chaynikov [a], Jean-François Thovert [b], Monica Riva [a,c], Alberto Guadagnini [a,c], Pierre M. Adler [d]

[a] Dipartimento Ingegneria Civile ed Ambientale Politecnico di Milano, Piazza L. Da Vinci, 32, I-20133 Milano, Italy
[b] Institut Pprime, CNRS, SP2MI, BP 30179, 86962 Futuroscope Cedex, France
[c] Department of Hydrology and Water Resources, University of Arizona, Tucson, AZ 85721, USA
[d] UPMC – Sisyphe, 4 Place Jussieu, 75252 Paris Cedex 05, France

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ABSTRACT

Focus of this study is a numerical investigation of a reactive transport problem involving an irreversible bimolecular reaction. The advection dispersion reaction equation (ADRE) is typically adopted to model and interpret these types of reactive transport scenarios in porous media at the continuum (Darcy) scale. It is well documented that the theoretical derivation of the ADRE from pore scale system dynamics requires a set of assumptions which are not always met in the context of laboratory and/or field scale applications. We start by recounting the various upscaled formulations which can be obtained through the volume averaging method in the space defined by the Damköhler (*Da*) and Péclet (*Pe*) numbers characterizing the phenomenon. The transport problem is then simulated numerically at the pore scale considering different models of disaggregated porous media. Simulation results provide a framework to discuss the key features and appropriateness of continuum scale formulations which can be employed to describe the target geochemical systems for these settings. The impact of *Pe*, *Da* and pore space configuration on the parameters embedded in the upscaled formulations is analyzed. Conditions under which such formulations hold are discussed, with emphasis on the critical and widely studied advection dominated scenarios associated with fast reactions (i.e., large values of *Pe* and *Da*). Main results include the quantitative assessment of the ability of recently proposed (Porta et al., 2012 [1]) and standard (e.g., ADRE) continuum formulations to quantify the effect of pore scale incomplete solute mixing on upscaled reaction rates.

1. Introduction

Reactive transport in porous media is governed by the pore scale feedback between advection, molecular diffusion and reactive processes. A direct pore scale solution of a typical reactive transport problem is generally not feasible because (i) the knowledge of the complex pore space morphology is incomplete and (ii) pore scale simulation of flow and transport settings which are relevant for laboratory/field scales is computationally prohibitive. Darcy (continuum) scale flow and transport models are then usually employed. Such models rely on approximate formulations that usually embed the effect of the pore scale structure within effective parameters. The latter can be formally derived through upscaling of the pore scale equations (e.g., [2,3]). A typically adopted continuum scale model for reactive transport process in porous media is the advection dispersion reaction equation, ADRE ([4,5] and references therein). Dispersive transport is usually described through the standard Fickian analogy, whereas reactions are modeled upon relying on kinetic coefficients/parameters which are often measured in batch reactors. Battiato and Tartakovsky [6] illustrated the set of sufficient conditions underlying the standard ADRE model. These include spatial scale separation and additional conditions expressed as a function of the Péclet (*Pe*) and Damköhler (*Da*) numbers characterizing the system. They note that reactive transport scenarios of practical interest may violate this specific set of assumptions.

This work focuses on a relatively simple reactive transport problem involving a bimolecular irreversible homogeneous reaction. While geochemical systems observed in real geologic media are often very complex, simplified conditions are usually considered to study the reliability of continuum scale reactive transport models from a theoretical standpoint. The bimolecular reactions of the kind $A + B \rightarrow C$ has been often analyzed as a benchmark problem. Pore scale numerical results are presented providing a detailed description of the evolution of the phenomenon. These

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* Corresponding author. Tel.: +39 0223996256; fax: +39 0223996298.
E-mail address: giovanni.porta@polimi.it (G.M. Porta).

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numerical results are then employed to assess the accuracy and applicability of continuum scale approximations which have been previously proposed for this specific setting [1].

