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**Pore and Continuum Scale Study of the Effect of Subgrid
Transport Heterogeneity on Redox Reaction Rates**

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ABSTRACT. A micromodel system, which corresponds to one or part of a numerical grid in the continuum model, was used to investigate the effect of subgrid transport heterogeneity on redox reaction rates. Hematite reductive dissolution by injecting a reduced form of flavin mononucleotide (FMNH₂) at variable flow rates was used as an example to probe the variations of redox reaction rates in different subgrid transport domains. Experiments, pore-scale simulations, and macroscopic continuum modeling were performed to measure and simulate in-situ hematite reduction and to evaluate the scaling behavior of the redox reaction rates from the pore to continuum scales. The results indicated that the measured pore-scale rates of hematite reduction were consistent with the predictions from a pore-scale reactive transport model. A general trend is that hematite reduction followed reductant transport pathways, starting from the advection-dominated pores toward the interior of diffusion-dominated domains. Two types of diffusion domains were considered in the micromodel: a micropore diffusion domain, which locates inside solid grains or aggregates where reactant transport is limited by diffusion; and a macropore diffusion domain, which locates at wedged, dead-end pore spaces created by the grain-grain contacts. The rate of hematite reduction in the advection-dominated domain was faster than those in the diffusion-controlled domains, and the rate in the macropore diffusion domain was faster than that in the micropore domain. The reduction rates in the advection and macropore diffusion domains increased with increasing flow rate, but were affected by different mechanisms. The rate increase in the advection domain was controlled by the mass action effect as a faster flow supplied more reactants, and the rate increase in the macropore domain was more affected by the rate of mass exchange with the advection domain, which increased with increasing flow rate. The hematite reduction rate in the micropore domain was, however, not affected by the flow rate because molecular diffusion limits reductant supply to the micropore domain interior. Domain-based macroscopic models were evaluated to scale redox reaction rates from the pore to continuum scales. Simulation results from the single domain model, which ignores subgrid transport heterogeneity, deviated significantly from the pore-scale results. Further analysis revealed that the rate expression for hematite reduction was not scalable from the pore to porous media using the single domain model. A three-domain model, which effectively considers subgrid reactive diffusion in the micropore and macropore domains, significantly improved model description. Overall this study revealed the importance of subgrid transport

58 heterogeneity in the manifestation of redox reaction rates in porous media and in
59 scaling reactions from the pore to porous media. The research also supported that the
60 domain-based scaling approach can be used to directly scale redox reactions in porous
61 media with subgrid transport heterogeneity.

1. INTRODUCTION

Scale-dependent behavior of geochemical reaction rates poses a critical challenge in extrapolating geochemical reactions and reaction parameters determined in laboratory for field-scale applications. The rates of geochemical reactions such as mineral dissolution, rock weathering, and sorption and desorption can vary in orders of magnitude from the molecular to field scales (Liu et al., 2013; Maher et al., 2004; Maher et al., 2006; Malmström et al., 2000; Miller et al., 2010; Navarre-Sitchler and Brantley, 2007; Swoboda-Colberg and Drever, 1993; White and Brantley, 2003). Various physical and chemical factors have been identified that may individually or collectively contribute to the scale-dependent behavior of geochemical reaction rates (Alekseyev et al., 1997; Lichtner and Kang, 2007; Liu et al., 2013; Liu et al., 2014; Maher, 2010; Meile and Tuncay, 2006; Miller et al., 2010; White and Brantley, 2003). These factors can generally be grouped into two types: 1) scale-dependent variation in mineral surface properties, such as surface roughness that controls reactive surface area, and secondary mineralization that alters surface reactivity (Alekseyev et al., 1997; Benner et al., 2002; White, 1995; White and Brantley, 2003), and 2) heterogeneous distribution of flow, transport, and chemical properties in subsurface environments (Li et al., 2006; Lichtner and Kang, 2007; Liu et al., 2013; Liu et al., 2014; Maher, 2010; Malmström et al., 2004; Meile and Tuncay, 2006; Shang et al., 2011; Zhang et al., 2013). These factors generally lead to the decrease in geochemical reaction rates as scale increases (Liu et al., 2013; Meile and Tuncay, 2006; Navarre-Sitchler and Brantley, 2007; Swoboda-Colberg and Drever, 1993). The magnitude of the decrease apparently depends on specific reactions and porous media where reactions occur. Quantitative prediction of the scale-dependent behavior of geochemical reaction rates is still a major challenge in reactive transport modeling.

Heterogeneous distribution of physical and chemical properties is a common phenomenon in subsurface environments. Large scale heterogeneity that can be spatially

87 resolved in characterization such as geological formations and facies may be explicitly
88 considered in reactive transport models by assigning facies or formation specific properties in
89 numerical grid cells for numerical simulations (Curtis et al., 2004; Davies, 1938; Malmström
90 et al., 2004; Navarre-Sitchler and Brantley, 2007). The effect of the large scale heterogeneity
91 on the scaling of geochemical reaction rates can thus be evaluated using reactive transport
92 models. On the other hand, fine-scale heterogeneity that is often at the subgrid scale and
93 below spatial resolution of characterization is the most challenging to be incorporated in
94 predictive reactive transport models (Baeumer et al., 2013; Liu et al., 2013; Meile and
95 Tuncay, 2006; Miller et al., 2010; Steefel et al., 2005). A recent study indicated that the
96 subgrid transport heterogeneity can significantly affect the manifestation of geochemical and
97 biogeochemical reactions, leading to a significant uncertainty in reactive transport model
98 prediction (Liu et al., 2014). The macroscopic rates of geochemical reactions have been
99 found to correlate with the distribution of flow and transport rates in heterogeneous porous
100 media (Baeumer et al., 2013; Li et al., 2011; Liu et al., 2013; Maher, 2010; Malmström et al.,
101 2004; Minyard and Burgos, 2007; Molins et al., 2012). Limited studies indicated that by
102 considering subgrid transport heterogeneity, even partially, in macroscopic continuum
103 reactive transport models can significantly reduce prediction uncertainty (Liu et al., 2014;
104 Zhang et al., 2013).

105 Pore-scale reactive transport simulations have been used to interpret microscopic
106 behavior of mixing and geochemical and biogeochemical reactions (Mo and Friedly, 2000;
107 Molins et al., 2012) and to provide insights into the macroscopic behavior of geochemical
108 and biogeochemical processes in reactive transport systems (Li et al., 2006; Liu et al., 2013;
109 Meile and Tuncay, 2006). Literature reports on the measurements of pore-scale reactive
110 transport were, however, limited, especially in porous media containing heterogeneous pore
111 structures, because of the difficulties in pore-scale experimental designs and in-situ reactive

species monitoring and quantification. The reactive transport equation (Eq 1), which includes advection, molecular diffusion, and local reactions, is commonly used in pore-scale reactive transport simulations (Bird et al., 2007; Liu et al., 2013; Porta et al., 2013; Willmann et al., 2008). It is, however, seldom validated by pore-scale reactive transport measurements in systems with complex pore structures. A micromodel represents an ideal system for measuring in-situ reactions and validating reactive transport simulations at the microscopic level (Willingham et al., 2008; Zhang et al., 2013).

