# SIMULATING MIXING LIMITED REACTIONS IN POROUS MEDIA USING FINITE DIFFERENCES

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## ABSTRACT

For systems with high second Damköhler number (reaction rate over diffusive mass transport rate) the reaction rate is limited by the mixing of the reactants. Instead of the reaction proceeding proportional to $t^{-1}$, the reaction proceeds at a rate proportional to $t^{-d/4}$, where $d$ is the dimensionality of the system. This has been shown analytically [7] and numerically, using particle tracking methods (*e.g.* [1]). This happens when reactants are initially segregated, or the forward progress of the reaction leads to the segregation of the reactants, which then diffuse back together.

Experiments have shown that even with highly homogeneous porous media, the observed reaction rate is less than expected if the reactants were mixed completely [4,5]. The experiments performed by [4] have been studied using numerical methods, most of which have used particle tracking methods (*e.g.* [2,3,8]). This work presents a finite difference formulation of a model which can reproduce systems in which reactions a limited by mixing on the sub discretization scale, and where imposed mixing rates of reactants leads to reactions proceeding at $t^{-d/4}$ over long timescales. This is achieved by simulating the mixing of reactants separately from the spatial discretization of the problem by separating each reactant into a mixed and unmixed fraction and defining rate laws to describe the transfer of reactants between the mixed and unmixed states.

The model developed is benchmarked against experimental data from [4] and produces a fit which compares well with outputs produced by other simulation studies.

**Key Words:** *mixing limited reactions, reactive transport, porous media, continuum methods*

## 1. Introduction

When well mixed batch reaction rates are used for simulations of solute reactions in porous media the simulation outputs often give a higher reaction rate than laboratory or field scale experimental studies. This has been attributed to the reaction rate being limited by the rate at which the reactants mix together [4,5]. To produce accurate results simulations must include some method of limiting the reaction rate. Studies such as [6] perform this by using a time dependent reaction rate coefficient of the form $K_r = \beta_0 t^{-m}$. Mixing limited reactions have been simulated using particle tracking methods (e.g. 2,3,8) which are effective, though these are computationally expensive and not well suited to large scale, complex, multicomponent reaction systems.

The classical solution of the reaction between two well mixed solutes of the form $A + B \rightarrow C$ is given by

$$\frac{dA}{dt} = -\Delta t K_r [A][B] \tag{1}$$

$$\frac{dB}{dt} = -\Delta t K_r [A][B] \tag{2}$$

$$\frac{dC}{dt} = \Delta t K_r [A][B] \tag{3}$$

where $K_r$ is the reaction rate coefficient and $[A]$ and $[B]$ are the concentrations of the solutes $A$ and $B$ respectively. This reaction system has a solution of the form

$$[A](t)/[A]_0 = ([A]_0 K_r t + 1)^{-1} \tag{4}$$

which give a long time reaction rate proportional to $t^{-1}$. Starting from a particle basis [7] showed that imperfectly mixed reactants will react at a rate proportional to $t^{-d/4}$, where $d$ is the dimensionality of the system and takes the form

$$\rho = \rho_0^{1/2}(2\pi)^{-3/4}(Dt)^{-1/4}, \tag{5}$$

$$\rho = \rho_0^{1/2}2^{-3/2}\pi^{-1}(Dt)^{-1/2}, \tag{6}$$

$$\rho = \rho_0^{1/2}2^{-7/4}\pi^{-5/4}(Dt)^{-3/4}, \tag{7}$$

where $\rho$ is the particle density, $\rho_0$ is the initial particle density, and $D$ is the diffusivity. The replication of this behaviour, as well as the production of a high quality experimental fit for a reaction-advection-dispersion system is the objective of the work presented here. By constrast, most previous studies have focussed solely on the quality of the experimental fit for a reaction-advection-dispersion system.

This paper presents a new method for limiting the reaction rate based on a conceptual model where each reactant is divided into two "pools", one of which is close to the other reactant, and so can take part in reactions, and one which is separate, and so cannot. The solutes are transported between these two pools, and the rate at which this occurs controls the reaction rate. This allows for the simulation of reactions where the reactants are partially segregated on the sub pore scale without the computational expense of pore scale simulations.

