INVESTIGATING THE ACCURACY OF A DARCY SCALE MODEL OF COMPETITIVE ADSORPTION IN A POROUS MEDIUM THROUGH SPH PORE SCALE MODELING

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Summary. *In this paper we investigate the accuracy of a Darcy-scale model for competitive adsorption in a porous medium through comparison with a smoothed particle hydrodynamics (SPH) pore-scale model. SPH is a Lagrangian, particle based modeling method which uses the particles as interpolation points to directly discretize the governing equations of the system. The models consider a binary system of competitively adsorbing species traveling through a porous medium due to advection and diffusion. The effects of Damköhler number and porous microstructure on the accuracy of the Darcy-scale model when compared to the pore-scale model are investigated. The comparison of the Darcy-scale model and the pore-scale model shows that the Darcy model overestimates the mass of a plume moving through the domain for all Damköhler numbers investigated and is not able to accurately predict the masses of both surface species in a reactive system.*

1 INTRODUCTION

Reactive transport in porous media occurs in many different fields of science and engineering, including subsurface transport[1], fuel cells[2], and biomedical systems. Understanding the transport and reaction mechanisms occurring within porous media can aid in the design of new systems, such as fuel cells, and in addressing current engineering problems, such as the remediation of contaminants in the subsurface. Computational modeling is a powerful tool for the investigation of porous media and reactive transport. Modeling can provide insight into the local conditions within porous media and the long term conditions in a system, which can be costly and time consuming to obtain through experimental means. We have developed a pore-scale smoothed particle hydrodynamics (SPH) model of reactive transport in porous media[3]. The model uses a discrete representation of the porous medium to explicitly model the surface reactions in a porous medium without

the need for effective parameters.

SPH is a grid free modeling method which discretizes the system with a set of particles which are used as interpolation points to directly solve the governing equations of the system. The Lagrangian nature of the SPH method makes it well suited for modeling complex geometry (such as porous media) and advecting systems. Its particle nature allows for easy implementation of physics and chemistry at the surfaces, such as the surface reactions discussed in this paper.

In this paper we investigate the accuracy of modeling reactive transport in a porous medium at the Darcy-scale by comparing the total mass and distribution of species predicted by the Darcy-scale model to a pore-scale SPH model for a competitively adsorbing binary system moving through a porous medium. The two models are laid out in this paper and the total mass and species distributions predicted by the models are compared for various Damköhler numbers. The paper is organized as: section 2 describes the pore-scale reactive transport model, section 3 describes the Darcy-scale model, section 4 discusses the simulation setup and the different conditions considered, section 5 presents the results, and the conclusions are discussed in the final section.

2 PORE-SCALE MODEL

The pore-scale model uses a discrete representation of the solid porous medium (Ω_S) and the fluid in the pore space (Ω_F) to model reactive transport in a porous medium Ω ($\Omega \in \Omega_S \cup \Omega_F$).The porous medium modeled in this paper is an idealized two dimensional porous medium consisting of circular solid grains placed in a square unit cell with a porosity of 0.42. The simulation domain is made up of four unit cells aligned along the flow direction (x). Two different porous microstructures are compared to the Darcy-scale model; a heterogeneous microstructure which has randomly placed solid grains and a homogeneous microstructure which has an ordered distribution of uniform radii solid grains, **Figure 2**.

