Reviews in Mineralogy & Geochemistry
Vol. 85 pp. 27-48, 2019

Multiscale Approaches in Reactive Transport Modeling

Sergi Molins
Lawrence Berkeley National Laboratory
Energy Geosciences Division
Berkeley, California 94720
USA

smolins@lbl.gov

Peter Knabner
Friedrich-Alexander-Universität Erlangen-Nürnberg
Applied Mathematics
91058 Erlangen
Germany

knabner@math.fau.de

INTRODUCTION

The field of reactive transport lies at the intersection of several disciplines in the Earth and Environmental sciences, including hydrology, geochemistry, biology and geology. The processes in natural and engineered media that are the focus of study of these disciplines take place over a wide range of spatial and temporal scales. Specifically, geological media are characterized by their physical and mineralogical heterogeneity at spatial scales from nanometers to hundreds of meters and beyond. Flow and advection of solutes take place at the scale of individual pores but are commonly represented at the Darcy scale where the porous medium is treated as a continuum. A large contrast is often observed between fluid residence times in regions of enhanced permeability such as fractures or macropores and less permeable media where diffusion may be the dominating solute transport process. Understanding of reactive processes, including those mediated by microorganisms, is often developed at the molecular scale in the laboratory but their impact in the environment is observed at larger spatial scales.

In addition to considering the scales of the individual processes, reactive transport must also consider how these different scales interact with one another to give rise to the overall coupled behavior. In fact, in many instances considering the processes at the observation (or native) scales has limited applicability in subsurface environments. For example, reaction rates derived from laboratory studies show large discrepancies from those observed in natural environments, where transport processes and accessibility to reactive areas control effective rates. Reactive transport models, thus, even in a simple form, must make assumptions regarding the scales associated with each process and how they interact with each other. Implicit in any model is also the assumption that the models for each process are applicable at the same spatial scale as the other processes represented. For example, local geochemical equilibrium may only be assumed where reaction rates are faster than transport rates such that the solution reaches equilibrium over a characteristic spatial scale.

Reactive transport modeling, as a tool to integrate knowledge and develop mechanistic understanding, seeks to incorporate improved process model representations that reflect our advances in fundamental understanding (Druhan and Tournassat 2019 and references therein).

1529-6466/19/0085-0002$05.00 (print)
1943-2666/19/0085-0002$05.00 (online)
http://dx.doi.org/10.2138/rmg.2019.85.2

The multiscale nature of reactive transport is one of the most prominent aspects in models and, hence, modeling approaches that address this multiscale nature are an increasingly important component of the toolset needed by researchers (Scheibe et al. 2015a). In particular, multiscale approaches make it possible to incorporate process representations at the appropriate native scale in models intended to simulate the coupled problem at a different spatial or temporal scale. A variety of approaches have been brought to bear that range from conceptual to mathematical to numerical. Specific goals of multiscale models are also diverse and include using the appropriate coupling between processes, capturing the processes at the relevant scale in different regions, capturing the physical and mineralogical heterogeneity at multiple scales or incorporating fine-scale information in larger-scale applications. Ultimately, there is the need to identify what processes and at what scale are controlling overall system behavior, and hence the appropriate spatial and temporal scales to represent each process.

Multiscale modeling is a very broad topic with applications across many disciplines (Tomin and Lunati 2013, 2016; Scheibe et al. 2015a; Amanbek et al. 2019). In this chapter, we specifically review multiscale approaches for reactive transport modeling from the conceptual and mathematical perspectives. Many of the approaches have also been used in the individual disciplines reactive transport draws from. They are here discussed in a general manner here but also specifically in relation to reactive transport applications. We include approaches where the multiscale nature is reflected in a continuum-mechanics-based model and we discuss numerical aspects of these approaches where needed. Approaches that incorporate upscaling procedures in the numerical solution process such as multiscale finite element or finite volume methods, or based on numerical upscaling however are not included, e.g., Efendiev and Hou (2009).

We start by establishing the equations that describe the processes of interest at a single scale and discussing the multiscale aspects associated with process coupling at a single scale. We relate these equations to the two scales commonly identified in porous media—the pore scale and the Darcy scale—but are generally applicable at a range of spatial scales, from fluid in pores to streams and rivers. Derivation of effective models by upscaling pore-scale equations to the Darcy continuum scale is used specifically to motivate the need for multiscale approaches. First, we describe approaches that use different scale representations in different regions in the domain. We continue with approaches based on the existence of two or more porous continua in the same region of the domain. We give examples of the use of the multiscale approaches described in selected literature applications before making some concluding remarks.

SINGLE-SCALE DESCRIPTION OF REACTIVE TRANSPORT

Reactive transport models simulate flow, solute transport and geochemical reactions. In this chapter, for simplicity, we will consider only single-phase (aqueous) flow and transport. These processes are typically described by two sets of equations, one for the conservation of mass and momentum of the fluid and the other for the conservation of mass of the reactive components. The form of these equations depends on continuum of reference for which they are written: a fluid continuum, a solid continuum or a continuum that includes both fluid and solid phases. For example, flow in streams and rivers may be represented by considering the fluid phase as the continuum of reference. In porous and fractured media in the subsurface, when the fluid and the solid are both treated as separate continua, we refer to the scale of observation as the pore scale, while when the porous medium is the continuum, we refer to it as the Darcy scale. For convenience, in the derivation that follows we will focus on porous and fractured media, but these single-scale equations can be read more generally as applicable at a range of spatial scales. Further, we will not consider here the scales where the medium is not characterized as a continuum. For example, we do not discuss characterizations at the molecular or atomistic scale, or the organism level in the case of microbial processes.

Separate fluid and solid continua: Pore-scale equations

When the individual pores are represented explicitly, and the solid–fluid interfaces are the boundaries of the domain considered (Fig. 1), flow may be described with the Stokes equations

$$\nabla \cdot \boldsymbol{u} = 0 \tag{1}$$

$$\nabla^2 \boldsymbol{u} = \frac{1}{\mu} \nabla p \tag{2}$$

where $\boldsymbol{u}$ is the fluid velocity (with $|\boldsymbol{u}|=0$ on the solid–fluid boundary), and μ, and p are the fluid viscosity, and pressure, respectively. The equations that describe the mass balance of chemical species subject to advective–diffusive transport and heterogeneous reactions at the fluid–solid surface may be written as

$$\frac{\partial c}{\partial t} = -\nabla \cdot \left(\boldsymbol{u} c\right) + \nabla \cdot \left(D \nabla c\right) \tag{3}$$

$$-D \nabla c \cdot \boldsymbol{n} = r \tag{4}$$

where c is the solute concentration, D is the diffusion coefficient of the solute in the solution, and r is the surface reaction rate. Equation (4) expresses the mass balance at the fluid–solid interface for the aqueous species involved in the heterogeneous reaction, where $\boldsymbol{n}$ denotes the unit normal pointing from solid to liquid.

Single porous continuum: Darcy-scale equations

When the porous medium is treated as a continuum, i.e., when within an elementary representative volume (or REV) properties that described the medium such as porosity (θ) or permeability ($\boldsymbol{k}$) may be assumed constant (Fig. 1), flow in porous media can be described by:

$$\frac{\partial \theta \rho}{\partial t} + \nabla \boldsymbol{q} = 0 \tag{5}$$

$$\boldsymbol{q} = -\frac{\boldsymbol{k}}{\mu} \left(\nabla p + \rho g z\right) \tag{6}$$

where $\boldsymbol{q}$ is the Darcy velocity vector, which is calculated with Darcy's law (Eqn. 6), θ is the porosity (water content in fully-saturated conditions), ρ is the fluid density, g is the gravitational constant, and z is the vertical coordinate. The equations that describe the mass balance of chemical species subject to advective-dispersive transport and heterogeneous reactions in porous media may be written as

$$\frac{\partial \theta C}{\partial t} = -\nabla \cdot \left(\boldsymbol{q} C\right) + \nabla \cdot \left(\boldsymbol{D}^{*} \nabla C\right) + R \tag{7}$$

where C is the concentration at the Darcy-scale, $\boldsymbol{D}^{*}$ is the effective diffusion/dispersion tensor, and R is the bulk reaction rate. In the view presented in this section, the properties that characterize the porous medium, i.e., θ, $\boldsymbol{k}$, or $\boldsymbol{D}^{*}$, or the bulk rates are assumed known (for example, empirically) and applicable at this scale. In general, however, they encapsulate information of the processes that take place at the scale of individual pores. In the section devoted to upscaling, we discuss how one may formally derive these parameters from the pore-scale description.

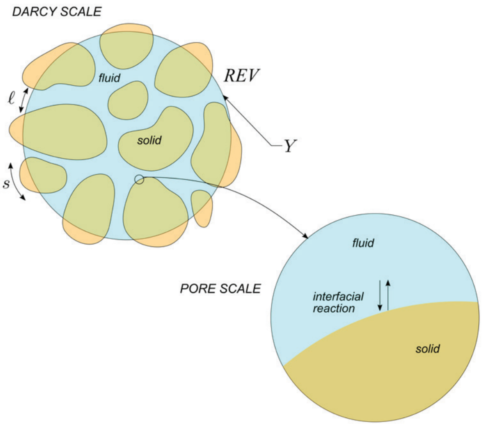

Figure 1. Conceptual representation of scales associated with interfacial (heterogeneous) reactions in porous media. The existence of an REV makes it possible to describe the medium as a continuum (left), while at the scale of individual pores interfacial reactions are explicitly described at the fluid–solid interface. Adapted from Wood et al. (2007).