The objective of this study is to systematically evaluate how the pore-scale subgrid heterogeneity in flow and transport affects reaction rates and to provide pore-scale insights into the factors controlling scale-dependent behavior of redox reactions using hematite reductive dissolution as an example. A hematite-coated micromodel system with a heterogeneous pore structure for flow and transport (Zhang et al., 2013) was used for both experiment and numerical studies. In this study, the term pore-scale refers to the spatial scale at which flow and reactive transport are explicitly resolved at a spatial resolution of 10^{-5} m in all the pore spaces within the micromodel; while the term continuum or macroscopic scale refers to the spatial scale at which average behavior of flow and transport within the micromodel is considered. Hematite reduction in the micromodel was initiated by injecting a reduced form of flavin mononucleotide (FMNH_2), which is an important electron carrying chemical in bacterial electron transport chain (Marsili et al., 2008). FMNH_2 is also one of the important biogenic extracellular chemicals with a redox potential ($E_0 = -0.22$ V) (Shi et al., 2012) facilitating microbial reduction of solid phase electron acceptors such as iron oxides. The flow rate of the injected FMNH_2 solution was varied to explore transport effect on the rate of hematite reduction by monitoring the in-situ rate of hematite reductive dissolution and effluent concentration of reduction product Fe(II) . Pore-scale flow and reactive transport simulations were performed to interpret the experimental data and to derive pore-scale

reactive transport data under other flow conditions. The pore-scale experiment and simulation results were then used to evaluate domain-based continuum models for scaling redox reaction rates from the pores to continuum scales.

2. MATERIALS AND METHODS

2.1 Materials and micromodel fabrication

FMNH₂ stock solution (2.4×10^{-2} M) was prepared in an anoxic glovebox (100% N₂, 21 °C) following a protocol described elsewhere (Shi et al., 2012). The stock solution was diluted to 1×10^{-4} M with 3×10^{-2} M deoxygenated acetate pH-buffer to maintain pH 5.0. The mild acid solution was used in the experiments to eliminate thermodynamic (equilibrium) constraint on the rates of hematite reduction (Zhang et al., 2013). The low pH condition can also minimize Fe(II) sorption or formation of a passive film of Fe(II) precipitation on hematite surfaces (Burgos et al., 2003; Liu et al., 2007).

The design and fabrication of the micromodel, hematite deposition procedures and characterization, and the analysis of the pore size and distribution in the micromodel were described elsewhere (Zhang et al., 2013). Briefly, a binary image of 2-dimensional pore network structures, which were derived from an SEM image of sediment grains (Liu et al., 2013), was used to shape the micropore domains. The derived binary image was replicated and packed as shown in Figure 1 to form a pore structure ($L = 8.1 \times 10^{-3}$ m, $W = 4.4 \times 10^{-3}$ m and the porosity $\theta = 0.435$). The micromodel is composed of an advection domain in the center, two macropore diffusion regions located in the middle of upper and bottom sides, and four micropore regions located at the four corners of the micromodel. The macropore diffusion regions were designed to mimic the dead-end or wedged pore spaces created by the grain-grain contacts in sediments. The micropore diffusion regions were to represent

intragranular or intra-aggregate pore spaces. The pore structure was transferred onto silicon wafers by photolithographic techniques (Willingham et al., 2008; Zhang et al., 2013). In brief, the skeletal frame of the silicon matrix was protected by a layer of photoresist materials. The pore network was etched into exposed Si substrates with inductively coupled plasma (ICP) etching method. The depth (d) of the pore network was 2.8×10^{-5} m. A layer of thin hematite film ($\sim 2.3 \times 10^{-7}$ m) was then sputter-deposited onto the bottom and side wall surfaces of the etched pores using Fe_2O_3 target (purchased from Kurt J. Lesker). The thickness of the thin hematite film was determined by X-ray reflectometry. After hematite deposition, the photoresist layer was removed, Si substrate was drilled to create inlet and outlet ports, and pore network in the Si substrate was covered with a Pyrex glass wafer by anodic bonding. The inlet and outlet ports were equipped with Nanoport connectors for fluid delivery.

2.2 Micromodel experiments

Micromodel experiments were conducted to measure hematite reduction in different transport domains in an anoxic glovebox. Before the experiment, CO_2 was purged through the micromodel overnight, followed by hundreds of pore-volume flush of deionized water to saturate the pore network. For each hematite reduction experiment, working solution (1×10^{-4} M FMNH₂ in 3×10^{-2} M acetate pH-buffer at pH 5.0) was pumped through the micromodel at constant flow rates using a milliGAT smooth low flow pump (Global FIA). Two volumetric flow rates, i.e. 2.70×10^{-7} and $1.08 \times 10^{-6} \text{ m}^3 \cdot \text{h}^{-1}$, were applied to study the influence of flow rate on hematite reduction. The effluent solutions were collected every 1 to 4 h for Fe(II)(aq) analysis using the ferrozine assay (Stookey, 1970). The residual hematite in the micromodel was quantified every 1 to 8 h with optical microscopic imaging as described below and the result was verified by in-situ backscattering Raman spectroscopy (Zhang et al., 2013).

2.3 In-site residual hematite quantification

The micromodel was mounted onto a Nikon Eclipse TE2000 microscope equipped with an automated stage and a 10× inverted objective with a resolution of $6.4 \times 10^{-7} \text{ m} \cdot \text{pixel}^{-1}$. At select times, the entire micromodel was scanned and 10×8 gray-scale images were recorded by a charge-coupled device (CCD) camera. Artifacts of the images caused by nonuniform illumination were rectified by shading correction. All the images were montaged into one large image that captured the entire field of the pore network. The pixel intensity of gray-scale images of hematite were found to be linearly correlated with the Raman signal intensity of residual hematite film ($R^2 = 0.9993$). The linear correlation relationship was validated by integrating effluent Fe(II)(aq) mass, which increased over time with decreasing total residual hematite in the micromodel. Using the linear correlation, the pixel intensity of hematite was used to estimate residual hematite distribution in the micromodel (Zhang et al., 2010; Zhang et al., 2013).

The initial hematite surface concentration, which was estimated from the hematite crystal density ($5242 \text{ kg} \cdot \text{m}^{-3}$) and the thickness of hematite coating ($2.3 \times 10^{-7} \text{ m}$) in the micromodel, was $7.6 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2}$. This value was close to the average initial hematite surface concentration ($7.3 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2}$) extrapolated from the linear correlation relationship described above. The slight difference between these two values in initial hematite concentration suggested that the sputter-coated hematite film might be less than the density of hematite crystal. A value of $7.3 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2}$ was used in the reactive transport simulations and data analysis in this study.

2.4 Pore-scale flow simulations

Steady-state flow velocity field in the micromodel was derived by solving the Navier-Stokes equations using a 2-D lattice Boltzmann method (LBM) with nine-speed algorithm (D2Q9)(Sukop and Thorne, 2007). The total numerical nodes were 356252 with a fixed numerical grid size ($\Delta x = 1.0 \times 10^{-5} \text{ m}$). The convergence criterion is 10^{-7} . When the relative

difference between two consecutive iterations was less than 10^{-7} at all numerical nodes, the simulation was considered to be convergent and moved to the next time step. The LBM method uses dimensional flow velocity. The dimensional velocity field was calculated by multiplying the simulated dimensionless velocity field by the lattice velocity, $\Delta x/\Delta t$, where Δx is the dimensional lattice spacing of the numerical LB algorithm (1×10^{-5} m) and $\Delta t = (\Delta x)^2(\tau - 0.5)/3\gamma$ (τ is relaxation time and γ is kinematic viscosity) (Hilpert, 2011). Pressure boundary condition was used for both flow inlet and outlet in the LBM simulations (Maier et al., 1996). The inlet pressure was fixed and the outlet pressure was adjusted to match desired flow rates at the inlet. Steady-state flow velocity fields corresponding to the influent flow rates ranging from 2.7×10^{-8} to $1.08 \times 10^{-6} \text{ m}^3 \cdot \text{h}^{-1}$ were obtained using the LBM and used for numerical simulations of reactive transport. These flow rates are equivalent to the average pore water velocities ranging from 0.5 – 20.0 $\text{m} \cdot \text{h}^{-1}$. The average pore velocities in x and y directions were calculated by independently summing the pore-scale velocity in x and y directions. The overall velocity was calculated using average velocity in x and y directions (i.e., $\sqrt{v_x^2 + v_y^2}$). The lower range of flow rates ($< 2.70 \times 10^{-7} \text{ m}^3 \cdot \text{h}^{-1}$), which are more relevant to field flow condition (Gelhar et al., 1992), is experimentally difficult to achieve and maintain in the micromodel experiments. Consequently, only high flow rates (2.7×10^{-7} and $1.08 \times 10^{-6} \text{ m}^3 \cdot \text{h}^{-1}$) were used in the experiments.