## 2. Method

The mixing limited reaction system is simulated by conceptually separating each reactant into into a mixed and an unmixed fraction, denoted using the subscripts $m$ and $u$ respectively. The formulation for a zero dimensional reaction system of the form $A + B \rightarrow C$ is given as

$$\frac{\mathrm{d}A_u}{\mathrm{d}t} = -\Delta t \cdot K_m \left[A_u\right]^M, \tag{8}$$

$$\frac{\mathrm{d}B_u}{\mathrm{d}t} = -\Delta t \cdot K_m \left[B_u\right]^M, \tag{9}$$

$$\frac{\mathrm{d}A_m}{\mathrm{d}t} = \Delta t \left(K_m \left[A_m\right]^M - K_r \left[A_m\right]\left[B_m\right]\right), \tag{10}$$

$$\frac{\mathrm{d}B_m}{\mathrm{d}t} = \Delta t \left(K_m \left[B_m\right]^M - K_r \left[A_m\right]\left[B_m\right]\right), \tag{11}$$

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \Delta t \cdot K_r \left[A_m\right]\left[B_m\right], \tag{12}$$

where $K_m$ is the mixing rate, $K_r$ is the reaction rate, and $M$ is an exponent used to control the rate of mixing. When $M$ is set to unity the mixing rate is exponential and so the limiting factor becomes the reaction rate, leading to a reaction rate proportional to $t^{-1}$. The mixing limited reaction rates for different dimensionalities, proportional to $t^{-1/4}$, $t^{-1/2}$, and $t^{-3/4}$, can be achieved by setting $M$ to 5, 3, and 7/3 respectively.

This model makes the assumption that the reactants are initially poorly mixed or totally separate, as it incorporates no method to segregate the reactants on the sub pore scale. The experiment used for benchmarking is a simulation of two totally separate reactants which mix imperfectly as they disperse, meaning that the assumption of perfect mixing leads to an overestimation of the reaction rate. The model is able to simulate this system but needs expanding to be able to simulate systems where mixing limited reactions a caused by the forward progress of the reaction segregating the reactants.

## 3. Results

The model is benchmarked by comparison with experimental results from [4]. A 36 cm by 5.5 cm by 1.8 cm porous medium is saturated with a 0.02 Mol solution of $CuSO_4$, which is displaced by a 0.02 Mol solution of $Na_2EDTA^{2-}$ at a constant flow rate of 2.67 mLmin$^{-1}$. The flow field is one dimensional, along the long axis of the domain. The reaction between the two solutes is given as

$$Na_2EDTA^{2-} + CuSO^4 \rightarrow CuEDTA^{2-} + Na^+ + SO_4^{2-} \qquad (13)$$
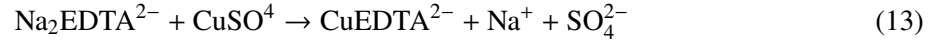
and is assumed to be instantaneous in well mixed systems. To simulate this system dispersive transport is added to the formulation above. The constant flow field allows for advection to be neglected for the sake of simplicity. This is done by centering the domain around $vt$. When plotted the product concentration profile is shifted along the $x$-axis by $vt$ to fit to the experimental data and for clarity of viewing rather than being plotted with the same centre point.

Figure 1 shows the best fit simulation results and the experimental data from [4]. As the bulk flow field is one dimensional the problem is simulated as a one dimensional problem using finite differences.The initial conditions are $[A_m]_0 = [B_m]_0 = 0$, $[A_u]_0 = 0$ from $0 \leq x < \ell/2$, $[A_u]_0 = 0.02$ from $\ell/2 \leq x \leq \ell$, and $[B_u]_0 = 0.02 - [A_u]_0$ from $0 \leq x \leq \ell$. The simulation setup has; domain length $\ell = 36$ cm, $\Delta x = 0.1$ cm, $D_h = 1.75 \times 10^{-3}$ cm$^2$s$^{-1}$, $K_m = 75$ mol$^{1-M}$cm$^{3M-1}$s$^{-1}$, $K_r = 10$ cm$^3$mol$^{-1}$s$^{-1}$, and $M = 3$. The best fit is achieved by having a two dimensional mixing regime ($M = 3$). The dimensionality of the mixing regime affects the rate at which the peak product concentration changes. A good fit to the data at $t = 619$s can be achieved with any of the mixing regimes, but a fit to all three can only be achieved with a two dimensional mixing regime.