Multiscale aspects of process coupling

The flow equations and the reactive transport equations are in general coupled via the composition of the fluid, as well as hydraulic and geometric properties of the porous medium. For example, changes in the fluid composition caused by geochemical reactions affect the fluid density, or dissolution–precipitation reactions change the pore space geometry which in turn affects the fluid velocity. The evolution of these properties is in many applications relatively slow compared to flow and transport and the coupling is assumed weak. In some other applications, the feedback processes are significant and are addressed specifically in the chapter devoted to porous media evolution in this volume (Seigneur et al. 2019, this volume).

Here we will briefly focus on the coupling of time scales associated with transport and reactions and how they affect the process representation at a specific spatial scale. For convenience, we re-write Equation (7) generically as

$$\frac{\partial \theta C}{\partial t} = \mathcal{L}(C) + \mathcal{R}(C) \tag{8}$$

where $\mathcal{L}()$ is the transport operator and $\mathcal{R}()$ the reaction operator. Transport is important as it provides the driving force for reaction but also because it provides a characteristic time scale to which the time scale of the reaction is compared. In an open system, as implied by Equation (8), if the characteristic time of transport (for a given characteristic length scale), $\tau_{\mathcal{L}}$,is larger than that of the reaction, $\tau_{\mathcal{R}}$, the solution reaches equilibrium with itself or with a mineral phase. In Darcy-scale models, if this characteristic length scale is that over which the REV is defined, this makes it possible to assume local equilibrium. In the local equilibrium assumption (LEA) (Lichtner 1996), the rate of reaction is thus determined by the rate of transport of matter across the boundaries of the domain (Fig. 2a).

In pore-scale models (Eqns. 3–4 may also be written in a form similar to Eqn. 8), the concept of local equilibrium is different (Lichtner 1996). At the Darcy scale, geochemical equilibrium is attained at the REV scale which includes many pores. At the pore scale, the detailed pore space geometry plays a role. Although equilibrium may be attained at mineral surfaces, geochemical gradients may still be present in individual pores (Fig. 2b).

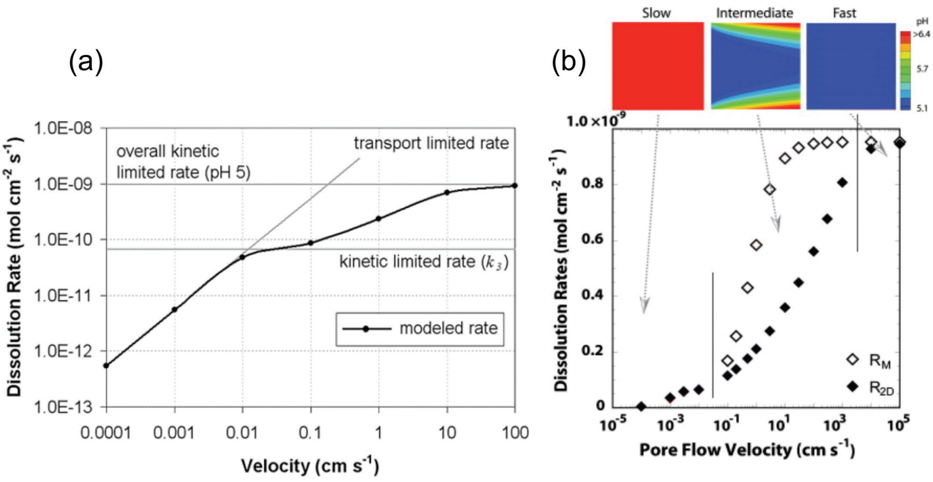

Figure 2. (a) Steady state calcite dissolution rates as a function of the flow velocity (using a double logarithmic scale) from a 1-D continuum model of transport and calcite dissolution (implemented with a kinetic rate expression). For velocities between 0.0001 and approximately 0.01 cm/s the dissolution rate is controlled by transport, hence it is proportional to velocity. For faster flow velocities, the rate is controlled by both transport and the kinetic reaction. [Reprinted from (a) From Molins S, Trebotich D, Steefel CI, Shen C (2012) An investigation of the effect of pore scale flow on average geochemical reaction rates using direct numerical simulation. Water Resources Research, 48(3):W03527, Figure 6, with permission] **(b)** Steady-state calcite dissolution rates in a single cylindrical pore calculated from a 2D pore-scale model (R2D) and from a Well-Mixed Reactor model (RM) as a function of the pore flow velocity for a pore of 100 μm in length and diameter. At low pore velocities, conditions in the pore are in equilibrium and R2D and RM produce the same results. Only under intermediate flow conditions where concentration gradients develop do the reaction rates depend on the spatial scale and the rate discrepancy between the two models reaches a maximum. [Reprinted from Li L, Steefel CI, Yang L (2008) Scale dependence of mineral dissolution rates within single pores and fractures. Geochimica et Cosmochimica Acta 72(2):360–377, Figure 5, with permission of Elsevier, Copyright 2008.]

UPSCALING AND EFFECTIVE MODELS

The macro- (Darcy) scale model in Equations (5–6) and (7) may be formally derived by scaling-up the micro-(pore) scale Equations (1–2) and (3–4). Upscaling has been the subject of intensive research for at least 50 years, with volume averaging being a commonly used approach for this purpose. In classical averaging theory, concentrations and fluxes are averaged over an REV composed of fluid and solid phases. The averaging of the pore-scale equations makes it possible to write conservation equations for these averaged quantities (see, e.g., Gray and Miller 2014). In these equations, however, new terms appear that still depend on pore-scale quantities and hence for which closure relations must be postulated. The mathematical theory of (periodic) homogenization is used to solve the closure problem (Hornung 1997).

In the most simple form, periodic homogenization relies on the spatial periodicity of the domain Ω, which is conceived to be composed of shifted and ε-scaled copies Y_ε of an REV Y (Fig. 3). The REV Y is made up of solid (Y_s) and liquid (Y_l), separated by an interface Γ. Accordingly, the porous media domain Ω_ε is composed of solid phase, with $Y_{s,\varepsilon}$ being the union of the shifted and ε-scaled Y_s and the liquid phase. The subdomain $Y_{l,\varepsilon}$ is defined similarly and assumed to be connected such that flow can take place. Let's assume a coefficient (φ) that oscillates with a periodicity of length ε such as the diffusion coefficient D, with $D > 0$ in the fluid and $D = 0$ in the solid. The aim of homogenization is to consider $\varepsilon \to 0$ (i.e., to zoom out) in order to see what description holds for the emerging homogeneous medium. Formally, this can be done assuming a two-scale asymptotic expansion for all unknown quantities φ in the form

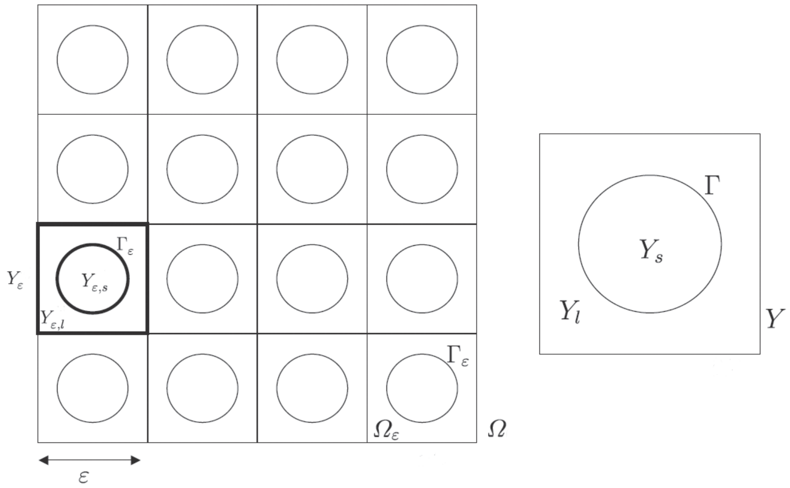

Figure 3. Two-dimensional domain Ω constructed by periodic repetition of a porous medium Ω_ε (left), represented by a unit cell *Y* composed of fluid and solid separated by a circular interface (right). Examples of other geometries used for unit cells are shown in Figure 4. [Modified from Ray N, van Noorden T, Frank F, Knabner P (2012) Multiscale modeling of colloid and fluid dynamics in porous media including an evolving microstructure. Transport in Porous Media 95(3):669–696, Figure 2, with permission of Springer Nature. Copyright 2012.]

$$\varphi_\varepsilon(x,t) = \varphi_0(x,t,y) + \varphi_1(x,t,y)\varepsilon + \varphi_2(x,t,y)\varepsilon^2 + \ldots \tag{9}$$

where $y := x/\varepsilon$ is a *fast* spatial variable in the sense that *y* covers *Y*, if *x* covers Y_ε. Depending on the problem, the interplay between the processes in ε and separation of scales, it is possible to derive equations in which only the *Y*-averaged 0-th order terms appear. This is done by inserting the expansion in the governing (pore-scale) equation such that each ε-power gives rise to a new equation for the coefficient that is being investigated.

For example, one can derive the upscaled, Darcy-scale form of the diffusion equation (i.e., Eqn. 7 with $\boldsymbol{q} = 0$ and no reaction term) from the pore-scale diffusion counterpart (i.e., Eqn. 3) with $|\boldsymbol{u}| = 0$). Solving the closure equations on *Y* numerically makes it possible then to obtain the effective diffusion tensor $\boldsymbol{D}^*$, which encodes the information about the pore geometry, see, e.g., Ray et al. (2018). The closure equations are typically solved using idealized or randomly generated porous geometries (Fig. 4). From these calculations, it is possible to describe the dependence on pore geometry solely by a macroscopic parameter such as porosity (Fig. 5).