2.5 Pore-scale reactive transport simulations

Pore-scale multi-species advection and diffusion equations in coupling with reactions were used to describe hematite reductive dissolution and reactive transport of reactants and reaction products:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i) - \mathbf{u} \cdot \nabla c_i + \sum_{j=1}^{N_r} v_{ij} r_j, \quad i=1, 2, \dots, N \quad (1)$$

233 where c_i is the concentration of aqueous species i (μM), $\mathbf{u}$ is the fluid velocity ($\text{m}\cdot\text{h}^{-1}$) from
 234 the pore-scale fluid simulations (section 2.4), D_i is the molecular diffusion coefficient of
 235 species i ($\text{m}^2\cdot\text{h}^{-1}$), r_j is the j^{th} reaction rate ($\mu\text{M}\cdot\text{h}^{-1}$), v_{ij} is the stoichiometry of species i in the
 236 j^{th} reaction, N_r is the total number of kinetic reactions, and N is the total number of species in
 237 the modeling system. Four aqueous species: FMNH_2 , FMN (oxidation product of FMNH_2),
 238 Fe(II) , and tracer Br^- , and one solid species Fe_2O_3 were considered in the modeling. For the
 239 solid species, both D_i and $\mathbf{u}$ are set to zero. A common diffusion coefficient ($D = 7.6 \times 10^{-6}$
 240 $\text{m}^2\cdot\text{h}^{-1}$) was used for all aqueous species in the simulations to simplify solving multispecies
 241 diffusion problems (Liu et al., 2011).

242 The pore-scale kinetics of hematite reduction by FMNH_2 in the micromodel was
 243 characterized previously under no flow-conditions as described elsewhere (Zhang et al., 2013)
 244 and can be briefly summarized using the following reaction stoichiometry and rate expression:

$$246 \quad r = k c_{\text{Fe}_2\text{O}_3} c_{\text{FMNH}_2} \left(1 - \frac{IAP}{K_{eq}} \right) \quad (3)$$

247 where k is the rate constant ($\mu\text{M}^{-1}\cdot\text{h}^{-1}$), IAP is the ionic activity product, and K_{eq} is the
 248 equilibrium constant of the redox reaction. The activity coefficients of aqueous species were
 249 calculated using the Davies equation. The values of k ($0.00435 \mu\text{M}^{-1}\cdot\text{h}^{-1}$) and $\log K_{eq}$ (19.96)
 250 were previously determined from a batch study by exposing the sputter-deposited hematite in
 251 a well-mixed bulk solution (Zhang et al., 2013). The rate expression and parameters
 252 estimated from the batch study were directly used in the pore-scale reactive transport model.

253 The multi-species reactive transport problem (Eq 1) was solved using finite volume
 254 method. In this method, Eq 1 was discretized to establish a mass balance equation for each
 255 species within each numerical node. The same node size used for solving flow field as

described before was used for solving Eq 1. Consequently, the flow velocity field from the LBM was directly used for solving Eq 1. The influent concentrations of chemical species were the same as those used for the micromodel experiments (section 2.2). A constant surface concentration ($7.3 \times 10^{-3} \text{ mol/m}^2$) was used as the initial hematite concentration on each pore surface in the micromodel as described in section 2.3. In this study, each numerical node contains a bottom wall coated with hematite and can potentially contain 0 to 4 hematite-coated side walls dependent on the number of walls surrounding the node. The surface area is $1.0 \times 10^{-10} \text{ m}^2$ for the bottom wall and $2.8 \times 10^{-10} \text{ m}^2$ for each side wall. The tracer and Fe(II)(aq) concentrations in effluent solutions were calculated by flux-averaging concentrations in the pore nodes at the outlet.

2.6 Domain-based modeling

Single domain and triple domain models were used to analyze the averaged behavior of pore-scale hematite reduction in the micromodel. The averaged behavior in porous media such as species concentrations, reaction rates, and fluxes are typically observed, measured or simulated in continuum reactive transport systems. Using the domain-based models to analyze the pore-scale data is to provide insights into the scaling behavior of redox reactions from the pore to continuum scales. The single-domain model assumes that the entire pore network in the micromodel can be treated as one well-mixed system for reactions and mass exchange with the influent solution. The triple domain model considers subgrid heterogeneity in reactive transport by dividing and aggregating the pore network into three operational domains. Mathematically, the domain-based models are described using the following mass balance equations:

1) *Single domain model:*

$$\theta \frac{\partial C_i}{\partial t} = \frac{q}{V} (C_i^{in} - C_i) + \theta R_i \quad i = 1, 2, \dots, N \quad (4)$$

280 where θ is the porosity; q is the flow rate ($\text{m}^3 \cdot \text{h}^{-1}$), V is the volume of the micromodel (m^3),

281 C_i (μM) is the average concentration of species i in the micromodel, C_i^{in} (μM) is the

282 concentration of species i in the influent solution, and R_i is the average reaction rate of

283 species i .

284 2) Triple domain model:

285 2a) Advection domain:

$$\begin{aligned}
 \theta_{adv} \frac{\partial C_i^{adv}}{\partial t} + \frac{\theta_{mic} f_{adv}}{f_{adv} + f_{mac}} \frac{\partial \overline{C_i^{mic,adv}}}{\partial t} &= \frac{q}{V} (C_i^{in} - C_i^{adv}) + \theta_{adv} R_i^{adv} \\
 -k_a \theta_{mac} (C_i^{adv} - C_i^{mac}) + \frac{\theta_{mic} f_{adv}}{f_{adv} + f_{mac}} \overline{R_i^{mic,adv}} &
 \end{aligned}
 \tag{5}$$

287 2b) Macropore domain:

$$\begin{aligned}
 \theta_{mac} \frac{\partial C_i^{mac}}{\partial t} + \frac{\theta_{mic} f_{mac}}{f_{adv} + f_{mac}} \frac{\partial \overline{C_i^{mic,mac}}}{\partial t} &= k_a \theta_{mac} (C_i^{adv} - C_i^{mac}) + \theta_{mac} R_i^{mac} \\
 + \frac{\theta_{mic} f_{mac}}{f_{adv} + f_{mac}} \overline{R_i^{mic,mac}} &
 \end{aligned}
 \tag{6}$$

289 2c) Micropore domain:

$$\frac{\partial C_i^{mic,adv}}{\partial t} = D_{eff} \frac{\partial^2 C_i^{mic,adv}}{\partial x^2} + R_i^{mic,adv}
 \tag{7}$$

$$\frac{\partial C_i^{mic,mac}}{\partial t} = D_{eff} \frac{\partial^2 C_i^{mic,mac}}{\partial x^2} + R_i^{mic,mac}
 \tag{8}$$

