Lagrangian simulation of multi-step and rate-limited chemical reactions in multi-dimensional porous media

Bing-qing Lu [a], Yong Zhang [a,*], Hong-guang Sun [b], Chun-miao Zheng [c]

[a] *Department of Geological Sciences, University of Alabama, Tuscaloosa, AL 35487, USA*
[b] *College of Mechanics and Materials, Hohai University, Nanjing 210098, China*
[c] *School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China*

Abstract

Management of groundwater resources and remediation of groundwater pollution require reliable quantification of contaminant dynamics in natural aquifers, which can involve complex chemical dynamics and challenge traditional modeling approaches. The kinetics of chemical reactions in groundwater are well known to be controlled by medium heterogeneity and reactant mixing, motivating the development of particle-based Lagrangian approaches. Previous Lagrangian solvers have been limited to fundamental bimolecular reactions in typically one-dimensional porous media. In contrast to other existing studies, this study developed a fully Lagrangian framework, which was used to simulate diffusion-controlled, multi-step reactions in one-, two-, and three-dimensional porous media. The interaction radius of a reactant molecule, which controls the probability of reaction, was derived by the agent-based approach for both irreversible and reversible reactions. A flexible particle tracking scheme was then developed to build trajectories for particles undergoing mixing-limited, multi-step reactions. The simulated particle dynamics were checked against the kinetics for diffusion-controlled reactions and thermodynamic well-mixed reactions in one- and two-dimensional domains. Applicability of the novel simulator was further tested by (1) simulating precipitation of calcium carbonate minerals in a two-dimensional medium, and (2) quantifying multi-step chemical reactions observed in the laboratory. The flexibility of the Lagrangian simulator allows further refinement to capture complex transport affecting chemical mixing and hence reactions.

1. Introduction

Accurate simulation of reactive transport in natural media remains one of the greatest challenges in hydrology, mainly due to its multi-scale process including molecular-scale reaction and the representative elementary volume (REV)-scale transport (Dentz et al., 2011). Recent efforts have focused on the fundamental, second-order bimolecular reaction $A + B \rightleftharpoons C$ (Willingham et al., 2008; Luo et al., 2008; Benson and Meerschaert, 2008; Bolster et al., 2017). To predict the concentration evolution of compounds undergoing bimolecular reaction in laboratory- and regional-scale porous media, the following advection-dispersion-reaction (ADR) continuum model combining transport and reaction at the same REV scale has been widely used (e.g., Ham et al., 2004):

$$
\begin{cases}
\dfrac{\partial C_\text{A}(x,t)}{\partial t} = -v\dfrac{\partial C_\text{A}(x,t)}{\partial x} + D\dfrac{\partial^2 C_\text{A}(x,t)}{\partial x^2} - K_\text{f}C_\text{A}(x,t)C_\text{B}(x,t) + K_\text{r}C_\text{C}(x,t) \\[2mm]
\dfrac{\partial C_\text{B}(x,t)}{\partial t} = -v\dfrac{\partial C_\text{B}(x,t)}{\partial x} + D\dfrac{\partial^2 C_\text{B}(x,t)}{\partial x^2} - K_\text{f}C_\text{A}(x,t)C_\text{B}(x,t) + K_\text{r}C_\text{C}(x,t) \\[2mm]
\dfrac{\partial C_\text{C}(x,t)}{\partial t} = K_\text{f}C_\text{A}(x,t)C_\text{B}(x,t) - K_\text{r}C_\text{C}(x,t)
\end{cases}
\tag{1}
$$

where v [LT^{-1}] is the mean flow velocity; D [L^{2}T^{-1}] is the macrodispersion coefficient; K_f [M^{-1}L^{3}T^{-1}] and K_r [T^{-1}] are the forward and reverse kinetic coefficients of reaction, respectively; and $C_\text{A}(x, t)$, $C_\text{B}(x, t)$, and $C_\text{C}(x,t)$ [ML^{-3}] denote the concentrations of species A, B, and C, respectively, at time t and position x.