The competitive adsorption of two species (A and B) moving through the porous medium via advection and diffusion is modeled with both the Darcy- and pore-scale models. Competitive adsorption is the adsorption of two or more species to the same adsorption sites on a surface. In the pore-scale model competitive adsorption occurs on the surfaces of the solid grains, Γ, and is modeled with the Langmuir adsorption model,[5]

$$R_S^a(\bar{x}_s,t) = k_a^+ c^a(\bar{x}_s,t)\left[1-\theta^a(\bar{x}_s,t)-\theta^b(\bar{x}_s,t)\right]^g - k_a^-\left(\theta^a(\bar{x}_s,t)\right)^g \qquad \bar{x}_s \in \Gamma \qquad (1)$$

where $\bar{x}_s$ is a point on Γ, c^a is the aqueous concentration of species a ($a=A,B$), θ^a is the normalized concentration of adsorbed species a, k_a^+ and k_a^- are the adsorption and desorption rate coefficients, respectively, and g is the number of adsorption sites needed by each species. For generality, in the simulations presented here species A is assumed to adsorb to two sites ($g=2$); while species B is assumed to adsorb to three sites ($g=3$).

The porous medium initially contains species A at equilibrium and at $t=0$ species B is introduced to the system with the fluid entering the domain. A steady state incompressible fluid flowing from right to left in the domain is modeled using the momentum and mass

conservation equations. A no-slip, no-flow boundary condition is applied at the solid grains and the flow is periodic in the x- and y-directions.

The transport of species A and B in the porous medium is described by the advection-diffusion equation,

$$\frac{Dc^a(\bar{x},t)}{Dt} = \nabla \cdot (D(\bar{x})\nabla c^a(\bar{x},t)) \qquad \bar{x} \in \Omega_F \tag{2}$$

where D is the diffusion coefficient.

The species are periodic in the y-direction and a no mass flux boundary condition is applied at $x=0$. Species B is introduced to the system with the flow at $x=H$, where H is the length of the domain, for an initial period of time while species A has a no mass flux boundary condition at $x=H$. After the initial time period a no mass flux boundary condition is also applied to species B at $x=H$. The competitive adsorption surface reactions are applied as a boundary condition to Eq. (2) at the solid grains,

$$D\nabla c^a(\bar{x}_s,t) \cdot \bar{n}(\bar{x}_s) = R_S^a(\bar{x}_s,t) \qquad \bar{x}_s \in \Gamma \tag{3}$$

where $\bar{n}$ is the normal to the surface Γ and R_S^a is described by Eq.(1).

The solid grains of the porous medium are considered impermeable and as such the change in concentration of adsorbed species (s^a) in the system is only due to the adsorption reaction and from mass conservation will be,

$$\frac{ds^a(\bar{x}_s,t)}{dt} = R_S^a(\bar{x}_s,t) \qquad \bar{x}_s \in \Gamma \tag{4}$$

Flux boundary conditions, Eq.(3), are difficult to implement in numerical methods such as SPH, especially in systems with complex geometries such as a porous medium. We developed a novel model, the continuum surface reaction (CSR) model[3], to implement a flux boundary condition as a source term added to the governing equation (2),

$$\frac{Dc^a(\bar{x},t)}{Dt} = \nabla \cdot (D(\bar{x})\nabla c^a(\bar{x},t)) - R_V^a(\bar{x},t) \qquad \bar{x} \in \Omega_F \tag{5}$$

subject to

$$\bar{n}(\bar{x}_s) \cdot D\nabla c^a(\bar{x}_s,t) = 0 \qquad \bar{x}_s \in \Gamma \tag{6}$$

The CSR model recasts the sharp interface, Γ, as a diffuse interface over which a volumetric reaction term, R_V^a, is applied to the advection-diffusion equation[3]. Using a characteristic function, φ, which has a unique value on either side of the interface, the volumetric source term, R_V^a, is related to the surface reaction term, R_S^a, by,

$$R_V^a(\bar{x},t) = \int_{\Omega_S} \tilde{R}_S^a(\bar{x},\bar{x}',t)\left(\bar{n}(\bar{x})+\bar{n}(\bar{x}')\right)\left(\varphi(\bar{x}')-\varphi(\bar{x})\right)\nabla_{\bar{x}}W(\bar{x}'-\bar{x},h_r)d\bar{x}' \qquad \bar{x} \in \Omega_F \tag{7}$$