292 where C_i and R_i are, respectively, the concentration and reaction rate of species i in

293 subgrid transport domains; superscript *adv* and *mac* denote subgrid advection and macropore

294 domains, respectively; superscript *mic,adv* and *mic,mac* denote the fraction of the micropore

295 domain that is in mass exchange with the advection and macropore domains, respectively;

bar over the concentration and reaction variables denotes the average along diffusion path in the micropore domain; f_{adv} , f_{mac} , and f_{mic} are the porosity ratios for advection, macropore, and micropore domains, respectively; D_{eff} ($\text{m}^2 \cdot \text{h}^{-1}$) is the effective diffusion coefficient in the micropore domain; and k_a (h^{-1}) is the mass exchange coefficient between the advection and macropore domains. The same inlet and outlet boundary conditions for the pore-scale model were used for the domain-based models. For the micropore diffusion equations (Eqs 7 and 8), continuous concentration and flux boundary conditions were imposed at the interfaces between micropore and advection domains, and between micropore and macropore domains. In the triple domain model, the reaction and transport properties within each subgrid transport domain were considered homogeneous. In addition, mass transport/transfer within the advection or macropore domain were not considered in the model. In the micropore domain, the internal mass transport (diffusion) was represented by the slab diffusion model in porous media (Eqs 7 and 8).

The reaction rate expression and rate constant k (Eq 3) used for the pore-scale reactive transport simulations were also used in the domain-based models to evaluate the applicability of the pore-scale rate expression and parameters in the continuum models. For the single domain model, all other parameters (θ , V , and q) in Eq 4 were measured. For the triple-domain model, parameters f_{mic} and D_{eff} were assumed known, while parameters f_{mac} and k_a were not. In practice, parameters f_{mic} and D_{eff} can be independently determined from tracer transport in intra-granular domains using a well-mixing system (Hay et al., 2011; Liu et al., 2011), while parameters f_{mac} and k_a have to be determined by simulating tracer transport in flow-through systems (Liu et al., 2008). In this study, f_{mic} was estimated by counting the number of pore nodes in the intragranular domains (four corner regions in the micromodel). D_{eff} was then estimated by fitting Br^- diffusion in the micropore domain under no flow condition. Parameters f_{mac} and k_a were obtained by fitting the effluent Br^- concentrations

under flow conditions using the triple domain model (Eqs 5-7). The fitted value of f_{mac} was used to determine a flow velocity threshold, $v_{c,mac}$, so that the pore nodes with their pore-scale flow velocity above $v_{c,mac}$ are assigned to the advection domain, the rest pore nodes in the inter-granular domain are assigned to the macropore domain, and the ratio of total pore volume in the macropore domain vs the total pore volume in the micromodel = f_{mac} . The average flow velocities and the concentrations of reactants and reaction products in each subgrid domain are then calculated using simulated pore-scale concentrations.

2.7 Calculation of Reynolds, Péclet and Damköhler number

Reynolds (Re), Péclet (Pe) and Damköhler (Da) numbers were calculated using the diameter of the grain aggregates (3.92×10^{-3} m) as the characteristic length of the micromodel (l_l). The Pe and Da numbers in the advection, macropore and micropore domains were also calculated using the average pore throat in each subgrid domain as the characteristic length (l_j , $j = 2,3,4$), i.e., 1.4×10^{-3} , 1.4×10^{-3} and 4×10^{-5} m for the advection, macropore and micropore domains, respectively.

Re was calculated for the micromodel with the following equation:

$$Re = l_l v / \gamma \quad (9)$$

where l_l is the length scale of the micromodel, v is the average pore water velocity, and γ is kinematic viscosity. Pe was calculated for the micromodel and its three subgrid domains with the following equation:

$$Pe_j = l_j v_j / D_{eff} \quad (10)$$

where subscript $j = 1, 2, 3$, and 4 , corresponding to the entire micromodel, advection domain, macropore domain, and micropore domain, respectively; l_j is the characteristic length of domain j ; and v_j is the average pore water velocity in domain j . The average pore velocities in

each subgrid domain were calculated from the simulated flow field within corresponding subgrid domain (Table 1). Damköhler number (Da) is defined as the ratio between transport time scale and reaction time scale:

$$D_a^j = \tau_{tr}^j / \tau_{re} \quad (11)$$

where superscript j has the same meaning as defined for peclet number ; τ_{re} is the characteristic time scale of the hematite reduction reaction, $1/kC_{Fe_2O_3}^0$ ($C_{Fe_2O_3}^0$ is the initial concentration of hematite); and τ_{tr}^j is characteristic time scale of mass transfer in domain j , which is $\theta V / q$ for the micromodel, and L / v_{adv} (L is the length of advection domain, v_{adv} is the average pore water velocity in advection domain), $1/k_a$ (k_a is the mass transfer coefficient in the macropore domain) and L_{mic}^2 / D_{eff} (L_{mic} is the diffusion length scale of the micropore domain chosen as the radius of the grain aggregates, i.e. 1.96×10^{-3} m) for the advection, macropore and micropore domains, respectively.

3. RESULTS

3.1 Pore-scale modeling results of flow field and heterogeneity

Figure 1 shows two steady state scenarios of flow velocity fields corresponding to influent flow rates of $2.7 \times 10^{-8} \text{ m}^3 \cdot \text{h}^{-1}$ (Figure 1A) and $1.08 \times 10^{-6} \text{ m}^3 \cdot \text{h}^{-1}$ (Figure 1B), which are, respectively, the slowest and fastest flow rates applied in this study. The simulated pore-scale flow velocity varied significantly in different pore domains in the micromodel, showing higher velocity in the inlet (left) and outlet (right) of the flow paths (or pore throats), relatively slower flow velocity in the center (pore body), and very low flow velocity ($< 0.05 \text{ m} \cdot \text{h}^{-1}$) in the micropore domain. The streamlines and arrows (white lines) delineated flow paths and directions in the micromodel. Only the upper part of the streamlines was displayed

in Figure 1 and the bottom part was symmetric to the upper part. From these streamlines and their connectivity, the pore regions in the micromodel can be generally divided into three domains. The pore regions in the four corners of the micromodel are the micropore domain where flow bypasses and diffusion is expected to dominate the transport process. The pore region containing continuous streamlines from the inlet to outlet is the flow region where advection is expected to dominate. When the advection flow passed the grain, it created a space devoid of moving fluid at the downstream side of the grains. The pore region with swirling streamlines in the middle of the upper and bottom sides is the macropore domain, where transport is affected by both diffusive mass transfer and advection. The swirling streamlines were formed as a result of advective drag of the adjacent stagnant fluid in the macropore domain toward downstream so that the fluid in the deeper macropore domain flowed upstream to compensate for the mass loss due to the advective drag (Bear, 2013; Bird et al., 2007). Pe numbers, which denote the relative importance of different transport processes, differed by 5 orders of magnitude in different subgrid domains (Table 1), reflecting the subgrid transport heterogeneity in the micromodel.

