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Review article

Mixing, spreading and reaction in heterogeneous media: A brief review

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ABSTRACT

Geological media exhibit heterogeneities in their hydraulic and chemical properties, which can lead to enhanced spreading and mixing of the transported species and induce an effective reaction behavior that is different from the one for a homogeneous medium. Chemical heterogeneities such as spatially varying adsorption properties and specific reactive surface areas can act directly on the chemical reaction dynamics and lead to different effective reaction laws. Physical heterogeneities affect mixing-limited chemical reactions in an indirect way by their impact on spreading and mixing of dissolved species. To understand and model large-scale reactive transport the interactions of these coupled processes need to be understood and quantified. This paper provides a brief review on approaches of non-reactive and reactive transport modeling in geological media.

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1. Introduction

Observed chemical transport in heterogeneous media does not behave according to the transport laws established for homogeneous environments (Neuman and Zhang, 1990; Adams and Gelhar, 1992; Berkowitz and Scher, 1997; Steefel et al., 2005; Meile and Tuncay, 2006; Li et al., 2008). Geological media are in general heterogeneous, that is, the chemical and physical medium properties vary in space and in time. This variability leads to effective reaction and transport behaviors that are different from their microscale counterparts. In principle, full resolution of the spatial medium heterogeneity down to the pore scale would allow for a description of such transport features. However, numerical or analytical flow and reactive transport models in general cannot resolve all variation scales of the spatial medium fluctuations. This is mainly due to limitations in computer power and characterization techniques.

Thus, upscaling or coarse graining of the salient reaction and transport features to a practically relevant support scale is needed. Furthermore, apart from the question of computational efficiency, the upscaling exercise is a necessary step to understand phenomena observed on a large scale. The large-scale processes are collective phenomena which result from the interaction of heterogeneity with local-scale flow and transport processes. This coupling leads to enhanced mixing of transported chemical species in particular and in general to effective reaction and transport dynamics.

Effective conservative transport has been quantified in terms of upscaled equations for the average chemical concentration. Upscaling implies the reduction of degrees of freedom of the original problem, which typically involves averaging. Possible averages can be (suitably chosen) ensemble averages in a stochastic modeling framework or volume averages.

In general, upscaled equations are characterized by temporal and spatial non-locality, so called non-Markovian behavior (e.g., Kubo et al., 1991). The latter implies that the system state depends on the transport history. Geochemical reactions in heterogeneous media are traditionally upscaled in terms of effective reaction parameters that are obtained under well-mixed conditions. Under natural conditions, however, such well-mixed conditions are not always given, in fact, the mixing in natural systems depends strongly on the transport characteristics and the multiscale medium heterogeneity.

The combined upscaling of these processes is a highly non-trivial task due to the non-linear coupling between reaction and transport.

The objectives of this paper are to give a brief overview of approaches to model reactive transport from the pore to the field scale, discuss their validity and limitations and review the state of the art of combined reaction and transport upscaling in heterogeneous media. This paper tries to synthesize some of the work and approaches that have been dedicated to conservative and reactive transport upscaling and the quantification of mixing in heterogeneous media. Specifically, it aims at highlighting the coupling between geochemical reaction and solute mixing and spreading in heterogeneous media.

This brief review does not intend to exhaustively review all the work in the fields of reaction and transport modeling.

2. Reactive transport from pore to field scale

The following section introduces and discusses some approaches and their underlying assumptions to model transport and reaction in heterogeneous media. We discuss the interaction of transport, reaction and physico-chemical heterogeneity for homogeneous (fluid–fluid) and heterogeneous (fluid–solid) reactions. This leads to the question of how to quantify mixing, dispersion and effective transport and reaction laws, which will be discussed in Section 3.

2.1. Pore scale

Multispecies chemical reactions between aqueous species (homogeneous reactions) and between aqueous species and the solid phase (heterogeneous reactions) are pore-scale phenomena.

Here we review briefly a simplified pore-scale reactive transport formulation which allows discussing some of the features that are important when going from the pore to the continuum or Darcy scale.