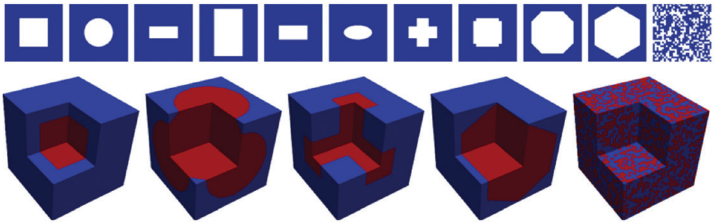

Figure 4. Representative elementary volumes in 2D: square, circle, rectangles, ellipse, crosses (type 1 and 2), octagon, hexagon, and random geometry (top), and representative elementary volumes in 3D: cube, sphere, 3D cross, hexagonal prism, and random (bottom) [Reprinted from Ray N, Rupp A, Schulz R, Knabner P (2018) Old and new approaches predicting the diffusion in porous media. Transport in Porous Media 124: 803–824, Figures 1 and 2, with permission of Springer Nature. Copyright 2018.]

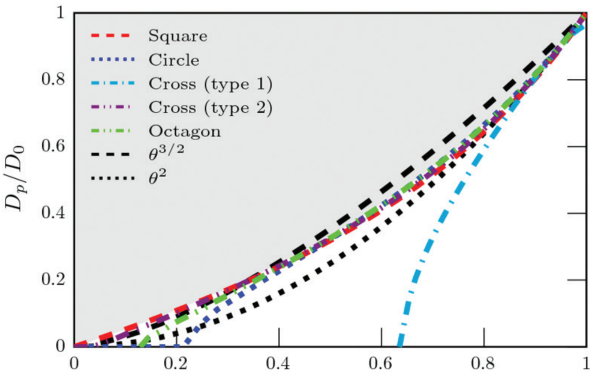

Figure 5. Scalar ratio between scalar representative effective diffusion (D_p) over intrinsic diffusion (D_0) as a function of porosity for isotropic geometries in 2D: square, circle, crosses (type 1 and 2, see Fig. 4), and octagon; Hashin–Shtrikman bound $\theta(2-\theta)$ (exclusion of gray area); and functional relations $\theta^{3/2}$ (Marshall 1959) and θ^2 (Buckingham 1904) [Reprinted from Ray N, Rupp A, Schulz R, Knabner P (2018) Old and new approaches predicting the diffusion in porous media. Transport in Porous Media 124: 803–824, Figures 1 and 2, with permission of Springer Nature. Copyright 2018]

The above procedure can be accomplished when there is scale separation (i.e., the micro- and macro-scales can be described independently from each other) but in general it also depends on the proper scaling of the parameters in the ε-problem. For example, to deduce Darcy's law from the Stokes equation at the pore scale (i.e., with a computable permeability), a scaling of the viscosity μ to εμ is required. Further, when several different processes are in play (e.g., advection and diffusion), characteristic numbers such as the Péclet number (Pe) may be needed in the efficient coefficients, e.g., in the derivation of mechanical dispersion (Mikelić et al. 2006). For reactive transport problems, efforts in upscaling have focused on heterogeneous reactions. Here we present a short derivation of upscaled relationships for (first-order) sorption reactions and dissolution-precipitation reactions first with non-evolving geometries and then with evolving geometries.

Upscaling interfacial reactions

We consider a surface reaction such that Equations (3–4) may be written on Γ_ε as

$$\frac{\partial c_m}{\partial t} = -\nabla \cdot \left(\boldsymbol{u} c_m - \boldsymbol{D} \nabla c_m \right) \text{in } Y_{l,\varepsilon} \tag{10}$$

$$D \nabla c_m \cdot \boldsymbol{n} = \varepsilon \cdot r \quad \text{on } \Gamma_{l,\varepsilon} \tag{11}$$

where c_m is the concentration in the fluid, and the rate is expressed as an exchange between the fluid and the surface concentration, $r=\alpha(c_m-c_{im})$, with the immobile concentration (c_{im}) being a surface concentration such that

$$\frac{\partial c_{im}}{\partial t} = \alpha \left(c_m - c_{im} \right) \tag{12}$$

where α is the rate of mass transfer between the bulk fluid and the surface, with $\alpha>0$. A no-flow boundary condition ($\boldsymbol{u}=0$) is assumed on $\Gamma_{\ell,\varepsilon}$. The upscaled model then takes the following form

$$\frac{\partial \left(\theta C_m \right)}{\partial t} - \mathcal{L}\left(C_m \right) = -\sigma R\left(C_m, C_{im} \right) \tag{13}$$

where σ is the specific surface ($\sigma=\Gamma/Y$, which along with θ and $\boldsymbol{D}^*$are computed from the pore geometry, and the macro-scale rate is described by

$$R\left(C_m, C_{im}\right) = \alpha\left(kC_m - C_{im}\right) \tag{14}$$

where micro- and macro-scale problems are separate. However, if surface diffusion is considered at Γ_ε such that the micro-scale Equation (12) is written as

$$\frac{\partial c_{im}}{\partial t} - \varepsilon^2 D_s \Delta_y c_{im} = \alpha\left(c_m - c_{im}\right) \tag{15}$$

where D_s, is the surface diffusion coefficient, it is not possible any longer to obtain the average of c_{im} and a coupled macro-scale/micro-scale model is obtained

$$\frac{\partial c_{im}\left(y,t;x\right)}{\partial t} - D_s \Delta_y c_{im} = \alpha\left(kC_m - c_{im}\right) \text{ for } y \in \Gamma, x \in \Omega \tag{16}$$

where the micro problem depends at every point x on the macroscopic concentration $C_m(x,t)$. (Note that the emerging equations for C_m and $C_{im} = C_{im}(y,t;x)$ read as Eqn. 35, with Γ in lieu of $\Omega_{\bar{x}}$).

Upscaling interfacial reactions with evolving geometries

Precipitation–dissolution reactions are of interest as they change the pore geometry and can have a positive feedback on flow and transport processes, leading in some case to clogging or wormholing. In the classical approach this is reflected in the change of porosity as described by Ray et al. (2015)

$$\frac{\partial \theta}{\partial t} = \frac{1}{\rho_s} R \tag{17}$$

where ρ_s is a surface density used as conversion factor between mass and volume. To close the model, the specific surface σ must be related to θ, which requires assumptions on the evolving micro geometry. In the case of known geometries (e.g., spheres, cubes, etc), this leads to the commonly used relation (Lichtner 1996)

$$\sigma = \beta C_{min}^{3/2} \tag{18}$$

where C_{min} is the mineral concentration and β is a factor to convert from units of mass to volume

The evolution of the interface as a result of the reaction can be described with a sharp interface approach (e.g., a level set) or approximated by a phase field model (Bringedal et al. 2019). The normal component of the velocity of the interface is denoted by $\nu_{n,\varepsilon}$

$$v_{n,\varepsilon} = \varepsilon \frac{1}{\rho_s} R\left(c_m\right) \tag{19}$$

This velocity is a function of the reaction rate R and the density of the precipitate ρ_s. Considering the reaction to be a single-component reaction for simplicity, Equation (11) can be replaced with

$$\boldsymbol{D} \nabla c_m \cdot \boldsymbol{n} = v_{n,\varepsilon}\left(c_m - \rho_s\right) \tag{20}$$

where the precipitate can form the outer surface of the solid grain. By upscaling we can again recover Equation (13), but here the closure comes from a detailed description of the interface via the evolution of a level-set function L_0 in the REV Y, described by (Ray et al. 2015)

$$\frac{\partial}{\partial t} L_0 - \frac{1}{\rho} R\left(C_m\left(x,t\right)\right)\left|\nabla_y L_0\right| = 0 \text{ in } Y \tag{21}$$

yielding θ, σ, $\boldsymbol{D}$ needed in Eqn. 13 but dependent now on the macroscopic concentration $C_m(x, t)$. Thus, we obtain again a coupled micro-macro model. The solution of Equation (21) is not straight-forward and can be derived by a two-scale asymptotic procedure (Ray et al. 2015).

Extension of this approach to multicomponent problems that include homogeneous and heterogeneous reactions, in equilibrium or kinetic, is still in the early stages of development. While homogeneous or sorption reactions are tractable, development of passivation layers in systems with multiple mineral reactions, e.g., Daval et al. (2009), is considerably more difficult to handle in this framework.

COMBINING SCALE REPRESENTATIONS

The ability of pore-scale models to explicitly resolve individual pores make them suitable to simulate flow and reactive transport without using bulk parameters to characterize the medium. The computational cost of pore-scale simulations, however, is very high if one wants to cover volumes of porous media large enough for relevant applications. As noted in the previous section, the macro (Darcy)-scale problem can only be formulated separately from the micro (pore)-scale problem under a number of simplifying assumptions, see also Battiato and Tartakovsky (2011). Rather than formulating and solving closure equations for periodic unit cells of idealized geometries in these cases, one may want to solve the pore-scale problem directly. In applications where the pore-scale characterization is needed only in certain regions rather the entire domain, an attractive approach is then to combine a pore-scale description in these regions and revert to a Darcy-scale description elsewhere. Broadly, two approaches have been used for this purpose: hybrid models and the Darcy–Brinkman–Stokes approach.

Hybrid multiscale models

Hybrid multiscale models combine different scale representations in a single simulation (Battiato et al. 2011; Roubinet and Tartakovsky 2013; Yousefzadeh and Battiato 2017). In this approach, the domain is divided in two or more regions where different scale representations are used (Fig. 6a). Because often this implies that different process models, and thus potentially also the numerical solution method, are used in each of the regions, hybrid models are sometimes known as multi-algorithm or algorithm refinement models. An advantage of hybrid models from the multi-algorithm perspective is that it is possible to consider different spatial and temporal discretization in different portions of the domain, or the use of different dimensionality for each of the sub-domains (e.g., Fig. 6b).