The flow velocity distributions were generally similar when different flow rates were applied for the influent solution (Figure 1). However, the flow velocity gradient from the advection domain toward the macropore domain increased with increasing flow rate because the flow velocity in the advection domain increased with flow rate, but the flow velocity at the middle of upper and bottom boundaries in the micromodel remained zero (no slip boundary). At a low flow rate, the streamlines in the downstream side were generally symmetric to the upstream side (Figure 1A). When a high flow rate was applied, the streamlines skewed toward downstream (Figure 1B). As a result of the changes in flow velocity gradient and streamline skewness, the macropore domain became slightly larger and skewed toward upstream when a higher flow rate was applied (Figure 1). The size of the

macropore domain and flow velocity gradient toward the advection domain have important implication for the mass exchange between the macropore and advection domains as discussed in later sections. Figure 1 only shows two flow rate scenarios. Flow velocity fields corresponding to other flow rates between 27 to 1080 $\mu\text{L/h}$ were also simulated. The results (not shown) are between those for the two scenarios shown in Figure 1.

3.2 Experimental results of hematite reduction in the micromodel

Hematite reduced and dissolved quickly in the advection domain as the reductant (FMNH_2) carried by fluid interacted with hematite on the bottom wall in the advection domain (Figure 2A1-2A4). The hematite reduction in the advection domain was relatively homogeneous. The slight nonuniform color distribution, reflecting residual hematite concentration in the advection domain, was caused by imaging collection and processing as discussed in method section 2.3. Over 90% of hematite in the advection domain was reduced within 7 hours. The reduction front then migrated from the advection domain to the macropore and micropore domains as FMNH_2 diffused into these domains. Figure 2 only shows the results at flow rate $2.70 \times 10^{-7} \text{ m}^3 \cdot \text{h}^{-1}$. Similar trend of the reduction front migration was observed at flow rate $1.08 \times 10^{-6} \text{ m}^3 \cdot \text{h}^{-1}$ (not shown).

Hematite in the advection domain depleted within 12 hours of reductive interactions with influent reductant FMNH_2 (Figures 2A4, 3A1 and 3B1). Most hematite in the macropore domain was reduced and dissolved within 30 hours. In contrast, the hematite in the micropore domain only partially reduced at the end of the experiment (51 hours) because of the slow diffusion of FMNH_2 . The reduction rate in the advection and macropore domains was relatively faster when a faster flow rate was applied (Figures 3A1 and 3B1). This is because the faster flow supplied more reductant to interact with the hematite in the micromodel. When the rate was normalized to pore volume (PV), however, the rate was slower under the faster flow rate. For example, the hematite in the advection domain depleted within 10 hours

or 20000 PVs at $1.08 \times 10^{-6} \text{ m}^3 \cdot \text{h}^{-1}$ flow rate as compared to 15 hours or 7000 PVs at $2.70 \times 10^{-7} \text{ m}^3 \cdot \text{h}^{-1}$. This is because a slower flow rate provided a longer residence time for the interaction of influent reductant FMNH₂ with hematite. The reduction rate in the micropore domain was, however, not influenced by the flow rate (Figures 3A1 and 3B1).

The accumulated mass of Fe(II) in the effluent solution (Figures 3A2 and 3B2) reflected the macroscopic behavior of pore-scale hematite reduction in the micromodel. The effluent Fe(II) profiles showed a faster macroscopic rate of Fe(II) production from time 0 to 5 hours, an intermediate stage from 5 to 10 hours, and a slower rate after 10 hours. The varying rate of total Fe(II) production was consistent with the decrease in the residual hematite in the micromodel and reflected varying Fe(II) contribution from different transport domains at different times (Figure 3A1 and 3B1).

3.3 Pore-scale modeling results of hematite reduction and reactive transport

The simulated reductive dissolution of hematite (Figure 2B1-2B4) using the pore-scale model (Eq 1) was generally consistent with the experimental observations in the micromodel (Figure 2A1-2A4). As observed in the experimental measurements, the simulated results also showed domain-based reduction behavior, with a faster reduction rate in the advection domain, followed by reduction in the macropore domain, and then in the micropore domain. The simulated reduction rate in the macropore domain was, however, slower than the measured. At flow rate of $2.70 \times 10^{-7} \text{ m}^3 \cdot \text{h}^{-1}$, model calculations showed that about 30% hematite was reduced in the macropore domain after 12 h of reaction (Figure 2B4). Experimental results, however, showed more than 75% hematite was reduced in the same domain (Figure 2A4). This discrepancy was attributed to several factors. The first is the effect of the molecular diffusion coefficient used in simulating the reactive transport in the macropore domain by assuming that the diffusive mixing was a molecular process that was superimposed on the swirling flow paths (Figure 1). If the flow in the experimental systems

did not follow the simulated swirling flow paths; for example, swirling flow paths broke down, causing eddy mixing (Bear, 2013; Bird et al., 2007), then the molecular diffusion would under-estimate the mixing in the experiments. The eddy mixing would increase the mass transfer rate of reductant from the advection domain to the macropore domain, leading to a faster hematite reduction in the macropore domain than that predicted from the pore-scale model. Two-dimensional simulations were used in this study, which ignored vertical variations in flow and solute concentrations. This may have also contributed to the discrepancy. The pore depth is 2.8×10^{-5} m in the micromodel, which is larger than the lattice size used in the pore-scale simulations (1.0×10^{-5} m), suggesting that a 2-D model may not fully represent the experimental system. The vertical mixing, such as Taylor dispersion caused by flow rate variance in vertical direction, may have enhanced the mass exchange rate between the advection and macropore domains, thus enhancing the rate of hematite reduction in the macropore domain. The third factor is the image processing. In the experimental micromodel, the light reflected by hematite dissolution front would lead to the underestimation of residual hematite concentrations in the adjacent area (Figure 2A2-4). As the dissolution front rapidly progressed into the macropore domain, hematite reduction in the macropore domain may have been overestimated in general.

The transport of reductant FMNH_2 was significantly retarded by the hematite redox reaction which consumed the reductant (Figure 4). Compared with tracer Br^- transport, the rate of FMNH_2 was retarded by 3 orders of magnitude, even in the advection domain. The transport of Fe(II) was, however, much faster than that of FMNH_2 as it was produced along flow paths, and carried by flow and diffusion from upstream. Significant amount of Fe(II) diffused into the micropore domain after 1 hour of hematite reduction when FMNH_2 was still associated with the advection domain. The result indicated that local redox reaction along FMNH_2 transport pathways only minorly affected Fe(II) transport. The pore-scale transport

of conservative tracer, Br^- , in the micromodel was fast (Figure 4C). Its concentration equaled to the influent level after 10s of seconds in the advection domain, 10s of minutes in the macropore domain, and a few hours in the micropore domain.

4. Discussions

4.1 Pore-scale reactive transport measurements and modeling

By taking advantage of advanced mineral deposition technology in the micromodel design, we are able to coat the hematite on pore walls that allow us to *in situ* measure the rates of hematite reduction in different pore domains through imaging and digital image processing. Comparison of the measured and simulated results indicated that reactive transport equation with parameters independently estimated generally consistent with the experimental measurements. This consistency indicated that the simple mass balance equation (Eq 1) can effectively describe pore-scale reactive transport, and illustrated that the rate expression (Eq 3), which was derived from well-mixed, batch reactors, can be directly applied in the pore-scale reactive transport models. Discrepancies did exist between the measured and simulated results (Figures 2), apparently caused by the imaging processing in the experimental measurements and inadequate model consideration of flow-induced mixing mainly in the macropore domain as described in the results section. The discrepancies emphasized the importance to improve both experimental measurement methods and pore-scale modeling techniques in describing reactive transport, especially in porous media with heterogeneous structures.