In Eq.(7), W is the SPH smoothing function[6] and R_S^a which was defined on the surface Γ has been replaced with $\tilde{R}_S^a$, which is defined throughout the diffuse interface as,

$$\tilde{R}_S^a(\vec{x},\vec{x}',t) = k_a^+ c^a(\vec{x},t)\left[1 - \tilde{\theta}^a(\vec{x}',t) - \tilde{\theta}^b(\vec{x}',t)\right]^g - k_a^-\left(\tilde{\theta}^a(\vec{x}',t)\right)^g \quad \vec{x} \in \Omega_F, \ \vec{x}' \in \Omega_S \quad (8)$$

where θ^a has been replaced with $\tilde{\theta}^a$ which is defined throughout the solid side of the diffuse interface and is defined by the concentration of adsorbed species as $\tilde{\theta}^a(\vec{x},t) = \dfrac{\tilde{s}^a(\vec{x},t)}{\tilde{s}_{max}^a(\vec{x})}$, where $\tilde{s}_{max}^a$ is the maximum concentration of adsorbed species in CSR form. In the CSR form s^a is replaced with $\tilde{s}^a$ which is defined throughout the solid side of the diffuse interface as,

$$\frac{d\tilde{s}^a(\vec{x},t)}{dt} = \int_{\Omega_F} \tilde{R}_S^a(\vec{x}',\vec{x},t)\left(\vec{n}(\vec{x}) + \vec{n}(\vec{x}')\right)\left(\varphi(\vec{x}') - \varphi(\vec{x})\right)\nabla_{\vec{x}}W(\vec{x}' - \vec{x},h_r)d\vec{x}' \quad \vec{x} \in \Omega_S \quad (9)$$

The SPH method is used to discretize the governing equations of the pore-scale model. In the SPH method the domain is divided into a discrete number of particles. In our model the system is divided into two sets of particles: Ω_S is discretized with "solid" particles and the aqueous phase occupying Ω_F is discretized with "fluid" particles. The positions of solid particles are fixed in time and fluid particles move through the domain with the fluid velocity.

Using the SPH discretization scheme[6] the species governing equations of the pore-scale model can be written for species A and B from the Eqs.(5) and (9) as[3],

$$\frac{DX_i^a}{Dt} = \frac{1}{m_i}\sum_{j \in fluid} \frac{D_i(m_id_i + m_jd_j)}{d_id_j}\left(X_i^a - X_j^a\right)\frac{\vec{x}_{ij}}{\vec{x}_{ij}^2}\nabla_iW(\vec{x}_{ij},h)$$
$$- \sum_{k \in solid}\left[k_a^+ X_i^a\left[1 - \tilde{\theta}_k^a - \tilde{\theta}_k^b\right]^g - \frac{k_a^-}{d_im_i}\left(\tilde{\theta}_k^a\right)^g\right]\frac{2\left(\varphi_i - \varphi_k\right)\left(\vec{n}_i + \vec{n}_k\right)}{d_k + d_i}\nabla_iW(\vec{x}_{ik},h_r) \quad (10)$$

$$i \in fluid \ particles$$

$$\frac{d\tilde{Y}_k^a}{dt} = \sum_{i \in fluid}\left[k_a^+ X_i^a\left[1 - \tilde{\theta}_k^a - \tilde{\theta}_k^b\right]^g - \frac{k_a^-}{d_im_i}\left(\tilde{\theta}_k^a\right)^g\right]\frac{2\left(\varphi_k - \varphi_i\right)\left(\vec{n}_i + \vec{n}_k\right)}{d_k + d_i}\nabla_kW(\vec{x}_{ki},h_r) \quad (11)$$

$$k \in solid \ particles$$

where $\vec{x}_{ij} = \vec{x}_i - \vec{x}_j$, $\vec{x}_i$ is the position of particle i, D_i is the diffusion coefficient of particle i, X_i^a is the aqueous mass fraction of species a of particle i, $\tilde{Y}_k^a$ is the adsorbed mass fraction of species a of particle k, d_i is the particle number density of particle i and $\tilde{\theta}_k^a$ is the normalized adsorbed mass fraction of species a of particle k. Due to the form of φ, only solid particles have non-zero contributions to the reaction terms of (10) and are included in the summation and only fluid particles have non-zero contributions to the reaction terms of (11).