A hybrid model of reactive transport on a domain Ω composed of a pore-scale domain Ω_p and a Darcy-scale domain Ω_D, such that $\Omega = \Omega_p \cup \Omega_D$, entails the solution of Equations (1–4) in Ω_p and Equations (5–7) in Ω_D. The pore-scale and Darcy-scale simulations are coupled by enforcing the continuity of mass (concentration) and mass flux (its normal component) along the interface Γ between Ω_p and Ω_D:

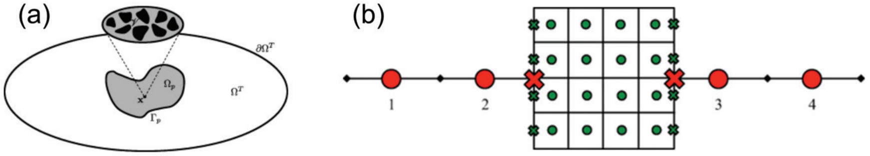

Figure 6. (a) Schematic representation of the pore-(Ω_p) and Darcy-scale ($\Omega_p = \Omega^T - \Omega_p$) domains [Reprinted from Battiato I, Tartakovsky DM, Tartakovsky AM, Scheibe TD (2011) Hybrid models of reactive transport in porous and fractured media. Advances in Water Resources, 34(9), 1140–1150, Figure 1, with permission of Elsevier. Copyright 2013.] **(b)** Hybrid finite-volume discretization. The (small green and big red) circles indicate nodes at which the (pore-scale and Darcy-scale) unknowns are computed with a regular finite-volume method. The (big red and small green) crosses denote extra nodes used to enforce the continuity conditions at the hybrid's interfaces. [Reprinted from Roubinet D, Tartakovsky DM (2013) Hybrid modeling of heterogeneous geochemical reactions in fractured porous media. Water Resources Research, 49(12), 7945–7956, Figure 1, with permission.]

$$C(\boldsymbol{x},t) = \frac{1}{|\Gamma|}\int_{\Gamma} c(\boldsymbol{X},t)\,ds \tag{22}$$

$$Q^D(\boldsymbol{x},t) = \frac{1}{|\Gamma|}\int_{\Gamma} Q^p(\boldsymbol{X},t)\,ds \tag{23}$$

where $Q^p(\boldsymbol{x}, t)$ and $Q^D(\boldsymbol{x}, t)$ are the normal components of the pore-scale and Darcy-scale mass fluxes , $Q^p(\boldsymbol{x}, t) = \boldsymbol{u}c - \boldsymbol{D}\nabla c$ and $Q^D = \boldsymbol{q}C - \boldsymbol{D}^*\nabla C$, respectively.

From a numerical perspective, hybrid models need to consider the interface between the sub-domains explicitly and coupling the sub-problems at the interface. Typically, concentrations and fluxes are used as coupling unknowns for Equations (22) and (23). This adds some complexity in the implementation of hybrid models, especially when the dimensionality or discretization on both sides of the interfaces are different. An example of a numerical method designed to handle these exchanges in a general and flexible way is the mortar method (Balhoff et al. 2008; Mehmani et al. 2012). In this method, coupling between sub-domains is accomplished by using finite-element (FEM) spaces to determine interface conditions (Fig. 7). Using the flow problem as example (with pressure being the unknown of the problem), the pressure field in the mortar space (noted by p) is a linear combination of finite element (FE) basis functions (ϕ_ι):

$$p = \sum \zeta_i \, \phi_i \tag{24}$$

The basis functions may be constant, linear, quadratic, or higher order functions. The solution is obtained by determining the coefficients (ζ_ι) that result in matching of fluxes at interface. The mortar solution then describes the pressure field only at the interface which is used as a boundary condition and projected onto the individual sub-domain. The sub-models are then solved using the appropriate algorithm.

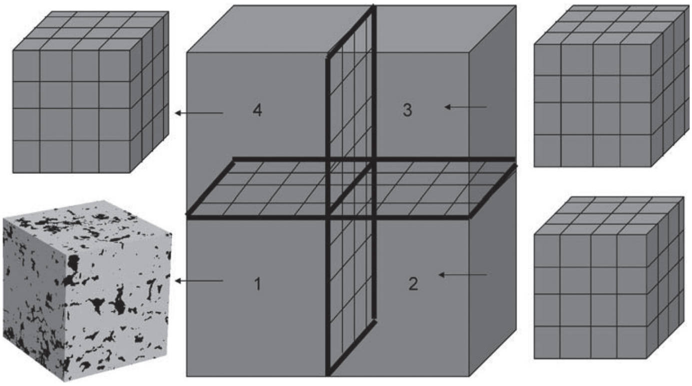

Figure 7. Schematic showing one pore-scale model and three Darcy-scale models arranged using 4×4 quadratic mortars. [Reprinted from Balhoff MT, Thomas SG, Wheeler MF (2008) Mortar coupling and upscaling of pore-scale models. Computational Geosciences 12(1):15–27, Figure 7, with permission of Springer Nature. Copyright 2008.]

Darcy–Brinkman–Stokes approach

An approach for combining pore- and Darcy-scale representations that has received increasing attention is the one conceptualized by the Darcy–Brinkman–Stokes equation (Golfier et al. 2002; Popov et al. 2009; Gulbransen et al. 2010; Yang et al. 2014; Soulaine and Tchelepi 2016; Soulaine et al. 2017). Darcy–Brinkman–Stokes describes flow in open pore space and in a porous continuum with a single equation (written here to recover the transient incompressible Navier–Stokes equations in the fluid domains in lieu of Eqn. 2):

$$\frac{1}{\varepsilon}\left(\frac{\partial \rho \boldsymbol{u}}{\partial t}+\nabla\cdot\left(\frac{\rho}{\varepsilon}\boldsymbol{u}\boldsymbol{u}\right)\right)=-\nabla p+\frac{\mu}{\varepsilon}\nabla^2\boldsymbol{u}-\mu\boldsymbol{k}^{-1}\boldsymbol{u} \tag{25}$$

where ε is the porosity of the medium, with $\varepsilon=1$ in the pore spaces, $0<\varepsilon<1$ in a porous continuum and $\varepsilon=0$ in the solid phase. The permeability $\boldsymbol{k}$ of the medium requires a constitutive relation linking it to ε, for example the Kozeny–Carman equation. As a result, the terms associated with porous-media flow become negligible in the pore scale, while the terms associated with pore-scale flow become negligible in the porous continuum or the solid phase (Fig. 8). The transport of the aqueous species is described by a locally averaged equation

$$\frac{\partial \varepsilon C}{\partial t}+\nabla\cdot\left(\boldsymbol{u}C\right)-\nabla\cdot\left(\varepsilon\boldsymbol{D}^{*}\nabla C\right)-R \tag{26}$$

where dissolution is here described as a source-sink term (R) as in Equation (7).

The use of a single equation simplifies the numerical implementation of this method. Further, it does not require explicit representation of an interface between pore-scale and Darcy-scale, which is especially convenient in problems with evolving media. In fact, the distinction between pore-scale and Darcy-scale is only conceptual. In the pore-scale limit, i.e., when ε and $\boldsymbol{k}$ are very small, Equations (25) and (26) recover the pore-scale description in Equations (1–3) and it may be used as a pore-scale method (Golfier et al. 2002; Soulaine et al. 2017).

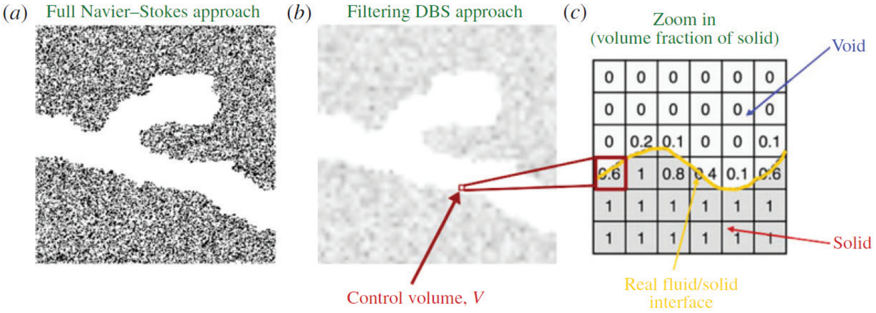

Figure 8. Conceptual representation of the void and solid in the pore-scale approach in contrast to the Darcy–Brinkman–Stokes (DBS) approach. **(a)** In the former, solid grains are explicitly described, the flow is governed by Navier–Stokes everywhere in the void. **(b)** In the latter, a cutoff length is introduced by means of the control volume V and the void is represented by the volume fraction ε, **(c)** discretized representation of the medium near the fluid–solid interface where the volume fraction of the solid ranges from 0 (pore space) to 1 (solid). [Reprinted from Soulaine C, Roman S, Kovscek A, Tchelepi HA (2017) Mineral dissolution and wormholing from a pore-scale perspective. Journal of Fluid Mechanics 827:457–483, Figure 2, with permission.]

MULTI-RATE AND MULTI-CONTINUA MODELS

Natural porous media are characterized by the existence of porosity at multiple spatial scales. The conceptual model presented in Figure 1 only considers inter-granular porosity, that is, porosity available between solid grains where in general fluid velocities are appreciable. We update here this model to include intra-granular porosity, that is, porosity that exists at small spatial scales in regions, which we will for convenience refer to as aggregates, where fluid flow is in general very slow and transport processes are dominated by diffusion (Fig. 9). In this media, the mass of each constituent is distributed between inter-porosity and intra-porosity, or mobile and immobile regions, between which mass is exchanged.

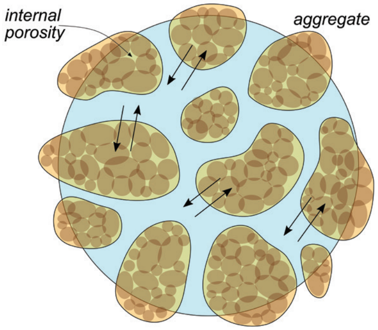

Figure 9. Conceptual representation of media with porosity at multiple spatial scales, showing mass exchange fluxes between internal porosity in aggregates and inter-granular porosity.