The assumption underlying the ADR model (Eq. (1)) is the perfect mixing of reactants, which has been found to be invalid for groundwater, since the saturated porous medium is usually inhomogeneous (Tartakovsky et al., 2009; Barnard, 2017). The incomplete mixing of reactant particles also explains the well-known fact that the reaction rate measured with batch experiments (in solutions) is much higher than that observed in sand columns, and the reaction rate measured in the laboratory (under the condition of complete mixing) is typically much higher than that observed in the field (Kapoor et al., 1997; Raje and Kapoor, 2000; Cirpka, 2002; Gramling et al., 2002), challenging the application of the continuum model (Eq. (1)) in quantifying real-world reactive kinetics in aquifers (Cirpka and Valocchi, 2016).

Full particle tracking-based Lagrangian approaches have been developed by various researchers for decades to quantify the imperfect mixing of reactants undergoing bimolecular reactions, or the so-called diffusion-controlled bimolecular reaction kinetics in porous media. For example, Smoluchowski (1918) assumed that two reactant molecule particles can react whenever they are close to each other. Gillespie (1977) developed perhaps the first random walk-based stochastic approach to simulate coupled chemical reactions with inherent fluctuations and correlations in spatially homogeneous systems. Toussaint and Wilczek (1983) quantified kinetics of diffusive particles undergoing irreversible annihilation. The pioneering work of Smoluchowski (1918) motivated various stochastic simulation algorithms in the chemical physics and biology communities (Erban and Chapman, 2009), including, for example, the compartment models (where molecules within the same compartment can react) (Hattne et al., 2005; Isaacson and Peskin, 2006) and the grid-free methods for the simulation of motion of individual molecules (Andrews and Bray, 2004; Tournier et al., 2006; Gillespie, 2009). Recently, in the hydrological community, Benson and Meerschaert (2008) have developed a probability-based scheme by accounting for the overlapped effective volume of two reactant molecules. Edery et al. (2009, 2010)

introduced a memory function into stochastic simulation algorithms, to capture the non-Fickian transport missed by previous simulations. Ding et al. (2013) developed a particle tracking scheme using two probabilities dictated by the physics of transport and energetics of reaction. Paster et al. (2013) proved theoretically that the particle method proposed by Benson and Meerschaert (2008) does match the governing equations for chemical transport. Benson et al. (2017) compared Lagrangian schemes and Eulerian nonlinear reactive transport in two-dimensional (2D) porous media. Engdahl et al. (2017) then modeled multicomponent reactions in one-dimensional (1D) media. Most of the previous Lagrangian approaches have been limited to bimolecular reactions and/or numerical analysis. To the best of our knowledge, none of the previous Lagrangian solvers has been checked against real world, complex (such as multi-step or higher than second-order) chemical reactions, and most successful applications are limited to 1D media. These limitations motivated this study.

The rest of this paper is organized as follows: Section 2 describes how the Lagrangian framework was developed to approximate reversible, multi-step chemical reactions, including derivation of the spatial range in any dimension where reaction may occur. A fully Lagrangian scheme is then described in section 3, as used to model the coupled advection, dispersion, and reaction at two different scales (i.e., the molecular-scale reaction and REV-scale transport). In section 4, we check reactive kinetics against classical rate equations in both one and two dimensions, and the application of the Lagrangian approximation of diffusion-controlled chemical reactions to simulate a two-step reaction as observed in the literature (Oates and Harvey, 2006) and a 2D mineral precipitation process. In section 5, we discuss the ways reaction kinetics change with medium dimensions and possible model extensions. Conclusions are drawn in section 6.

2. Methodology development: Derivation of interaction radius

This study conceptualized chemical reaction as a random process, for the following reasons. According to collision theory (Trautz, 1916), reactant particles can collide if their nuclei get closer than a certain distance, which is called the interaction radius, denoted as R (Fig. 1). Chemical reactions