Several works analyze the interaction between diffusion and reaction in the chemical setting we consider (e.g., [7–10]). It is found that the reaction rate evolves in time due to the effect of local fluctuations of the concentration. Experimental observations [11–13] and numerical pore scale simulations [14] show that the assumption of complete mixing at the pore level may vastly overestimate the concentration of the reaction product for fast reactions and advection-dominated transport (i.e., for a large *Pe*, *Da*). In this context, the experimental results provided by Gramling et al. [13] have been interpreted resorting to different approaches which are reviewed in [15]. Edery et al. [16,17] model the experiment through a continuous time random walk (CTRW) particle tracking method where space–time particle transition rates are sampled from a truncated power law distribution. Ding et al. [18] analyze the same experimental data through an advective–diffusive particle-based approach, where the total number of particles employed in the simulation is appropriately selected.

Continuum models have been adopted to reproduce the experiment of [13] by Rubio et al. [19], Sanchez-Vila et al. [20] and Chiogna and Bellin [21]. Chiogna and Bellin [21] employ an analytical approach assuming that (i) calibration of the dispersion coefficient can be performed through a nonreactive experiment, and (ii) local scale reactants concentration are represented by the Beta probability density function. The results of [19] rely on the segregation factor concept introduced in [22]. A time dependent reaction rate coefficient embedded in the standard ADRE formulation is employed by Sanchez-Vila et al. [20]. These authors embed a multirate mass transfer conceptualization of the transport process in the effective reaction rate of the model. Their results suggest that calibration of the dispersion coefficient against non reactive data might not always be appropriate to interpret reactive transport experiments. The model formulations provided by Rubio et al. [19], Sanchez-Vila et al. [20] and Chiogna and Bellin [21] compare favorably against most of the key features of the tested experiments in spite of (a) the lack of a rigorous theoretical foundation and (b) the adoption of very different modeling assumptions. The work of Porta et al. [1] attempts to reconcile these results through the application of the standard volume averaging technique. It is shown that (i) volume averaged continuum scale approximations of passive transport can be recast in terms of a nonlocal in time equation, which naturally tends to recover the format of the standard advection dispersion equation (ADE) for long times; and (ii) a workable continuum approximation may be formulated in the presence of fast reactions by assuming a reaction-based closure of the governing system of equations. The validity of this continuum scale model has been assessed in [23] for a simplified geometry, corresponding to flow within a plane channel. The pore scale simulation of bimolecular reaction in two-dimensional porous media has been recently presented in [24]. Main results of this work include the formulation of an empirical relationship which is based on the segregation intensity factor introduced in [22] and links the effective reaction rate and *Da* for a prescribed *Pe*. It is shown that the reaction constant introduced in the continuum scale model has a limited impact on the global product of the reaction in a replacement setting because the reactive process tends to be dispersion limited for long times.

Here, we focus on bimolecular reaction processes taking place within a set of two-dimensional disaggregated porous media. We consider various (Da, Pe) combinations. Pore scale numerical simulations are performed with the aim of (i) providing a detailed description of the process in fully controlled systems, and (ii) assessing the validity of the assumptions underpinning the upscaled model presented in [1]. Specific attention is devoted to the analysis of the upscaling of the reaction term and in particular to assess the soundness of the reaction-based closure proposed in [1]. Since nonlocal terms are shown to have a negligible impact in the considered two-dimensional systems, the full nonlocal formulation presented in [1] is not solved. The impact of the temporal behavior of the dispersion coefficient on the globally observed product of the reaction is analyzed and compared against numerical results and the analytical solution presented in [13]. With respect to recent contributions (e.g., [24]), the main distinctive features of our work include (i) a detailed documentation of the processes that occur at the pore scale (ii) the assessment of the ability of the upscaled model presented by [1] to incorporate incomplete mixing at the continuum scale, (iii) the quantification of the effect of incomplete mixing on upscaled quantities as a function of both *Da* and *Pe* numbers as well as of the porosity of the medium.