Multi-rate models

The concept of mass exchange between mobile and immobile regions is analogous to considering heterogeneous reactions between a mobile and immobile species, such as in sorption reactions, see Equations (10–12). We will use this idea here to present single- and multi-rate models, see, e.g., Haggerty and Gorelick (1995), Hollenbeck et al. (1999). We start by writing the mass balance of a species as (omitting the species index for simplicity)

$$\frac{\partial \theta_m C_m}{\partial t} + \frac{\partial \theta_{im} C_{im}}{\partial t} = \mathcal{L}\left(C_m\right) \tag{27}$$

where C_m and C_{im} are the mobile and immobile concentrations of the species, where we assume the immobile concentration is not subject to transport $\mathcal{L}()$. The mobile (θ_m) and immobile (θ_{im}) porosities are the corresponding conversion factors to normalize the concentrations to the volume of an REV (if C_{im} is a surface concentration, then $\theta_{im}=\rho_b$, with ρ_b being the bulk density). Equation (27) needs a closure relation that links the two concentrations, which may be a quasi-stationary approximation

$$C_{im} = \kappa C_m \tag{29}$$

describing a linear equilibrium sorption reaction ($\kappa \equiv K_d$), or a first-order kinetic exchange such as

$$\frac{\partial C_{im}}{\partial t} = \alpha\left(\kappa C_m - C_{im}\right) \tag*{(29)}$$

Integration of Equation (29) makes the memory effect of the linear mass transfer process evident

$$C_{im}\left(x,t\right) = e^{-\alpha t} C_{im}\left(0,t\right) + \int_0^t e^{-\alpha(t-s)} \alpha \kappa C_m\left(x,s\right) ds \tag{30}$$

For more flexibility in the description of this memory (or tailing) effect, C_{im} can be further subdivided in different fractions (β_k) with different kinetic behavior in a multi-rate formulation. Equations (27) and (29) can be generalized to

$$\frac{\partial \theta_m C_m}{\partial t} + \sum_{k=1}^{N} \beta_k \frac{\partial \theta_{im} C_{im,k}}{\partial t} = \mathcal{L}\left(C_m\right) \tag{31}$$

$$\frac{\partial C_{im,k}}{\partial t} = \alpha_k\left(\kappa_k C_m - C_{im}\right) \qquad k = 1,..,N \tag{32}$$

with $\beta_k \geq 0, \sum_{k=1}^{N} \beta_k = 1$.

Applying (30) to each of the fraction and expanding the sum in (31), one can see that the exponential kernel in the memory term becomes multimodal. The model can be also used to describe physical non-equilibrium, where now the mass transfer is between the mobile region and each of the fractions of the immobile region (or classes of micro-porosity, each giving a different memory effect). All these fractions (or sorption sites in the sorption interpretation), exchange mass with the mobile region directly based on the same C_m.

A generalization of Equations (31) and (32) is given by extending them from a finite number of fractions (i.e., sorption sites/micro-porosity classes) to an infinite number (or a continuum) of them by re-writing them as

$$\frac{\partial \theta_m C_m}{\partial t} + \int_0^\infty \beta(k) \frac{\partial \theta_{im} C_{im,k}}{\partial t} dk = \mathcal{L}(C_m) \tag{33}$$

$$\frac{\partial C_{im}}{\partial t} = \alpha(k)(\kappa_k C_m - C_{im}) \qquad k \geq 0 \tag{34}$$

with $\int_0^\infty \beta(\mathrm{k}) \mathrm{dk} = 1$

Extension of multi-rate mass transfer models to multicomponent reactive transport is possible; see, e.g., Donado et al. (2009) where the equilibrium is assumed in each the mobile and immobile domains such that Equations (27) and (30) may be written in terms of total concentrations and speciation calculations performed once the equations are solved for these total concentrations.

Multi-continua models

Multi-rate models are derived for two continua: a mobile and immobile region. This can be generalized for any number of continua. One can transition from multi-rate models to multi-continua models (MC). We can start by assuming that in one aggregate class the diffusive transport within the aggregate is taken into account. For the ease of notation, we consider only one rate ($N=1$) . The averaged concentration $C_{im} = C_{im}(x,t)$ is now replaced by $c_{im} = C_{im}(y,t;\bar{x})$, $y \in \Omega_{\bar{x}}$ where $\Omega_{\bar{x}}$ is a representative aggregate and the total mass conservation from (31) reads

$$\frac{\partial \theta_m C_m}{\partial t} + \frac{\partial \left(\int_{\Omega_{\bar{x}}} \theta_{im} c_{im} dy \right)}{\partial t} = \mathcal{L}(C_m) \tag{35}$$

Equation (31) is substituted by a partial differential equation on $\Omega_{\bar{x}}$

$$\frac{\partial \theta_{im} c_{im}}{\partial t} - d_{im} \Delta_y c_{im} = 0 \tag{36}$$

$$d_{im} \nabla_y c_{im} \cdot n_y = \alpha\left(C_m(\bar{x},t) - c_{im}(y,t;\bar{x})\right) \text{ for } y \in \partial\Omega_{\bar{x}} \tag{37}$$

where $d_{im} > 0$ denotes the molecular diffusion coefficient in the aggregate and n_y is the unit normal at $\partial\Omega_{\bar{x}}$ pointing out of $\Omega_{\bar{x}}$.

If we have several points $\bar{x} = x_k$, where the detailed dynamics must be considered, we go from a two-continuum/region model to a multiple continuum/regions models with a considerable increase in numerical complexity. The extreme is to do this for every (discretization) point $\bar{x} = x \in \Omega$. In this case, we can again arrive at a micro-macro model as in Equations (13) and (16). To avoid enormous numerical complexity in simulating such a model, on can try solving Equations (36) and (37) analytically with appropriate initial conditions. This is possible in special cases, e.g., when $\Omega_{\bar{x}}$ is a sphere. This solution representation, which depends on $c_m(x,t)$, may be viewed as analogous to the multi-model extension of Equation (30), where now the integral in (30) has to be substituted by an integral of the type

$$\int_{\Omega_x} \theta_{im} c_{im}\left(y,t;x\right)dy = \int_0^t G\left(x,t-s\right)C_m\left(x,s\right)ds \tag{38}$$

to close the relation in Equation (35), with $c_m\left(y,0,x\right)=0$ for simplicity.

Multiple interacting continua

The multiple interacting continua (MINC) is a multi-continuum approach developed specifically as a discretization method for fractured media. In this approach, the matrix is represented by multiple continua, each one further away from the fracture continuum. The idea is that changes in fluid conditions propagate more slowly in less permeable matrix blocks compared to the smaller fracture volumes. This approach allows for accurate resolution of the gradients in pressures and concentrations into the matrix. It is distinct from the MRMT in that matrix continua are connected in series to account mass transfer between, while in the MRMT mass transfer is always between the mobile region and the immobile region according to a number of parallel rates. While the MINC method was developed for fractured media, it may be used as general multi-continuum discretization approach, and in some MINC implementations multi-rate mass transfer models can be obtained as a specific case.

MULTISCALE MODEL APPLICATIONS

In the previous sections, we have reviewed approaches to simulate reactive transport processes in media characterized by the multiplicity of scales. These approaches have been brought to bear on several applications in the field. Here we presented a selection of applications where one or more of these approaches have been used. In some of these applications, to evaluate the ability of multiscale methods to capture the processes of interest, they are compared to micro-scale simulations, macro-scale simulations, or simulations with other multiscale approaches. We organize this section by first distinguishing between applications in granular porous media and fractured media. We move on to applications in integrated hydrology that connect surface and subsurface compartments, which share similarities to the multiscale concepts discussed in this chapter.

Granular porous media

Dissolution of rocks often involves the development of altered rinds in the grains that make up the rock, e.g., Navarre-Sitchler et al. (2009). These layers may be characterized by changes in porosity or diffusivity that determine the rate at which reactant accesses the reactive mineral. Rates of dissolution observed at the large scale depend on diffusion-reaction processes that take place at the scale of micrometers. Although the method of multiple interacting continua was developed for fractured media it can be viewed as similar to the "shrinking core" model (Wunderly et al. 1996). In this view, the grains can be conceptualized as consisting of several continua connected in series. Aradóttir et al. (2013) used this approach to capture the microscopic dynamics of basaltic glass dissolution in a Darcy-scale model (Fig. 10). The MINC method involves dividing the system up to ambient fluid and grains, using a specific surface area to describe the interface between the two. The various grains and regions within grains can then be described by dividing them into continua separated by dividing surfaces. Millions of grains can thus be considered within the method without the need to explicitly discretizing them. Four continua were used for describing a dissolving basaltic glass grain; the first one describes the ambient fluid around the grain, while the second, third and fourth continuum refer to a diffusive leached layer, the dissolving part of the grain and the inert part of the grain, respectively.