The term $d_i m_i$ dividing k_a^- in Eqs.(10) and (11) comes from writing the advection-diffusion equation (5) in terms of mass fraction. The benefit of writing the equation in terms of the mass fraction rather than the concentration is that the mass fraction of the particles does not change due to advection, it changes only as a result of the diffusion and reactions. As a result, for a given velocity field the advection of the solute is treated exactly.

The accuracy of the SPH-CSR model has been evaluated with analytical and finite difference solutions[3], which show that the SPH-CSR model is accurate up to the SPH discretization error and is independent of spatial and temporal resolution.

3 DARCY-SCALE MODEL

The Darcy-scale model uses a continuum description of the porous microstructure to model reactive transport in a porous medium. The model relies on the effective properties, such as the effective diffusion coefficient, effective reaction rates and effective surface area, to model the transport and surface reactions. The Darcy-scale model presented in this paper is a hybrid Eulerian-Lagrangian finite difference model with constant transport properties[4].

Reactive transport on the Darcy-scale is described by the advection-dispersion equation,

$$\frac{\partial \hat{X}^a(\vec{x},t)}{\partial t} = \boldsymbol{D}\nabla^2 \hat{X}^a(\vec{x},t) - U\nabla\hat{X}^a(\vec{x},t) - \frac{A_S}{V_P}\left[k_a^+ \hat{X}^a(\vec{x},t)\left[1 - \hat{\theta}^a(t) - \hat{\theta}^b(t)\right]^g - \frac{k_a^-}{\bar{\rho}}\left(\hat{\theta}^a(t)\right)^g \right] \quad (12)$$

$$\vec{x} \in \Omega$$

and the governing equation for the mass fraction of adsorbed species,

$$\frac{\partial \hat{Y}^a}{\partial t} = k_a^+ \hat{X}^a(\vec{x},t)\left[1 - \hat{\theta}^a(t) - \hat{\theta}^b(t)\right]^g - \frac{k_a^-}{\bar{\rho}}\left(\hat{\theta}^a(t)\right)^g \quad \vec{x} \in \Omega \quad (13)$$

where $\boldsymbol{D}$ is the dispersion coefficient, U is the average velocity, A_s is the total surface area (length in 2D) of the solid grains, V_P is the pore volume (area in 2D) of the porous domain and $\hat{X}^a$ and $\hat{Y}^a$ are the aqueous and adsorbed mass fractions, respectively.

The finite difference model used to solve the Darcy-scale model is an extension of a two dimensional hybrid Eulerian-Lagrangian model of Tartakovsky et al[4]; the numerical accuracy of the model has been validated via analytical solutions. Because of the uniform Darcy velocity field in the considered examples, the grid does not become distorted and in the Lagrangian framework the advection in Eq.(12) is modeled exactly.

The model uses a Lagrangian moving grid to discretize the advection-dispersion equation for the aqueous species and a stationary grid to calculate the mass fractions of adsorbed species. The stationary mass fractions of adsorbed species are interpolated onto the moving grid of the aqueous species to calculate the reaction term of Eq.(12) and the aqueous mass fractions are interpolated onto the stationary grid to calculate the mass fractions of adsorbed species from Eq.(13).

The transport properties of the Darcy-scale model are taken from the conservative tracer simulations of Tartakovsky et al[4] for the heterogeneous porous microstructure.