In the following the pore space is denoted by Ω_f, the solid space by Ω_s. For simplicity, the solid grains here are assumed to be impermeable. Flow in the pore space is governed by the Navier–Stokes equation. We assume that the fluid density is constant, that is, the system is assumed to be isothermal and the concentrations of the dissolved species are small enough not to affect the fluid properties. For low enough Reynolds numbers (less than unity) inertia effects can be disregarded and so the flow equation simplifies to the Stokes equation

$$\mu\nabla^2\mathbf{v}(\mathbf{x}) = \nabla p(\mathbf{x}) - \rho_f\mathbf{g}, \tag{1}$$

where $\mathbf{v}(\mathbf{x})$ is the pore velocity, μ is the fluid viscosity and $p(\mathbf{x})$ the fluid pressure, ρ_f is the fluid density and $\mathbf{g}$ is gravity acceleration. Since we assume that the fluid density is constant in time and space, fluid mass conservation implies $\nabla\cdot\mathbf{v}(\mathbf{x}) = 0$. For the solution of the flow problem, one typically specifies no-slip conditions on the (impermeable) solid grains

$$\mathbf{v}(\mathbf{x})|_{\mathbf{x}\in\partial\Omega_s} = 0. \tag{2}$$

We consider a multicomponent reactive system representing both homogeneous reactions between aqueous species and heterogeneous reactions involving aqueous and solid species. The aqueous species concentrations $C_i(\mathbf{x}, t)$ obey the mass balance equation (e.g., Saaltink et al., 1998)

$$\frac{\partial C_i(\mathbf{x},t)}{\partial t} + \nabla\cdot[\mathbf{v}(\mathbf{x})C_i(\mathbf{x},t) - D\nabla C_i(\mathbf{x},t)] = \sum_j \nu_{ij} r_j[\{C_n(\mathbf{x},t)\}], \tag{3a}$$

where D is the molecular diffusion coefficient, which we assume here to be the same for all species. This assumption is valid for dilute solutions. The reaction rate for the jth homogeneous reaction is given by $r_j[\{C_n(\mathbf{x}, t)\}]$, ν_{ij} are the stoichiometric coefficients. The reaction rate depends in general on the concentrations of all the aqueous species as expressed by its argument. This formulation accounts for fast and slow chemical reactions in the fluid phase. Whether a chemical reaction is slow or fast can be determined by the Damköhler number. The latter compares a typical reaction time scale τ_j of the jth reaction with a typical mass transfer or transport time scale τ_t,

$$Da_j = \frac{\tau_t}{\tau_j}. \tag{3b}$$

Fast reactions imply $Da \gg 1$. The reaction time scale is inversely proportional to the kinetic rate constant of the specific reaction. For fast reversible reactions, indexed in the following by f, the reaction rates $r_f[\{C_n(\mathbf{x},\ t)\}]$ can be approximated by their limit for $Da_f \to \infty$

$$r_f^{e}(\mathbf{x},t) = \lim_{Da_f \to \infty} r_f[\{C_n(\mathbf{x},t)\}]. \tag{3c}$$

where $r_f^{e}(\mathbf{x},\ t)$ is the equilibrium reaction rate of the fth reaction. The right side of Eq. (3a) can then be written as (e.g., Saaltink et al., 1998)

$$\sum_j \nu_{ij} r_j[\{C_n(\mathbf{x},t)\}] = \sum_f \nu_{if} r_f^{e}(\mathbf{x},t) + \sum_s \nu_{is} r_s[\{C_n(\mathbf{x},t)\}]. \tag{3d}$$

where we indexed the slow reactions by s. Fast reactions can be characterized by the mass action law (e.g., Steefel and MacQuarrie, 1996; Saaltink et al., 1998)

$$\prod_i \left[\gamma_i c_i(\mathbf{x},t)\right]^{\nu_{fi}} = K_f, \tag{3e}$$

where K_f is the equilibrium constant of the fth equilibrium reaction, and the γ_i are the activity coefficients of the ith species. They depend in general on all species concentrations. Here we assume them to be constant. Fast equilibrium reactions are mixing-limited, that is these reactions can only occur when different waters mix. As such, these reactions depend on the (physical) mixing properties of solute in the flow through the heterogeneous pore space.