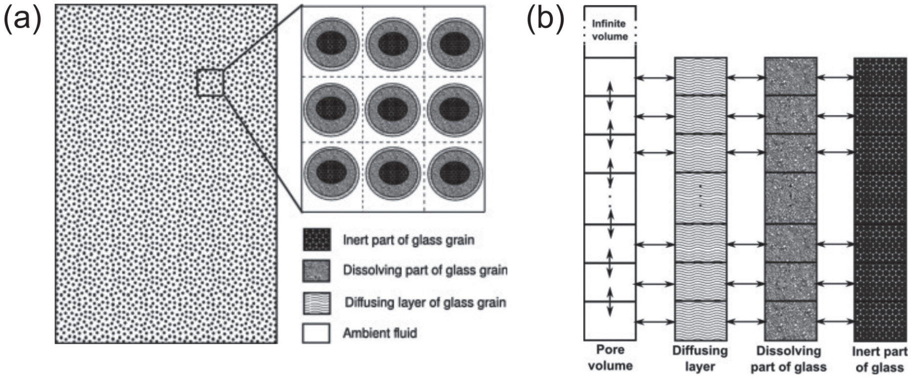

Figure 10. (a) Four-dimensional MINC interpretation of basaltic glass dissolution in the context of a column flow through experiment, **(b)** Schematic illustration of elements and connections in the four-dimensional MINC setup. Columns represent different continua, each of which has a number of elements (represented by boxes). Arrows show connections between elements and continua. [Reprinted from Aradóttir ESP, Sigfússon B, Sonnenthal EL, Björnsson G, Jónsson H (2013) Dynamics of basaltic glass dissolution–Capturing microscopic effects in continuum scale models. Geochimica et Cosmochimica Acta 121:311–327, Figures 2 and 5, with permission of Elsevier. Copyright 2013.]

The physical heterogeneity of natural porous media often leads to poorly mixed conditions such that different conditions exists within relatively small volumes of the media. From a reactive transport perspective, the existence of micro-environments implies that geochemical gradients can develop. For example, diffusion-dominated micro-environments conditions may be at equilibrium or close to equilibrium with certain minerals, while in advection-dominated pore spaces reactions are far from equilibrium. Mineralogical heterogeneity at different scales compounds to this effect where a correlation may exist between a certain mineralogy and enhanced reactivity due to availability of micro-porosity (Landrot et al. 2012). Poorly mixed conditions may also exist within individual pores, which under certain conditions lead to scale dependent rates (Li et al. 2008).

Although pore-scale simulations make it possible to reproduce geochemical gradients at the micrometer scale (Molins et al. 2012), multiscale models offer an alternative that is less computationally demanding. Liu et al. (2015) designed a micromodel experiment coated with hematite where macro- and micro-porosity domains where present (Fig. 11a). Three separate models were used to describe transport processes and reductive dissolution of hematite: a pore-scale model, a 1D single-continuum model, and a 1D triple-continua model. The predictions from the pore-scale reactive transport model predicted reasonably well the measured pore-scale rates of hematite reduction. Geochemical gradients within the domain (Fig. 11a) made it necessary to divide the domain in three continua: one that captured advection-dominated domain, one to capture the diffusive gradients within the macro-pore and a third on to capture diffusive limitations in the micro-pores. While the rate of hematite reduction in the advection-dominated and macro-pore domains was affected by the flow rate, the rate in the micropore domain was not, however, as reactant diffusion was rate-limiting. Results from the single domain model deviated significantly from the pore-scale results.

Pore-scale is not always available due to the large dimensions of the domain and the associated large computation costs. In these circumstances, multiscale approaches that retain a pore-scale description for part of the domain while using Darcy-scale for the rest help bridge the trade-off between process resolution and domain size. Yan et al. (2017) used a Darcy–Brinkman–Stokes-based approach to simulate biogeochemical reaction rates in heterogeneous sediments. An X-ray computed tomography image was used to construct a

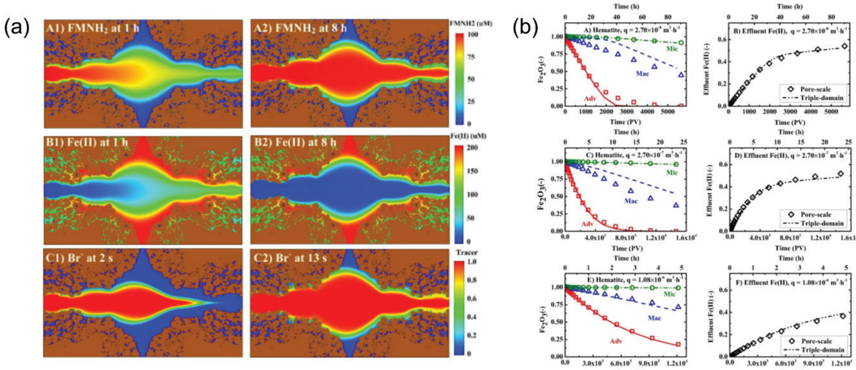

Figure 11 (a) Pore-scale simulation results for selected components and **(b)** Hematite concentration normalized to initial values in triple-continua domains (A, C and E), and accumulated Fe(II) mass in effluent (normalized to initial hematite-Fe in the micromodel) (B, D and F). Symbols denote calculated results from pore-scale simulations, and lines denote predicted results from the triple-domain model. [Reprinted from Liu Y, Liu C, Zhang C, Yang X, Zachara JM (2015) Pore and continuum scale study of the effect of subgrid transport heterogeneity on redox reaction rates. Geochimica et Cosmochimica Acta 163:140–155, Figures 4, 8, with permission of Elsevier. Copyright 2015.]

3D multiscale domain where ε was assigned a value from grayscale image (Fig. 12a), and in turn, a permeability value calculated from ε. A critical aspect of the model was, however, the assumption that the distribution of soil organic carbon (SOC) and biomass was correlated inversely with ε. That is, these variables were high near or on solid surfaces while low in large pore spaces. Additional simulations with single- and dual-domain models were performed to test this assumption. These simulations show that only when a large fraction of the soil organic carbon and biomass was placed in the immobile domain, dual-domain models were able to capture effluent concentrations of nitrate (Fig. 12b). In fact, single-domain models captured well effluent concentrations for non-reactive tracers. The multiscale aspect of the problem appeared only in the reactive transport component.

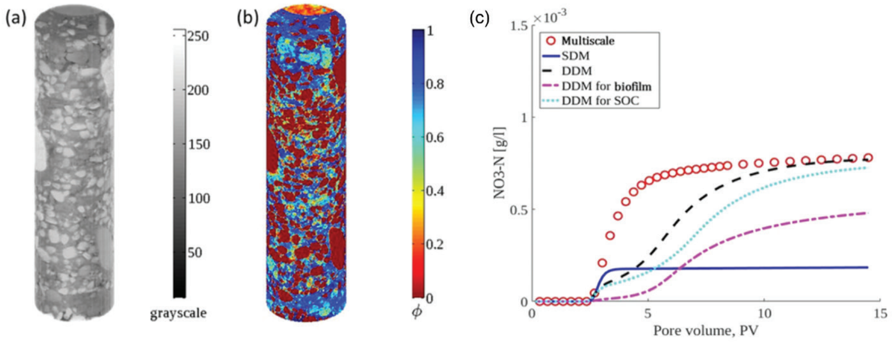

Figure 12 (a) An X-ray computed tomography image of a sediment column where a larger grayscale value indicates that the volume contains a higher content of solids; **(b)** porosity distribution converted from the left grayscale image where 0 denotes solid, 1 denotes pore, and other values between them denote the regions with mixed pores and solids, **(c)** Effects of biofilm and SOC heterogeneity on NO_3 reduction for the DBS-based model (Multiscale), the single-domain model (SDM), the dual-domain model (DDM) and two additional DDM, one where the positive correlation is only assumed for the biofilm (DDM for biofilm) and the other for the soil organic carbon (DDM for SOC). [Reprinted from Yan Z, Liu C, Liu Y, Bailey VL (2017) Multiscale investigation on biofilm distribution and its impact on macroscopic biogeochemical reaction rates. Water Resources Research 53(11):8698–8714, Figures 1, 9, with permission.]

These applications highlight the importance of mixing processes in reactive transport in heterogeneous porous media. In some instances, however, simulation of mixing processes in relatively homogeneous media may need of a multiscale approach when they are coupled to reactive processes. An example of this are mixing-controlled reactions. When two solutions mix such that a precipitate may form that has the potential to clog the pore space, it may be necessary to perform pore scale simulations. Scheibe et al. (2015b) presented a hybrid model that performed Darcy-scale simulations everywhere in the domain, and based on an incomplete mixing conditions, dynamically performed additional pore-scale simulations in a narrow region of the domain where precipitation occurred as a result of the mixing. This overlapping or hierarchical approach eliminated the need for matching boundary conditions between pore-scale and Darcy-scale domains. Hybrid simulations showed a sharper reaction front than equivalent Darcy-scale simulations, although some instabilities were observed in the hybrid approach (Fig. 13).

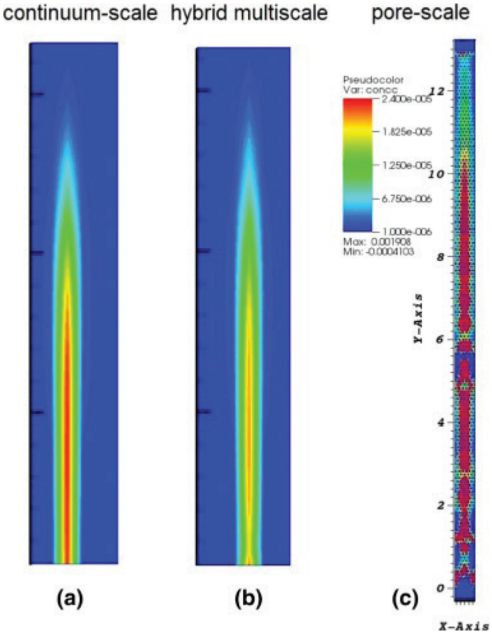

Figure 13. Concentration of product species *C* (mol/cm^3) in **(a)** a single-scale (Darcy-scale only) simulation, **(b)** hybrid multiscale simulation and (c) pore-scale simulation. [Reprinted from Scheibe, T. D., Schuchardt, K., Agarwal, K., Chase, J., Yang, X., Palmer, B. J., et al. (2015). Hybrid multiscale simulation of a mixing-controlled reaction. Advances in Water Resources 83:228–239, Figure 5, with permission of Elsevier. Copyright 2015.]