4   REACTIVE TRANSPORT SIMULATIONS

The Darcy-scale model was compared to two different pore-scale simulations for the case of reactive transport through a porous medium with a competitive adsorption boundary condition at the solid grains. The two pore-scale models use two different porous microstructures which have the same porosity, average grain size and total surface area, but different porous microstructures, **Figure 2**. A heterogeneous porous microstructure is simulated by randomly placing circular solid grains throughout the simulation domain, and a homogeneous microstructure is modeled by placing the solid grains uniformly throughout the domain. All three simulations (the Darcy- and two pore-scale models) were run for the same transport and reaction conditions by setting the Reynolds, Peclet and Damköhler numbers equal. Three different reaction cases were modeled for each of the Darcy- and pore-scale domains with various species B adsorption Damköhler numbers, **Table 1**. The Damköhler numbers are defined as,

$$Da_a^+ = \frac{Lk_a^+}{D} \tag{14}$$

$$Da_a^- = \frac{k_a^- L^2}{Ds_{max}^a} \tag{15}$$

where L is the characteristic length (grain diameter) and s_{max}^a is the maximum adsorbed concentration of species a.

Table 1: Adsorption and desorption Damköhler numbers for the reactive transport simulations

	Da_A^+	Da_A^-	Da_B^+	Da_B^-
Case 1	23.2	335.2	231.6	335.2
Case 2	23.2	335.2	2316.0	335.2
Case 3	23.2	335.2	3474.0	335.2

The simulation domain initially contains species A at equilibrium where the equilibrium mass fraction of adsorbed species is calculated from the initial aqueous mass fraction of species A and the reaction rates[5]. At $t=0$ species B is introduced to the system with the flow at $x=H$ for an initial period of time. The flow and species mass fractions are periodic in the y-direction. The flow is periodic in the x-direction and after the initial pulse of species B there is a no mass flux boundary condition at $x=0$ and $x=H$ for both species A and B.

5   RESULTS

The total mass and spatial distributions of each species predicted by the Darcy-scale model are compared to the two pore-scale models. As can be seen in **Figure 1**, for both porous microstructures the Darcy model under predicts the total mass of aqueous and adsorbed species A and over predicts the total aqueous and adsorbed mass of species B for Case 2 (Cases 1 and 3 show similar trends). In the Darcy-scale model the transport parameters are

based on the heterogeneous pore-scale microstructure. The L^1 error norms between the Darcy-scale model and the heterogeneous pore-scale model increase with increasing species B adsorption Damköhler number (from Case 1 to 3), **Table 2**. The total masses predicted by the two different pore-scale microstructures also differ significantly for both the aqueous and adsorbed masses of species A and B, **Table 2**.

Table 2: L^1 error norms for the total mass of aqueous (FA/FB) and adsorbed (SA/SB) species A and B predicted by the Darcy-scale and pore-scale models.

| | Darcy-Heterogeneous | | | | Heterogeneous-Homogeneous | | | |
	FA	FB	SA	SB	FA	FB	SA	SB
Case 1	2.4%	-6.1%	4.0%	1.3%	2.0%	11.3%	1.2%	-10.8%
Case 2	3.3%	-20.5%	5.3%	-3.9%	1.3%	16.4%	-2.6%	-5.5%
Case 3	3.4%	-22.9%	5.7%	-5.1%	1.3%	16.2%	-2.9%	-5.3%

The effects of the porous microstructure on the transport and reactions of species can be seen in the predictions of the spatial distribution of aqueous and adsorbed species B, **Figure 2**, by the three models for Case 2. The Darcy-scale model and the homogeneous pore-scale model predict a uniform, fully mixed (in the y-direction) plume of aqueous species B while the heterogeneous pore-scale simulation predicts an incompletely mixed plume. The heterogeneous pore-scale simulation also results in a non-Gaussian distribution of species B in the flow (x) direction while the Darcy-scale model predicts a Gaussian distribution of species B in the direction of flow. Although the two porous microstructures considered here have similar overall microstructural properties they produce very different flow patterns, which influence the movement of species A and B and their reactions with the solid surface; this level of detail is lost in the Darcy-scale model.