The paper is organized as follows. Section 2 provides the pore scale formulation of the system. Section 3 recalls the main conclusions of the volume averaging analysis of [1]. Section 4 presents key results of the pore scale simulations and of the numerical upscaling. Concluding remarks end the work.

2. Pore scale formulation

We consider a physical domain Ω filled by a fully saturated porous medium, consisting of a liquid (Ω) and a solid fraction (Ω_s). The liquid and the solid phases share a fully impermeable boundary surface, Γ_{ls}. The fluid phase is displaced through the pore space under the action of a steady three-dimensional velocity field $\hat{\mathbf{u}}(\hat{\mathbf{x}})$. Laminar flow is assumed and $\hat{\mathbf{u}}(\hat{\mathbf{x}})$ is governed by

$$\hat{\nabla}\hat{p} = \hat{\mu}\hat{\nabla}^2\hat{\mathbf{u}} - \hat{\rho}\hat{g}\mathbf{k}; \quad \hat{\nabla}\cdot\hat{\mathbf{u}} = 0 \tag{1}$$

Here, $\hat{p}$ is pressure, $\hat{\rho}$ and $\hat{\mu}$ are fluid density and viscosity, respectively; $\hat{g}$ is gravity and $\mathbf{k}$ is a unit vertical vector. No slip boundary conditions require $\hat{\mathbf{u}}(\hat{\mathbf{x}}) = 0$ at boundary Γ_{ls}. Here and in the following, all hat signed variables are dimensional. The external boundary Γ_{ext} can be subdivided into three parts according to the sign of $\hat{\mathbf{u}}(\hat{\mathbf{x}})\cdot\mathbf{n}_e$, i.e., Γ_{in} $(\hat{\mathbf{u}}(\hat{\mathbf{x}})\cdot\mathbf{n}_e > 0)$, Γ_{out} $(\hat{\mathbf{u}}(\hat{\mathbf{x}})\cdot\mathbf{n}_e < 0)$, and Γ_{imp} $(\hat{\mathbf{u}}(\hat{\mathbf{x}})\cdot\mathbf{n}_e = 0)$, $\mathbf{n}_e$ being the inward unit vector normal to the boundary. A bimolecular irreversible reaction of the kind $A + B \rightarrow C$ takes place in the liquid phase and it is assumed that the velocity field and the pore space geometry are not affected by the reaction. Molecular diffusion is modeled through the standard Fick's law. The local mass conservation for the three chemical species can be expressed through

$$\frac{\partial\hat{c}_A}{\partial\hat{t}} + \hat{\mathbf{u}}\cdot\hat{\nabla}\hat{c}_A = \hat{D}_A\hat{\nabla}^2\hat{c}_A - \hat{r}_{AB} \tag{2}$$

$$\frac{\partial\hat{c}_B}{\partial\hat{t}} + \hat{\mathbf{u}}\cdot\hat{\nabla}\hat{c}_B = \hat{D}_B\hat{\nabla}^2\hat{c}_B - \hat{r}_{AB} \tag{3}$$

$$\frac{\partial\hat{c}_C}{\partial\hat{t}} + \hat{\mathbf{u}}\cdot\hat{\nabla}\hat{c}_C = \hat{D}_C\hat{\nabla}^2\hat{c}_C + \hat{r}_{AB}, \tag{4}$$

where $\hat{c}_i$ $(i = A, B, C)$ are the dissolved solute concentrations; $\hat{D}_i$ $(i = A, B, C)$ are the molecular diffusion coefficients which are here assumed to be equal for the chemical species considered, i.e., $\hat{D}_i = \hat{D}$; $\hat{r}_{AB}$ is the reaction rate. Among the available reaction models (see, e.g., [25]), we select the widely used bilinear formulation for the reaction rate (e.g., [7–10,19–24,26–27])

$$\hat{r}_{AB} = \hat{k}\,\hat{c}_A\hat{c}_B, \tag{5}$$

where $\hat{k}$ ($\mathrm{m}^3/(\mathrm{mol\,s})$) is the reaction kinetic constant. The system (2)–(4) is cast into a dimensionless format and the conservative