Fractured media

Flow and transport in fractured media occur primarily through a network of fractures, while flow in the matrix may be significantly slower with transport dominated by diffusive processes. While the fractures account for most of the flow and transport they typically make up a small portion of the overall volume of the medium. One could argue that to simulate fracture systems and incorporate this disparate scale, most fracture models has in one way or other multiscale aspects. Specific approaches to simulate fractures are reviewed in detail in a chapter of this volume (Deng and Spycher 2019, this volume). Here we describe the work of Molins et al. (2019) to develop a hybrid multiscale of fractured media as an example of the two separate scales. In this hybrid model, a pore-scale component captures Navier–Stokes flow, multi-component transport and aqueous equilibrium in the fracture, while a Darcy-scale component captures multi-component diffusive transport, aqueous equilibrium and mineral reactions in the porous matrix (Fig. 14). The interface between the sub-models, the fracture surface, is represented by an embedded-boundary. To simplify exchange of concentrations and fluxes at this interface, adaptive mesh refinement is used such that resolutions of the sub-models match at the interface while still using coarser resolution away from the interface when not needed in the Darcy-scale domain. The multiscale model is capable to capture flow channelization observed in an experimental fractured core and, at the same time, limitations in the dissolution of calcite by diffusive transport through an altered porous layer.

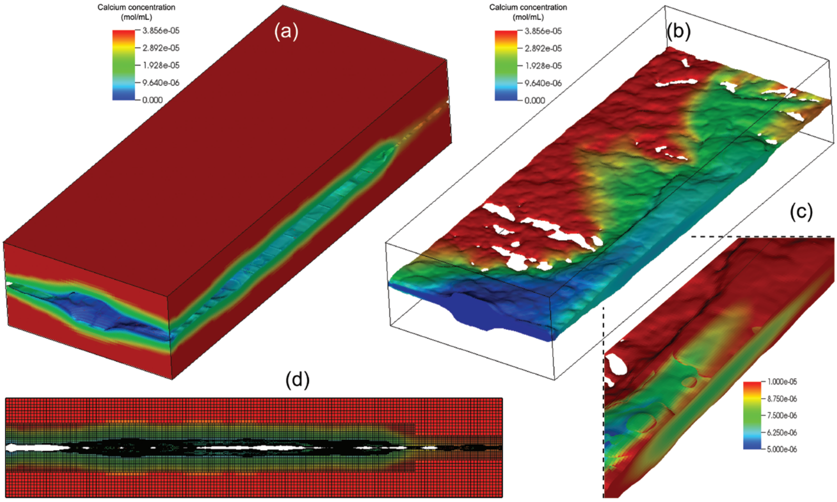

Figure 14. Steady-state calcium concentrations in the 3D simulations of the Duperow fracture experiment **(a)** in the Darcy-scale domain and **(b)** the pore-scale domain. **(c)** A close-up view of the pore-scale domain shows concentration gradients within the fracture opening, and **(d)** a side view of the Darcy-scale domains shows the embedded boundary and the mesh refinement around the fracture surface, where it interfaces with the pore-scale domain and steep concentration gradients develop. [Reprinted from Molins S, Trebotich D, Arora B, Steefel CI, Deng H (2019) Multi-scale model of reactive transport in fractured media: Diffusion limitations on rates, Transport in Porous Media 128:701–721, Figure 7, with permission.]

Surface–subsurface hydrologic coupling

Reactive transport of geochemical species in streams is result from an interplay between biogeochemical processes and mass exchange between the stream and the subsurface. The saturated sediment adjacent to the stream is therefore an important region for understanding the composition and evolution of water in the stream. For its role, the hyporheic zone has been the focus of study to understand flow and solute transport. Increasingly, there is interest to simulate reactive transport in the context of integrated surface–subsurface processes where both compartments are considered.

Although we have motivated the need for multiscale approaches in porous media from the pore- to Darcy-scale models in porous media, coupling of surface and subsurface processes requires the solution of similar equations in a coupled manner. The understanding of multiscale approaches in this sense is related to that of multi-physics, where the processes of interest are described by different equations. These processes may be characterized by different time scales, e.g., fast overland flow compared to long residence times for subsurface flow. Conceptually, these systems are similar to some of the subsurface systems considered in this chapter such as fractured media with fast flow in fractures compared to long residence times in the rock matrix. As a result, the approaches to coupling processes between the different compartments fall within those described in this review, including multi-rate approaches and hybrid approaches that require enforcement of continuity of mass and fluxes across interfaces. Examples of each of them are presented in what follows.

Painter (2018) use the residence time concept to develop a multiscale model for hyporheic exchange considering biogeochemical reactions. In this approach, the channel is a one-dimensional domain in which each cell of the discretization is connected to one dimensional sub-grid model for reactive transport (Fig. 15a), which are convolution representations of the exchange of solute with the hyporheic. This approach is mathematically equivalent to multi-rate mass transfer formulations such as Equations (33–34). In Painter (2018), the sub-grid model is generalized to include multicomponent reactive transport with general nonlinear reactions. Hyporheic zone denitrification is simulated with these non-linear models to demonstrate the approach (Fig. 15b).

Hybrid approaches are also being brought to bear on the surface–subsurface hydrologic exchange. Bao et al. (2018) developed a one-way coupled surface and subsurface water flow model to simulate a 7-km long reach along the Columbia River (Fig. 16). While the subsurface model is a Darcy-scale model, the surface component is solved with computational fluid dynamics software that solves a form of the Navier–Stokes equations with a free surface boundary. The model was employed to investigate surface water fluid dynamics and the impact of subsurface structures on the hydrologic exchange.

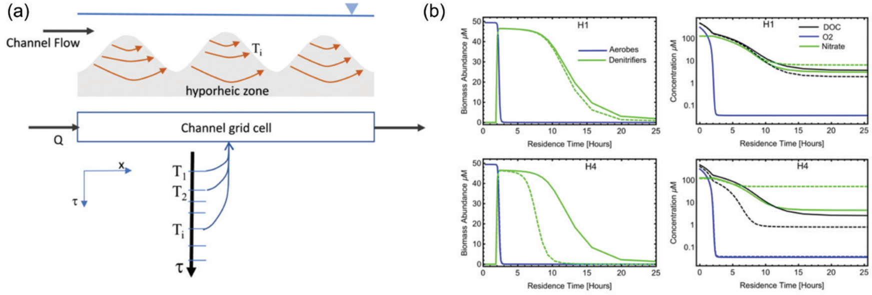

Figure 15. (a) Schematic of a multiscale representation of transport in a stream corridor. Hyporheic zone transport is represented by subgrid models in residence time formulation, which are coupled to the stream channel. The subgrid auxiliary equation associated with each channel grid cell is representative of the ensemble of pathways within the grid cell **(b)** Solutions of the subgrid reactive transport equations for biomass abundance (left column) and solute concentration (right column) versus residence time τ in the hyporheic zone at two channel locations and in steady state. Dissolved organic carbon (DOC) is consumed in the oxic zone at the downstream location leaving little DOC to fuel the denitrification reactions. [Reprinted from Painter SL (2018) Multiscale framework for modeling multicomponent reactive transport in stream corridors. Water Resources Research 54(10):7216–7230, Figures 1, 5, with permission.]

SUMMARY AND CONCLUSIONS

The issue of scale is central in reactive transport modeling and the different disciplines it draws from. It is often implicitly behind common assumptions used in most models, for example to couple different processes at the appropriate scale. The term *multiscale* is often used to specifically refer to applications that explicitly consider the different scales present in a given application. Here we have motivated the use of multiscale approaches by the need to scale-up processes that take place at the pore scale, where the medium is treated as composed of separate fluid and solid phases, to the Darcy-scale continuum, where the porous medium is characterized as a continuum. As shown, formally upscaling reactive transport only results in separate macro- and micro- problems under a limiting set of conditions. In general, however the macro and micro problem are coupled.

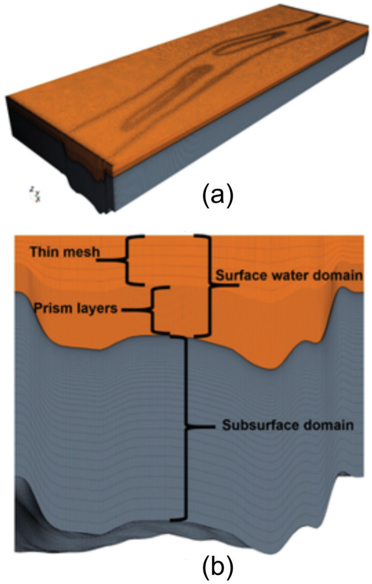

Figure 16. Meshes for the simulation domain of hydrologic exchange with a hybrid model. **(a)** Perspective view of the meshes. **(b)** Side view of the meshes for clarifying the mesh regions. [Reprint from Bao J, Zhou T, Huang M, Hou Z, Perkins W, Harding S, et al. (2018) Modulating factors of hydrologic exchanges in a large-scale river reach: Insights from three-dimensional computational fluid dynamics simulations. Hydrological Processes 32(23):3446–3463, Figure 2, with permission.]

Although insightful, mathematical methods for upscaling reactive transport rely on idealized representation of porous media and rarely used to investigate experimental or field systems. Simulation of these systems usually requires bringing to bear methods that use different scale descriptions within the same model such that micro-scale descriptions are used where it is needed; for example, to represent processes without making assumption of constitutive models for bulk parameters. Two approaches are prominent to simulate reactive transport in domains consisting of pore-scale and Darcy-scale sub-domains, one that uses a single equation to describe processes at both scales, and one that solves the problem in each domain separately and applies appropriate coupling conditions at the interface. These methods have also been used to find a compromise between the process and domain resolution and the size of domain that can be addressed with limited computational resources.

