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Scale dependence of reaction rates in porous media

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Abstract

Elemental turnover in porous media depends on substrate concentrations at the pore-scale. In this study, the effect of small scale variability in concentration fields on reaction rate estimates and the validity of the continuum approximation in reactive transport models are investigated via a pore-scale numerical model. Artificial porous media are generated using an identical overlapping sphere algorithm. By comparison between explicit pore-scale simulations and macroscopic continuum approximations, it is shown that inhomogeneous solute distribution within the pores can affect estimates of elemental turnover rates. The error associated with large scale rate estimates depends on the type of reaction, pore geometry, reaction kinetics and macroscopic concentration gradient. A correction term that involves a phenomenological parameter which can be evaluated numerically and macroscopic concentration gradients is introduced to improve the accuracy of upscaled homogeneous reaction rates. Implications for macroscopic descriptions of surface processes and surface attached microbial populations are discussed and it is shown that pore-scale heterogeneity can substantially affect estimates of heterogeneous reactions, while for homogeneous reactions, the error amounts to only a couple of percents.

Keywords: Porous media; Diffusion; Pore-scale modeling; Reaction rate; Upscaling

1. Introduction

In natural porous media, such as sediments or aquifers, complex reaction networks couple biogeochemical cycling of many elements. Prediction of the response to changes in environmental conditions requires an understanding of how individual processes contribute to the observed distribution patterns of chemical constituents. Reactive transport modeling permits a quantitative analysis of the interaction between transport and reaction processes and provides a framework to integrate insight gained both through laboratory experiments and field observations. A major obstacle to achieving prognostic power with simulations lies in the challenge to incorporate the effect of spatial heterogeneity on the system behavior. For example, at the field scale, modeled mineral weathering rates based on laboratory rates overpredicted actual field rates by 1–3 orders of magnitude [63,57,34]. Apart from differences of physico-chemical conditions in the laboratory compared to the field (e.g., temperature, pH), this has been attributed to a large extent to hydrological controls such as preferential flow patterns which reduce the mineral surfaces in contact with the percolating fluid.

At the pore-scale, limited exchange between macro- and micro-pores can lead to differences in the chemical environment. Modeling studies have shown the distribution of chemicals at the pore level to be important under advective flows (e.g., [13,30,50,58]). For fast bimolecular kinetics the effect of pore-scale reactant distribution on estimates of reaction rates has been studied in advection dominated laboratory systems. A distinct impact of reactant segregation, with roughly 20–50% difference

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between measured rates and those calculated based on average concentrations was observed [21,45]. In diffusion dominated settings, a theoretical analysis suggested only minor effect for reactions taking place in the pore fluid [39]. However, sub-millimeter scale heterogeneity has been observed for O_2 and trace metals in sediments and microbial mats (e.g., [20,16]; see also [12]). This suggests that in these settings, diffusion may be sufficiently slow such that the distribution of chemicals at the pore level can be heterogeneous.

Reactive transport models commonly employ a continuum description and rely on volume averages. In porous media, averages are taken over scales larger than typical grain sizes (e.g., [3,44,69]). Hence, spatial heterogeneity in concentration fields below the scale of volume averaging is not resolved explicitly. The effect of features which are not accounted for explicitly is typically represented by phenomenological parameters and a closure model [5,4]. Modeling pore-scale processes and subsequent upscaling to a macroscopic scale allows one to rigorously calculate macroscopic properties of complex porous media in terms of the statistical properties of the solution obtained at the pore-scale. To date, the majority of pore-scale modeling studies have focused on the basic transport properties of porous media including effective diffusion, conductivity, permeability and elasticity (among many, one may note [1,29,37, 49,35,40]).

In this communication, we investigate the effect of small-scale heterogeneity of reactants on estimates of reaction rates. We focus on settings where reactants are transported via diffusion (i.e., advective flow is negligible) which may include muddy sediments or soil aggregates (e.g., [24,62]). We use high resolution computational models that explicitly resolve small-scale heterogeneity in porous media and upscale the pore-scale simulation results. To that purpose, first an artificial porous medium is generated. Then, numerical simulations of concentration fields at the pore-scale are performed and effective diffusion coefficients are evaluated. We calculate the volume averaged reaction rates using the concentration field obtained with the pore-scale simulations and compare them with reaction rates based on average concentrations. We discuss the consequences for biogeochemically relevant reaction kinetics and introduce a macroscopic rate correction term for homogeneous reactions.

2. Methods

2.1. Porous media

Pore connectivity is a key parameter for solute transport and the geometrical arrangement of pores and solid entities is a central issue in the computational study of small-scale processes. Several methods have been applied in the computational reconstruction of porous media, including pore networks consisting of pores and connecting throats, random networks where connectivity is based on statistical image analysis image analyses, or sedimentation reconstruction methods (e.g., [7,9,68,43]; many others).

In this study, artificial porous media are generated by random placement of identical spherical particles, which are allowed to overlap, into the model domain. This model is commonly called overlapping (or penetrable) sphere model (Fig. 1). The analytical solution for the spatial correlation functions of this model was obtained by Weissberg [66], Doi [19], Torquato and Stell [59] and Berryman [8] and the expected value of porosity (ϕ) is related to the dimensionless radius of spheres ($r = r_{\text{grain}}/L$, where L is the length of one side of the cubic model domain and r_{grain} the grain radius), and the

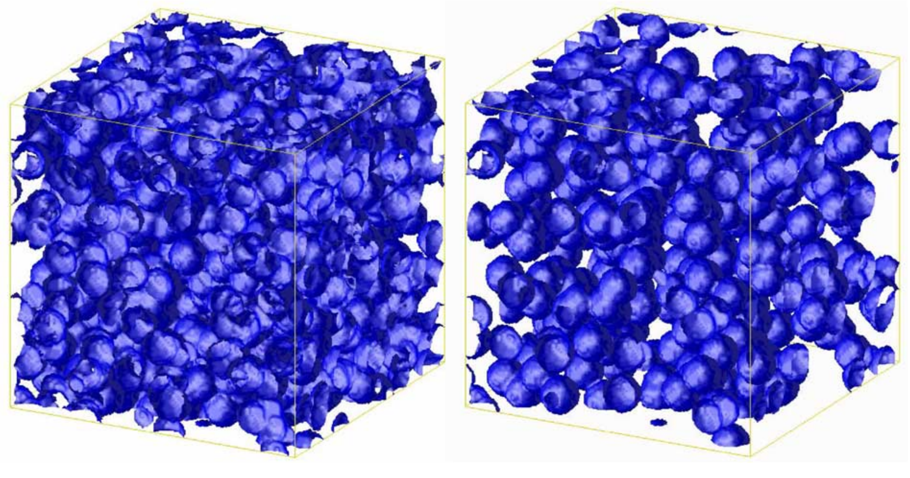

Fig. 1. Artificial porous media generated using the overlapping sphere method for porosities of 0.5 (left) and 0.8 (right). The width of a cube is set to 10 times the grain diameter.