4.2 Subgrid transport heterogeneity and apparent reaction rates in the single domain model

491 Solving a reactive transport equation such as Eq 1 requires discretizing simulation
492 domains into many numerical grid cells and assigning physical, chemical, and/or biological
493 properties to each grid cell. Subgrid heterogeneity describes the nonuniform distribution of
494 physical, chemical, and/or biological properties within the numerical grid cells. In the pore-
495 scale modeling, the numerical grid size is typically small so that subgrid heterogeneity can be
496 eliminated. In macroscopic systems, subgrid heterogeneity becomes an important
497 consideration when the numerical grid cell is large enough to include various pores, solid
498 grains, and transport domains, such as micropore and macropore domains in Figure 1. This is
499 because the reaction rates (e.g., r_j in the right hand side of Eq 1) were the average rates
500 defined on the numerical grid cells. The average rates can be significantly different from the
501 pore-scale rates. Assuming that the entire micromodel (Figure 1) is treated as one numerical
502 grid cell in continuum scale simulations, the reactive transport in the grid cell can be
503 described by a single domain model (Eq 4). Figure 5 showed that the results calculated from
504 the single domain model, with a reaction rate and rate constant determined from batch
505 experiment (Eq 3), deviated significantly from the experimental measurements (Figure 5A
506 and 5B) and those calculated from pore-scale simulations (Figure 5C and 5D). The deviation
507 increased with time, indicating that in order to fit the experimental results, the rate constant in
508 Eq 3 had to decrease with time. The decrease in average hematite reduction rate with time
509 reflected temporally varying contribution of hematite reduction from different subgrid
510 domains. Average hematite reduction rate in the micromodel (Figure 6), which was
511 calculated using the pore-scale simulations, was initially dominated by the contribution from
512 the advection domain. This contribution decreased with time as hematite reduced and
513 dissolved in the advection domain and reductant moved into the macropore and micropore
514 domains. The relative contribution from the macropore and micropore domains increased and
515 became dominant after 1000-10000 PVs for this specific case depending on flow rate. Faster

516 flow rate required more PVs of solution to deplete the hematite in the advection domain
 517 because of a shorter fluid residence time.

518 If the average rate expression for hematite reduction in the heterogeneous micromodel
 519 was assumed to be the same as for the pore-scale reaction (Eq 3), it would linearly correlate
 520 to $\langle c_{Fe_2O_3} \rangle \langle c_{FMNH_2} \rangle (1 - IAP/K_{eq})$ as shown in Eq 12.

$$521 \quad \langle r \rangle = k' \langle c_{Fe_2O_3} \rangle \langle c_{FMNH_2} \rangle (1 - IAP/K_{eq}) \quad (12)$$

522 where $\langle c \rangle$ and $\langle r \rangle$ are the average concentration of a reactant and rate in the micromodel
 523 calculated from the pore scale simulations, respectively, and k' is the apparent rate constant.
 524 Figure 7, however, showed that the average rate followed this linear relationship only for the
 525 initial period, corresponding to the initial stage of hematite reduction in the advection domain.
 526 The average rate became independent of $\langle c_{Fe_2O_3} \rangle \langle c_{FMNH_2} \rangle (1 - IAP/K_{eq})$, and even
 527 decreased with increasing $\langle c_{Fe_2O_3} \rangle \langle c_{FMNH_2} \rangle (1 - IAP/K_{eq})$ at later time. Multi-variant
 528 fitting was performed to correlate the average rate to the average concentrations of hematite
 529 and FMNH₂ using the following rate equation:

$$530 \quad \langle r \rangle = k' \langle c_{Fe_2O_3} \rangle^n \langle c_{FMNH_2} \rangle^m (1 - IAP/K_{eq}) \quad (13)$$

531 The results indicated that the average rate was first order with respect to reductant FMNH₂
 532 concentration ($m = 1$) and zero order with respect to hematite concentration ($n = 0$) during the
 533 initial linear stage (Figure 7), and become zero order with respect to both hematite and
 534 reductant FMNH₂ ($n = 0$ and $m = 0$), and zero order with respect to average FMNH₂ ($m =$
 535 0) and nearly five order with respect to average hematite concentration ($n > 5$) at the later
 536 time. The change in rate order with time resulted from the volume averaging of reactant
 537 concentrations in the micromodel. Initially, the hematite reduction by FMNH₂ only occurred

in the advection domain; however, the reduced amount in the advection domain was relatively small as compared to the overall residual hematite in the micromodel, leading to zero order with respect to average hematite concentration and first order to the average FMNH₂ concentration. With continued supply of FMNH₂ from the injected solution, the change in average FMNH₂ concentration in the micromodel became small, so that the rate order with respect to average FMNH₂ concentration also became zero. At the later time of the reduction, most hematite in the advection domain was reduced and dissolved, the decrease in residual hematite concentration in the macropore and micropore domains played important role in the change of average hematite concentration, leading to a higher order with respect to the average hematite concentration.

4.3. Subgrid domain-based approach for scaling reactions

As shown in section 4.2, the average reaction rate $\langle r \rangle$ calculated using the pore-scale reaction rates in the micromodel was slower than the reaction rate calculated using average concentrations of the reactants in the micromodel. Consequently, if a single domain model, which uses average concentrations of the reactants, was used to describe hematite reduction in the heterogeneous micromodel, the rate constant had to decrease with time. This rate change was dependent on flow velocity and likely also dependent on specific pore structures and the spatial distribution and variation of reactive transport properties, creating a significant challenge to derive quantitative relationship to scale reactions for predictive purpose. A triple domain model (Eqs 5-8), which considers the subgrid heterogeneity by grouping pore regions with similar pore-scale reactive transport properties into three subgrid domains, was evaluated to scale the reactions in heterogeneous porous media from the pores to continuum scale. The triple domain model has been successfully used to scale uranyl surface complexation reactions from intragranular pore scale to sediment cores under flow conditions (Liu et al., 2014; Liu et al., 2008; Shang et al., 2014). To apply the triple domain model, the

apparent diffusion coefficient in the micropore domain was first estimated using the pore-scale simulated tracer Br^- results in the micropore domains as described in section 2.6. The estimated D_{eff} (Eqs 7 and 8) was $2.6 \times 10^{-6} \text{ m}^2 \cdot \text{h}^{-1}$, which is lower than the diffusion coefficient ($7.6 \times 10^{-6} \text{ m}^2 \cdot \text{h}^{-1}$) used in the pore-scale simulations. The lower diffusion coefficient in the domain-based model reflected the tortuous nature of diffusion paths and pore connectivity limitation in the micropore domain (Figure 1). The estimated apparent diffusivity and diffusion equations for the micropore domain (Eqs 7 and 8) were then coupled with transport equations in the advection and macropore domains (Eqs 5 and 6) to estimate mass transfer parameter (k_a and f_{mac}) in Eq 5 and 6 using effluent Br^- concentrations that were simulated from the pore-scale reactive transport model. The estimated mass transfer and diffusion parameters for the macropore and micropore domains, and reaction parameters from the batch experiments, were then used by the triple domain model (Eqs 5-8) to predict temporal evolution of residual hematite concentrations in different subgrid domains and Fe(II) concentrations in the effluent solution.

The triple domain model provided a good prediction of the effluent Fe(II) concentrations and residual hematite in different subgrid domains estimated from the pore-scale simulations (Figure 8). The result indicated that the subgrid domain-based model effectively scaled the reaction rate from the pore to the porous media without need to change reaction expression and constants. The model performed better for the advection and micropore domains than for the macropore domain. The discrepancy between the pore-scale and triple-domain models in the macropore domain increased with decreasing flow rate (Figure 8). Similar trend was also observed for the advection domain, though at a less degree. The triple domain model under-predicted the hematite reduction in the macropore domain and over-predicted in the advection domain at the low flow rate. This difference suggested that separating the pore spaces in the inter-grain pore regions into two operationally defined

advection and macropore domains was not enough. More operationally defined domains would provide a better description, especially at a low flow rate. At a high flow rate, however, the flow-induced mass exchange would enhance the mass transfer in different inter-grain pore spaces, so that two operational domains well approximated pore-scale variations in reactive transport.