Multi-rate and multi-continua constitute another class of multiscale models that conceptualize the Darcy-scale porous medium as composed of two or more sub-regions that exists at each point in space and exchange mass according to a single-rate, multi-rate or continuum of rates. Mass exchanges between sub-regions or continua can represent micro-environments in which geochemical conditions may be different. Often these differences imply that a certain correlation exists between their hydrological accessibility and their mineralogical composition and reactivity.

Applications of these approaches in porous and fractured media show that often more than one approach can be used for a specific application. As application of reactive transport expands to consider surface processes, in addition to subsurface processes, available approaches are adapted and brought to bear on the surface–subsurface coupling. Generally multiscale approaches seek to represent processes at the appropriate scale, but different reasons are identified for this need. In some cases, the heterogeneous structure and composition of the porous medium necessitates micro-scale representation of the processes, while in other cases, the processes lead to the need for this micro-scale representation. For example, when solutions of different compositions mix, zones of active biogeochemical processes may require a micro-scale representation, especially when the media evolves as a result of it. While there is interest in capturing accurately these hot spots of biogeochemical activity, there is also interest in multiscale methods that can dynamically adjust process representation in time to capture periods of increased biogeochemical activity or hot moments.

ACKNOWLEDGMENTS

The contribution of Sergi Molins to this chapter was supported by the Interoperable Design of Extreme-scale Application Software Watersheds (IDEAS Watersheds) project funded by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research under Award Number DE-AC02-05CH11231.

REFERENCES

Amanbek Y, Singh G, Wheeler MF, van Duijn H (2019) Adaptive numerical homogenization for upscaling single phase flow and transport. J Comput Phys 387:117–133

Aradóttir ESP, Sigfússon B, Sonnenthal EL, Björnsson G, Jónsson H (2013) Dynamics of basaltic glass dissolution – Capturing microscopic effects in continuum scale models. Geochim Cosmochim Acta 121:311–327

Balhoff MT, Thomas SG, Wheeler MF (2008) Mortar coupling and upscaling of pore-scale models. Comput Geosci 12:15–27

Bao J, Zhou T, Huang M, Hou Z, Perkins W, Harding S, Titzler S, Hammond G, Ren H, Thorne P, Suffield S, Murray C, Zachara J (2018) Modulating factors of hydrologic exchanges in a large-scale river reach: Insights from three-dimensional computational fluid dynamics simulations. Hydrol Process 32:3446–3463

Battiato I, Tartakovsky DM (2011) Applicability regimes for macroscopic models of reactive transport in porous media. J Contam Hydrol 120–121:18–26

Battiato, Tartakovsky DM, Tartakovsky AM, Scheibe TD (2011) Hybrid models of reactive transport in porous and fractured media. Adv Water Resour 34:1140–1150

Bringedal C, von Wolff L, Pop IS (2019) Phase field modeling of precipitation and dissolution processes in porous media: Upscaling and numerical experiments. UHasselt Computational Mathematics Preprint Nr. UP-19-01.

Buckingham E (1904) Contributions to Our Knowledge of the Aeration of Soils. U.S. Government Printing Office

Daval D, Martinez I, Corvisier J, Findling N, Goffé B, Guyot F (2009) Carbonation of Ca-bearing silicates, the case of wollastonite: Experimental investigations and kinetic modeling. Chem Geol 265:63–78

Deng H, Spycher N (2019) Modeling reactive transport processes in fractures. Rev Mineral Geochem 85:49–74

Donado LD, Sanchez-Vila X, Dentz M, Carrera J, Bolster D (2009) Multicomponent reactive transport in multicontinuum media. Water Resour Res 45:W11402

Druhan JL, Tournassat C (2019) Reactive Transport in Natural and Engineered Systems. Rev Mineral Geochem Vol 85

Efendiev Y, Hou T (2009) Multiscale Finite Element Methods: Theory and Applications. Springer-Verlag, New York

Golfier F, Zarcone C, Bazin B, Lenormand R, Lasseux D, Quintard M (2002) On the ability of a Darcy-scale model to capture wormhole formation during the dissolution of a porous medium. J Fluid Mech 457:213–254

Gray WG, Miller CT (2014) Introduction to the Thermodynamically Constrained Averaging Theory for Porous Medium Systems. Springer International Publishing, Cham

Gulbransen AF, Hauge VL, Lie K-A, ICT S (2010) A multiscale mixed finite-element method for vuggy and naturally fractured reservoirs. SPE J 15:395–403

Haggerty R, Gorelick SM (1995) Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. Water Resour Res 31:2383–2400

Hollenbeck KJ, Harvey CF, Haggerty R, Werth CJ (1999) A method for estimating distributions of mass transfer rate coefficients with application to purging and batch experiments. J Contam Hydrol 37:367–388

Hornung U (ed) (1997) Homogenization and Porous Media. Springer-Verlag, New York

Landrot G, Ajo-Franklin JB, Yang L, Cabrini S, Steefel CI (2012) Measurement of accessible reactive surface area in a sandstone, with application to CO_2 mineralization. Chem Geol 318–319:113–125

Li L, Steefel CI, Yang L (2008) Scale dependence of mineral dissolution rates within single pores and fractures. Geochim Cosmochim Acta 72:360–377

Lichtner PC (1996) Continuum formulation of multicomponent-multiphase reactive transport. Rev Mineral Geochem 34:1–81

Liu Y, Liu C, Zhang C, Yang X, Zachara JM (2015) Pore and continuum scale study of the effect of subgrid transport heterogeneity on redox reaction rates. Geochim Cosmochim Acta 163:140–155

Marshall TJ (1959) The diffusion of gases through porous media. J Soil Sci 10:79–82

Mehmani Y, Sun T, Balhoff MT, Eichhubl P, Bryant S (2012) Multiblock pore-scale modeling and upscaling of reactive transport: application to carbon sequestration. Transp Porous Media 95:305–326

Mikelić A, Devigne V, van Duijn C (2006) Rigorous upscaling of the reactive flow through a pore, under dominant peclet and damkohler numbers. SIAM J Math Anal 38:1262–1287

Molins S, Trebotich D, Steefel CI, Shen C (2012) An investigation of the effect of pore scale flow on average geochemical reaction rates using direct numerical simulation. Water Resour Res 48:W03527

Molins S, Trebotich D, Arora B, Steefel CI, Deng H (2019) Multiscale model of reactive transport in fractured media: Diffusion limitations on rates, Transp Porous Media 128:701–721

Navarre-Sitchler A, Steefel CI, Yang L, Tomutsa L, Brantley SL (2009) Evolution of porosity and diffusivity associated with chemical weathering of a basalt clast. J Geophys Res 114:F02016

Painter SL (2018) Multiscale framework for modeling multicomponent reactive transport in stream corridors. Water Resour Res 54:7216–7230

Popov P, Efendiev Y, Qin G (2009) Multiscale modeling and simulations of flows in naturally fractured karst reservoirs. Commun Comput Phys 162–184

Ray N, Elbinger T, Knabner P (2015) Upscaling the flow and transport in an evolving porous medium with general interaction potentials. SIAM J Appl Math 75:2170–2192

Ray N, Rupp A, Schulz R, Knabner P (2018) Old and new approaches predicting the diffusion in porous media. Transp Porous Media 124:803–824

Roubinet D, Tartakovsky DM (2013) Hybrid modeling of heterogeneous geochemical reactions in fractured porous media. Water Resour Res 49:7945–7956

Scheibe TD, Murphy EM, Chen X, Rice AK, Carroll KC, Palmer BJ, Tartakovsky AM, Battiato I, Wood BD (2015a) An analysis platform for multiscale hydrogeologic modeling with emphasis on hybrid multiscale methods. Groundwater 53:38–56

Scheibe TD, Schuchardt K, Agarwal K, Chase J, Yang X, Palmer BJ, Tartakovsky AM, Elsethagen T, Redden G (2015b) Hybrid multiscale simulation of a mixing-controlled reaction. Adv Water Resour 83:228–239

Seigneur N, Mayer KU, Steefel CI (2019) Reactive transport in evolving porous media. Rev Mineral Geochem 85:197–238

Soulaine C, Tchelepi HA (2016) Micro-continuum approach for pore-scale simulation of subsurface processes. Transp Porous Media 113:431–456

Soulaine C, Roman S, Kovscek A, Tchelepi HA (2017) Mineral dissolution and wormholing from a pore-scale perspective. J FLUID Mech 827:457–483

Tomin P, Lunati I (2013) Hybrid Multiscale Finite Volume method for two-phase flow in porous media. J Comput Phys 250:293–307

Tomin P, Lunati I (2016) Spatiotemporal adaptive multiphysics simulations of drainage-imbibition cycles. Comput Geosci 20:541–554

Wood BD, Radakovich K, Golfier F (2007) Effective reaction at a fluid–solid interface: Applications to biotransformation in porous media. Adv Water Resour 30:1630–1647

Wunderly MD, Blowes DW, Frind EO, Ptacek CJ (1996) Sulfide mineral oxidation and subsequent reactive transport of oxidation products in mine tailings impoundments: A numerical model. Water Resour Res 32:3173–3187

Yan Z, Liu C, Liu Y, Bailey VL (2017) Multiscale investigation on biofilm distribution and its impact on macroscopic biogeochemical reaction rates. Water Resour Res 53:8698–8714

Yang X, Liu C, Shang J, Fang Y, Bailey VL (2014) A unified multiscale model for pore-scaleflow simulations in soils. Soil Sci Soc Am J 78:108

Yousefzadeh M, Battiato I (2017) Physics-based hybrid method for multiscale transport in porous media. J Comput Phys 344:320–338