6   CONCLUSIONS

A new modeling method for reactive transport pore-scale modeling was presented and compared to a Darcy-scale model. Two different porous microstructures were modeled to investigate the accuracy of the Darcy-scale model for modeling the reactive transport of a plume moving through a porous medium due to advection and diffusion. The Darcy-scale model with constant transport and reaction properties has difficulty accurately modeling the reaction dominant systems presented in this paper.

The simulations show that the Darcy-scale model has trouble accurately predicting the aqueous and adsorbed masses of both species A and B for all three cases considered and that the accuracy of the Darcy-scale model decreases with increasing Damköhler number. The spatial distributions of species B predicted by the three models demonstrate how the detailed microstructure can affect the predicted aqueous and adsorbed mass fraction distributions in the system and how this level of detail can be lost in the Darcy-scale model.

The accuracy of the Darcy-scale model could be improved by using variable transport properties based on the heterogeneous microstructure. However, these parameters would depend on the specific reactions and flow in the system via the dimensionless numbers of the system (*Da*, *Pe*) and so the predictive abilities of the Darcy-scale model would be decreased.

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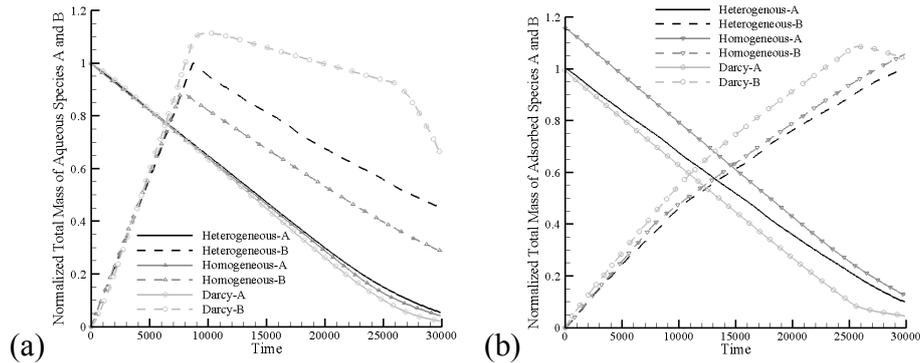
Figure 1: Total mass for the aqueous (a) and adsorbed (b) species for Case 2.
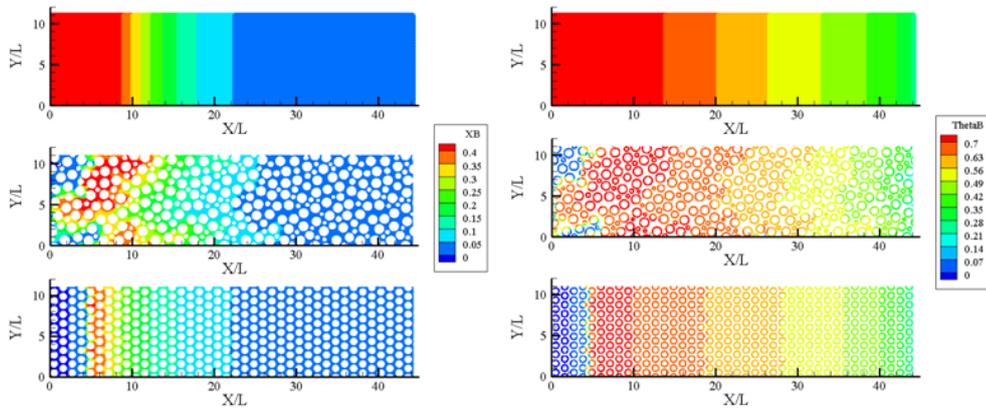
Figure 2: Contour plots of aqueous (left) and adsorbed (right) species B for the Darcy-scale model (top), Heterogeneous (middle) and Homogeneous (bottom) pore-scale microstructure models.