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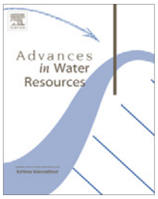

Modeling bimolecular reactions and transport in porous media via particle tracking

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ABSTRACT

We use a particle-tracking method to simulate several one-dimensional bimolecular reactive transport experiments. In our numerical scheme, the reactants are represented by particles: advection and dispersion dominate the flow, and molecular diffusion dictates, in large part, the reactions. The particle/particle reactions are determined by a combination of two probabilities dictated by the physics of transport and energetics of reaction. The first is that reactant particles occupy the same volume over a short time interval. The second is the conditional probability that two collocated particles favorably transform into a reaction. The first probability is a direct physical representation of the degree of mixing in an advancing interface between dissimilar waters, and as such lacks empirical parameters except for the user-defined number of particles. This number can be determined analytically from concentration autocovariance, if this type of data is available. The simulations compare favorably to two physical experiments. In one, the concentration of product, 1,2-naphthoquinoe-4-aminobenzene (NQAB) from reaction between 1,2-naphthoquinone-4-sulfonic acid (NQS) and aniline (AN), was measured at the outflow of a column filled with glass beads at different times. In the other, the concentration distribution of reactants ($CuSO_4$ and $EDTA^{4-}$) and product ($CuEDTA^{2-}$) were quantified by snapshots of light transmitted through a column packed with cryolite sand. These snapshots allow us to estimate concentration statistics and calculate the required number of particles. The experiments differ significantly due to a $\sim 10^7$ difference in thermodynamic rate coefficients, making the latter experiment effectively instantaneous. When compared to the solution of the advection–dispersion-reaction equation (ADRE) with the well-mixed reaction coefficient, the experiments and the particle-tracking simulations showed on the order of 20–40% less overall product, which is attributed to poor mixing. The poor mixing also leads to higher product concentrations on the edges of the mixing zones, which the particle model simulates more accurately than the ADRE.

1. Introduction

As groundwater moves through an aquifer, it often undergoes chemical reaction as it mixes with chemically dissimilar water or encounters reactive solids. The reactions are local phenomena, but predictions of reactive transport are often made at much larger scales. This mismatch of scales has been found to degrade the predictions of reaction. In particular, the reaction rates at the larger scale are found be be much less than those measured in the laboratory [1–4]. To make predictions, a Fickian transport equation is typically coupled to a chemical reaction equation to form the advection–dispersion-reaction equation (ADRE):

$$\partial C_i/\partial t = -\nabla \cdot (\mathbf{u}C_i - D\nabla C_i) - r_i \tag{1}$$

where $C_i(\mathbf{x},t)$ is the concentration, t is time, $\mathbf{u}(\mathbf{x},t)$ is the Darcy scale pore water velocity, $D(\mathbf{x},t)$ is the hydrodynamic dispersion tensor, and $r_i(\mathbf{x},t,C_1,C_2,\ldots)$ is the reaction rate of species i. The reaction rate, a crucial term in ADRE, is commonly estimated from batch tests under perfect mixing conditions of the same reaction [5,6,4,7,8,3]. When this reaction rate is used in Eq. (1) to predict miscible displacement and reaction in column- and field-scale tests, the observed reaction rate is generally much smaller [6,9–11]. An effective reaction coefficient (<1), is commonly applied to the last term of ADRE to account for the over-estimated reaction [12,7,6,13]. Unfortunately, the coefficient value is difficult to determine and varies from case to case (and scale to scale) [6,8].

Laboratory and numerical experiments (e.g., [8,5,12]) revealed that incomplete mixing is primarily responsible for the reduced reaction rates. The dispersion term in Eq. (1) simultaneously describes both spreading of, and mixing among, solute fronts between dissimilar water. But in real-world and synthetic tests, the spreading rate is found to be greater than the mixing rate [14,11,15–19]; therefore, an equation that correctly simulates spreading will overpredict the mixing of the water. For example, Kapoor et al. [8] theorized (and showed numerically) that the simple bimolecular reaction ($A + B \rightarrow C$) for Poiseuille flow and Taylor

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dispersion within a single tube would result in reduced reaction relative to the well-mixed rate. In a series of numerical and laboratory experiments, Raje and Kapoor [5] constructed a glass bead-filled column and showed that the product concentration in the column was approximately 40% less than what was predicted by Eq. (1) in one-dimension (1*D*). Gramling et al. [12] found overall product production of approximately 20% less in their column than predicted by Eq. (1) based on experiments at different flow velocities. These observations point to several deficiencies of the ADRE: (i) the deterministic concentration neglects small-scale fluctuations [5,12,7,20]; (ii) the reactants are assumed to be well-mixed, which is unusual under natural conditions [6,20,21]; and (iii) the dispersion term is forced to account for both the spreading and the dilution, or mixing, of the species [22,23].

The mixing that leads to reaction is often limited to transverse dispersion and diffusion. In porous media, these mechanisms are orders-of-magnitude lower than longitudinal dispersion [5,24,22,14]. In recent studies, both Edery et al. [20] and Tartakovsky et al. [21] noticed that the slow diffusion of the reacting species into and out of plume boundaries determines the reaction rate and explains why averaged concentration models over-predict the amount of reaction. A variety of studies (e.g. [25–28]) demonstrate that reactants are not perfectly mixed and diffusion is a limiting process even in free fluid flow without the structure imposed by porous media.