The quality of the fit produced is superior to methods where the reaction rate is reduced by reducing the reaction rate coefficient. [6] are able to produce a comparable quality fit for $t = 619$s, though this is achieved by reducing the coefficient of dispersivity by ~25%, and are unable to reproduce the increase in peak product concentration observed in the experimental results presented by [4]. The quality of the fit also compares well with results presented in numerical studies using particle tracking methods, which are intrinsically capable of simulating mixing limited reaction systems [1,2].
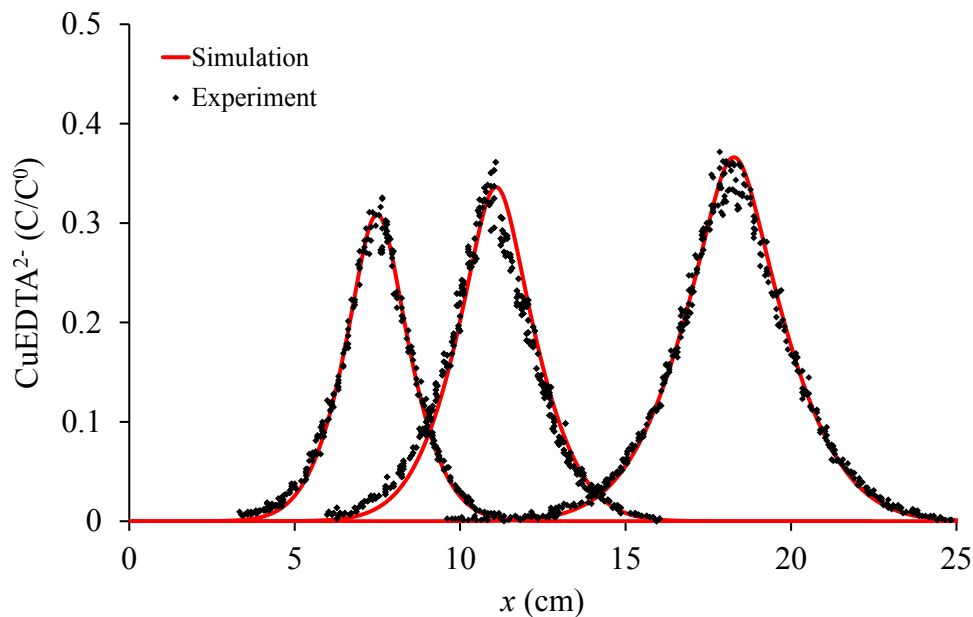


Figure 1: Comparison of the reactive transport simulation utilizing $t^{-0.5}$ mixing with the experimental data from [4] at times 619 s, 916 s, and 1510 s (left to right).

## 4. Conclusions

In this article a new method for simulating mixing limited reaction using continuum methods has been presented. This method is based around the separation of each reactant into two fractions to represent the mixed and unmixed reactants, and a formulation for the transfer of reactant from the unmixed to the mixed fraction and *vice versa*. This method reproduces the $t^{-d/4}$ mixing regime, rather than altering the reaction rate coefficient as other studies have. The quality of the fit to an widely used experimental benchmark is good and compares favourably with other studies. The method makes the assumption that the reactants are initially either poorly mixed or entirely separated, as this is sufficient for the simulation of the experiments presented in [1]. Despite this the action of the reaction process to resegregate the reactants is an important aspect in the behaviour of mixing limited reaction systems. As such the next step is to expand the formulation to include a segregation term.

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