The mass transfer parameters for the macropore domain estimated from the tracer data were a function of flow velocity (Figure 9). Increasing flow rate (or Re) increased both the domain size and mass transfer coefficient for the macropore domain. Good correlations were observed between f_{mac} and Re ($f_{mac} = 0.05 \times \log(Re) + 0.09$ with R^2 of 0.95) and between k_a and Re ($k_a = 16.5 \times Re + 18.4$ with R^2 of 0.98) (Figure 9). The positive correlations indicated the increasing role of flow-induced mass exchange between the macropore and advection domains with increasing flow rate. These correlations were, however, established for the specific pore geometry in this study, and are expected to change for different pore structures in sediments. The macropore domain was termed as the immobile pore domain in the inter-granular regions in sediments, which can significantly affect the scaling behavior of reactions from a well-mixed system to heterogeneous sediments (Liu et al., 2014). The results here indicated that the mass transfer parameters in the inter-granular, immobile domain will change with flow velocity.

Using a diffusion model (Eqs 7 and 8) to describe reactive transport in the micropore domain is an important consideration for the domain-based model to scale reactions in the micropore regions. Lichtner and Kang (Lichtner and Kang, 2007) reported that a dual continuum model, which used a 1-D diffusion model in the secondary continuum domains connected to a primary continuum domain, significantly improved the simulations for tracer and reactive transport in heterogeneous porous media as compared to a single continuum model. A linear, first-order reaction was considered in that study, while in this study a

nonlinear reaction rate was evaluated in the scaling. Similar results from both studies that subgrid domain-based models provide a much improved result of reactive transport in heterogeneous porous media indicated that subgrid domain-based approach is an effective approach in scaling reaction rates. In this study, calculated pore-scale Da number in the micropore domain was 4579 (Table 1), suggesting that hematite reduction in the micropore domain was limited by the diffusion of reactants. Consequently, molecular diffusion mechanism needs to be explicitly considered in the model. Here, the diffusion model and parameters (D_{eff} and micropore porosity) were estimated using the pore-scale diffusion simulations in the micropore domain. In practice, the diffusion parameters in the micropore domain can be independently estimated from batch reactors that eliminate mixing effect in grain exterior regions (Hay et al., 2011; Liu et al., 2011).

The triple domain model was also used to predict the experimental observations of hematite reduction in the micromodel and effluent Fe(II) concentration profiles. The model, however, under-predicted the hematite reduction in the macropore domain. The under-prediction was attributed to parameter k_a , which was estimated from the pore-scale simulations of tracer Br^- transport in the micromodel. The pore-scale simulations used a molecular diffusion coefficient. As described before, the swirl streamlines in the macropore domain (Figure 1) suggested that effective diffusion coefficient should be larger. A larger diffusion coefficient would lead to a larger mass transfer coefficient (k_a) between the advection and macropore domains, which would increase the reduction rate in the macropore domain. It is, however, impractical to experimentally measure tracer transport in the different pore domains and in the effluent in this study because tracer transport was faster and effluent concentration reached the plateau within five pore volume, i.e. around $2 \times 10^{-9} \text{ m}^3$ (about 7 to 29 seconds). To describe the experimental results in the macropore domain, the mass transfer coefficient (k_a) in the triple domain model was refitted by matching experimental

measurements of hematite loss. The refitted k_a values (Figure 9) were, as expected, larger than those estimated from pore-scale simulations of tracer transport. The triple domain model with refitted k_a provided a good description to the residual hematite concentrations in the macropore and other domains (Figure 10). The predicted effluent Fe(II) concentration still deviated from the measurements although the results showed a significant improvement as compared to the single-domain model (Figure 5). The mismatch was primarily attributed to the measurement inconsistency as discussed in the result section.

5. CONCLUSIONS

This study investigated the effect of subgrid heterogeneity in pore structures on solute transport, which in turns affected the manifestation of a pore-scale redox reaction in the heterogeneous porous media. The pore-scale simulations revealed complex flow velocity fields and velocity gradient-induced mass exchange in and between different pore domains that depended on overall, macroscopic flow rate. This type of pore-scale flow and transport heterogeneity has long been recognized as an important mechanism causing the scale-dependency of geochemical and biogeochemical reaction rates as observed at different spatial scales (Liu et al., 2013; Liu et al., 2014; Maher, 2010; Malmström et al., 2004). This study revealed that such pore-scale heterogeneity in flow and transport, if not explicitly considered in reactive transport models, can significantly affect the predictability of mechanistic reaction models and parameters that often characterized using well-mixed reactors. Reaction rates and rate parameters will become scale-dependent if the pore-scale transport heterogeneity is implicitly included or explicitly lumped into reaction rates. This study also revealed that the reaction rate law with respect to reactants and reaction products may change with increasing scale as a result of volume averaging of reactant and reaction product concentrations across transport domains with different transport properties.

Pore-scale heterogeneity in flow and transport is often below spatial resolution of characterization and modeling at the macroscopic scales. Explicit inclusion of the pore-scale heterogeneity is consequently infeasible in macroscopic reactive transport models. This study demonstrated that a domain-based model, which divided and aggregated subgrid pore regions into three domains with each domain having its own features in reactive transport mechanisms, provided an effective approach to integrate mechanistic reactions into reactive transport models. The important features of the domain-based model include that: 1) the physical parameters may be independently determined through tracer experiments; and 2) reaction rates and parameters determined from the well-mixed reactors can be directly used in the domain-based model. Three domains are needed, which represents advection-dominated domain, diffusion-dominated domain in intragranular/intra-aggregate regions if these pore spaces contain reactive surfaces, and an inter-granular immobile domain to represent dead-end/wedged pores or low flow velocity regions in sediments. The importance and characterization of these domain properties have been described previously (Hay et al., 2011; Lichtner and Kang, 2007; Liu et al., 2013; Liu et al., 2014; Liu et al., 2008). A new finding from this research is that the mass transfer properties in the macropore domain are a function of flow velocity that can affect the manifestation of reactions in the macropore and its transport-connected domains.

A micromodel system with heterogeneous pore structures was used to investigate redox reaction between hematite and FMNH_2 under flow conditions. The micromodel system allows in-situ monitoring the redox reaction at the pore scale using imaging and spectroscopy analysis besides measuring the effluent solutes that reflect aggregated behavior of the pore scale reactions. Consequently the micromodel system represents an ideal system to investigate the scaling behavior of reactions by comparing the pore scale and aggregated behavior. In addition, the pore structure in the micromodel can be explicitly integrated into

pore-scale reactive transport models for model validation and data interpretation under experimental conditions. Various experimental limitations exist, however, in using micromodel systems to study reactive transport and reaction rate scaling. These limitations include a difficulty to control flow rate, especially for low flow rates; errors from imaging collection and processing; and small volumes of effluent samples available for chemical analysis. Pore scale models can be used to complement micromodel experiments as shown in this study. Combining pore scale measurements and modeling presents a potentially powerful tool to evaluate pore scale reaction behavior and its macroscopic manifestation.