A series of theoretical studies [6,29,9] showed that the upscaled equations of reaction in the presence of diffusion are different from the perfectly-mixed equation and uniquely defined by the transport mechanism. These studies showed that it not necessarily proper to arbitrarily combine transport and reaction equations. Various reactive transport models have been proposed [30–32,10,33,4,21,34] and a variety of laboratory (e.g. [5,12,35]) and field studies (e.g. [36–40]) have been conducted to test the validity of various modeling approaches that separately account for mixing, reaction, and transport. One approach is a Lagrangian particle tracking (PT) method. The general Lagrangian framework has given rise to several algorithms that represent smaller-scale physics in different ways. For example, the smoothed particle hydrodynamics method simulates a given partial differential equation (PDE) on moving particles instead of on a fixed grid [41,42,10]. This method rests on the assumption that the chosen PDE for transport and reaction is the correct one at some smaller scale.

A different Lagrangian model from Benson and Meershaert [29] makes no assumption about the form of the governing equation for reaction. Their PT method simulates chemical reactions through probabilistic rules of particle collisions, interactions, and transformations. The method is based on an explicit calculation of the probability that any two particles will be co-located in any time interval, in combined with the independent probability that two particles, upon co-location, will react. The second probability is the well-mixed reaction rate scaled appropriately by the number of particles and the volume associated with that rate. Benson and Meerschaert's [29] method is an extension of Gillespie's [43], which uses a well-mixed assumption to calculate the probability of particle co-location (and leads to the classical mass-action reaction equations [44]). It was shown recently by Paster et al. [45] that at the limit of infinitely small time step and infinite number of particles, the PT method converges to the well-mixed ADRE (1) using the classical law of mass action for a bimolecular reaction.

Other approaches have also been proposed, such as different forms of underlying transport [9,46,47], time dependent reaction rate coefficients [48,49], stochastic perturbation models [7], and multi-rate mass transfer [50,51]. These models can be calibrated to simulate the reactive transport successfully by reproducing anomalous flux-averaged breakthrough curves [52,21]. However, as indicated by Tartakovsky et al. [21], these approaches require additional effective parameters, which can only be obtained from calibration with experimental data.

In this study, we test the hypothesis that the bulk of the experimental observations can be explained by the application of simple, physically-based rules of transport and reaction within a Lagrangian framework. The transport algorithm is based on Fickian dispersion with a mean advective drift, and the bimolecular reactions use the PT method from Benson and Meerschaert [29], in which the reaction probability only depends on the thermodynamic rate of the chemical reaction and the distribution of particles in both space and time.

2. Methods

2.1. Summary of column experiments

We consider the column experiments conducted by Raje and Kapoor [5] and Gramling et al. [12], which are widely regarded as benchmarks of reactive transport in porous media [53,20,49,46]. Raje and Kapoor [5] used a spectrophotometer to obtain the outflow concentrations of product from the transport and reaction of 1,2-naphthoquinone-4-sulfonic acid (NQS) and aniline (AN) in a column filled with glass beads. They ran two experiments, each with different flow rates and concentrations of reactants. Gramling et al. [12] took images of light transmitted through a colorimetric reaction between aqueous $CuSO_4$ and $EDTA^{4-}$ within a translucent chamber packed with cryolite sand to observe the concentration distribution of compounds within the column. They ran three experiments at three different velocities with all other parameters held constant. The physical setup of all of the experiments considered here was similar. Initially, the columns were saturated with one species at concentration C_0, and the other reactant was introduced at the inlet at a constant rate and the same constant concentration C_0. Peclet numbers of both experiments were high, but Reynolds numbers were sufficiently low to ensure laminar flow.

Before performing the column experiments, the reaction rate constants were obtained with high confidence from well-mixed batch experiments. Dispersion coefficients at each velocity were measured via conservative tracer, and diffusion coefficients were gathered from the literature. Hydrodynamic dispersion dominated over diffusion in spreading the inert tracer at all velocities. The parameters from the two experiments under different flow conditions are summarized in Table 1.

Primarily because of the different reactions rates, different solution methods were used to evaluate the experimental results in these two studies, even though both assumed one-dimensional flow. For a well-mixed system, the law of mass action for the irreversible reaction $A + B \rightarrow P$ can be expressed as $r_A = r_B = -r_P = dC_A/dt = -k_f C_A C_B$. Both groups used this law in the ADRE (1) to compare to experimental results. Raje and Kapoor [5] solved the ADRE (1) at the outflow using the finite difference (FD) scheme. Gramling et al. [12] used an analytical solution by assuming the reaction was instantaneous and the boundaries remote. Their solution is

$$\frac{C_P}{C_0} = \frac{1}{2}\operatorname{erfc}\left(\frac{|x - ut|}{\sqrt{2Dt}}\right), \tag{2}$$

where $C_P(x, t)$ is product concentration, and C_0 is the constant flux concentration of the injected reactant at the inlet boundary [12]. We also use an FD solution to compare to Raje and Kapoor's [5] data and the analytic solution (2) for Gramling et al.'s [12] data.

2.2. Methodology of particle reaction and transport

Our particle tracking algorithm separately simulates transport and reactions in any given time step. For reaction, the model assumes that molecular diffusion dictates the probability that