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 810

Figure

813

814 Figure 1. Simulated steady-state flow velocity field corresponding to influent flow rate of

815 $2.70 \times 10^{-8} \text{ m}^3 \cdot \text{h}^{-1}$ (A) and $1.08 \times 10^{-6} \text{ m}^3 \cdot \text{h}^{-1}$ (B). Blue color indicates lowest flow velocity and

816 red color indicates highest flow velocity, white lines and arrows denote streamlines and flow

817 directions, and brown color indicates the solid regions.

818

Table

819 Table 1. Average pore water velocities and dimensionless numbers of the micromodel
820 systems.

$q \text{ (m}^3\cdot\text{h}^{-1}\text{)}$	2.70×10^{-8}	5.40×10^{-8}	1.08×10^{-7}	2.70×10^{-7}	5.40×10^{-7}	1.08×10^{-6}
$v \text{ (m}\cdot\text{h}^{-1}\text{)}$	0.50	1.00	2.00	5.01	10.02	20.05
$v_{adv} \text{ (m}\cdot\text{h}^{-1}\text{)}$	7.49	15.36	31.24	79.38	165.02	327.15
$v_{mac} \text{ (m}\cdot\text{h}^{-1}\text{)}$	0.02	0.13	0.36	1.09	3.71	5.73
$v_{mic} \text{ (m}\cdot\text{h}^{-1}\text{)}$	0.015	0.015	0.015	0.018	0.024	0.043
Re	0.54	1.09	2.17	5.44	10.87	21.74
Pe	254	508	1015	2538	5076	10153
Pe_{adv}	1354	2778	5651	14358	29849	59174
Pe_{mac}	3.74	23.44	64.47	197.95	670.70	1036.00
Pe_{mic}	0.08	0.08	0.08	0.09	0.13	0.22
Da	23.96	11.98	5.99	2.40	1.20	0.60
Da_{adv}	1.02	0.50	0.25	0.10	0.05	0.02
Da_{mac}	36.99	48.43	26.64	14.53	5.97	3.67
Da_{mic}	4579	4579	4579	4579	4579	4579

821 The parameters, i.e. v , Re , Pe and Da , without subscripts are parameters of the entire
822 micromodel system; that with subscripts, i.e. adv , mac , and mic , correspond to the parameters
823 in the advection, macropore and micropore domains, respectively.

Figure

Figure 2. Snapshots of experimental measured (A1-A4) and pore-scale model simulated (B1-B4) residual hematite concentrations (normalized to local pore volume) after 0, 3, 7, and 12 hours of reaction with influent FMNH₂ in the micromodel at flow rate of $2.70 \times 10^{-7} \text{ m}^3 \cdot \text{h}^{-1}$. Blue color denotes initial hematite concentration, red color indicates that hematite was reduced/dissolved, and brown color denotes the solid regions.

Figure 3. Experimental results of hematite reduction in the micromodel at flow rates of $2.70 \times 10^{-7} \text{ m}^3 \cdot \text{h}^{-1}$ (A1 and A2) and $1.08 \times 10^{-6} \text{ m}^3 \cdot \text{h}^{-1}$ (B1 and B2). Figure A1 and B1 show the ratio of the total residual over total initial hematite concentration in the micromodel (solid red triangles), and the ratio of the residual over initial hematite concentration in the advection (blue diamonds), macropore (cyan circles) and micropore (olive squares) domains as a function of time (hour or pore volume). Figure A2 and B2 show the ratio of Fe(II) mass accumulated in the effluent solution over initial hematite-Fe in the micromodel.

Figure 4. Snapshots of FMNH₂ (A1 and A2), Fe(II) (B1 and B2) and Br⁻ (C1 and C2) concentrations in the micromodel simulated by the pore-scale reactive transport model at flow rate of $2.70 \times 10^{-7} \text{ m}^3 \cdot \text{h}^{-1}$.

848

849 Figure 5. Experimental results (A and B, solid symbols), pore-scale model simulations (C and
850 D, open symbols) and single-domain model simulations (lines) of hematite reduction in the
851 micromodel at flow rates of 2.70×10^{-8} (blue), 2.70×10^{-7} (green) and 1.08×10^{-6} (red) $\text{m}^3 \cdot \text{h}^{-1}$.
852 Panel A and C showing the ratio of total residual hematite over total initial hematite in the
853 micromodel; B and D showing the ratio of dissolved Fe(II) mass accumulated in the effluent
854 over total initial hematite-Fe in the micromodel.

855

856 Figure 6. Averaged hematite reduction rate in each subgrid domain as a function of time after

857 normalizing to the average hematite reduction rate in the entire micromodel. The average

858 hematite reduction rates in each subgrid domain and in the entire micromodel were calculated

859 from the pore scale reactive transport simulations at flow rate 2.70×10^{-8} (A), 2.70×10^{-7} (B)

860 and 1.08×10^{-6} (C) $\text{m}^3 \cdot \text{h}^{-1}$.

861

862 Figure 7. Average rate of hematite reduction ($\langle r \rangle$) calculated from pore-scale simulations at
863 flow rate of $q = 2.70 \times 10^{-8}$ (red) $\text{m}^3 \cdot \text{h}^{-1}$ as a function of $\langle C_{\text{Fe}_2\text{O}_3} \rangle \langle C_{\text{FMNH}_2} \rangle (1 - \langle IAP \rangle / K_{eq})$. There were three regions with different slopes. The values of parameters k' , n and m ,
864 that corresponded to each region in the figure were estimated by multi-variant regression of
865 $\langle r \rangle$ vs $\langle C_{\text{Fe}_2\text{O}_3} \rangle$ and $\langle C_{\text{FMNH}_2} \rangle$ using equation
866 $\langle r \rangle = k' \langle C_{\text{Fe}_2\text{O}_3} \rangle^n \langle C_{\text{FMNH}_2} \rangle^m (1 - IAP/K_{eq})$. In the fitting, IAP value was
867 calculated using $\langle C_{\text{Fe}_2\text{O}_3} \rangle$ and $\langle C_{\text{FMNH}_2} \rangle$.

869

870 Figure 8. Residual hematite concentration (normalized to initial hematite concentration) in
 871 three subgrid domains (A, C and E), and accumulated Fe(II) mass in effluent (normalized to
 872 initial hematite-Fe in the micromodel) (B, D and F). Symbols denote calculated results from
 873 pore-scale simulations, and lines denote predicted results from the triple-domain model at
 874 flow rates of 2.70×10^{-8} (A and B), 2.70×10^{-7} (C and D) and 1.08×10^{-6} (E and F) $\text{m}^3 \cdot \text{h}^{-1}$.

875
876 Figure 9. Porosity ratio (f_{mac}) for the macropore domain (A) and mass transfer coefficient (k_a)
877 between advection and macropore domains (B) as a function of Reynolds number. Symbols,
878 except green stars, denote the triple domain model estimated parameter values using the
879 pore-scale simulation results of tracer Br^- , and lines denote the linear fit to the estimated
880 parameter values. Green stars denote the estimated k_a using the experimental residual
881 hematite concentrations in the micromodel (see text).

882

883 Figure 10. Measured and simulated results of residual hematite concentrations in different
884 subgrid domains (A and C), and measured and predicted results of accumulated Fe(II) mass
885 in effluent (C and D) at flow rates of 2.70×10^{-7} (A and B) and 1.08×10^{-6} (C and D) $\text{m}^3 \cdot \text{h}^{-1}$.
886 Symbols for the experimental results, and lines for the model results. The residual hematite
887 concentration was normalized to the initial hematite concentration in each subgrid domain.
888 The accumulated Fe(II) in the effluent was normalized to the initial total hematite-Fe in the
889 micromodel.