Reactions between the fluid and solid phases take place at the fluid–solid boundaries where minerals are present. We consider here precipitation–dissolution reactions and adsorption to the solid matrix. Thus, the boundary conditions at the fluid–solid interface can be written as (e.g., Lichtner and Kang, 2007; Whitaker, 1999)

$$-\mathbf{n}_{\mathrm{fs}}(\mathbf{x}) \cdot D\nabla C_i(\mathbf{x},t)\big|_{\mathbf{x}\in\partial\Omega_s} = -\sum_m \nu_{im}\alpha_{\mathrm{m}}(\mathbf{x}) j_m[\{C_n(\mathbf{x},t)\}]\big|_{\mathbf{x}\in\partial\Omega_s} + \alpha_{\mathrm{ad}}(\mathbf{x})\frac{\partial S_i(\mathbf{x},t)}{\partial t}\bigg|_{\mathbf{x}\in\partial\Omega_s}, \tag{3f}$$

where $\mathbf{n}_{\mathrm{fs}}(\mathbf{x})$ is the unit normal vector on $\partial\Omega_{\mathrm{s}}$ pointing from the fluid into the solid phase; $\alpha_{\mathrm{m}}(\mathbf{x})$ is the relative mineral surface area. The first term on the left side models precipitation–dissolution reactions. The second term accounts for adsorption of species i at the solid surface. The adsorbed concentration $S_i(\mathbf{x}, t)$ is referred to the grain surface area, the relative surface area where the species can adsorb is denoted by $\alpha_{\mathrm{ad}}(\mathbf{x})$. The relative mineral surface area is non-zero only at these locations on the solid–fluid interface where the mineral is present. The reaction flux of the mth mineral at its surface is denoted by $j_m[\{C_n(\mathbf{x},\ t)\}]$. It depends on the aqueous concentrations at the solid surface. A discussion of the boundary conditions at the fluid–solid interface can be found in e.g., Knabner et al., 1995; van Duijn and Pop, 2004.

Based on transition state theory (e.g., Hänggi et al., 1990; Lasaga, 1998) the reaction flux $j_m[\{C_n(\mathbf{x}, t)\}]$ is often modeled as (e.g., Lichtner and Kang, 2007)

$$j_m[\{C_n(\mathbf{x},t)\}]\big|_{\mathbf{x}\in\Omega_s} = k_m(1-\Omega_m), \tag{3g}$$

where k_m is the kinetic rate constant. The saturation state Ω_m is given by

$$\Omega_m = K_m^{-1}\prod_j \left[\gamma_j C_j(\mathbf{x},t)\right]^{\nu_{jm}}, \qquad \mathbf{x}\in\Omega_s, \tag{3h}$$

where K_m is the equilibrium constant of the mth mineral reaction, ν_{jm} are the stoichiometric coefficients and γ_j denotes the activity coefficient of the jth aqueous species, which relate the activities of the species to their molal concentration. Note that the activity of the mineral species is equal to one (e.g., (Appelo and Postma, 2006), p. 130). The saturation state of the mth mineral reaction is 1 at local equilibrium. Then Eq. (3h) expresses the mass action law for the mth mineral reaction at the solid surface.

With respect to sorption at the solid surface, we consider here only the simplest case of linear equilibrium sorption for which the sorbed concentration is proportional to the aqueous concentration

$$S_i = k_{\mathrm{ad}} C_i, \qquad \mathbf{x}\in\partial\Omega_s, \tag{4}$$

where k_{ad} is assumed to be constant.

Here we assume that the solid matrix is impermeable. Thus, the flux at the grain surfaces is zero except at the locations where reactions occur. Mass transfer between the pores and the grains due to diffusion can be incorporated in the pore-scale transport model (Eqs. (3a)–(3h)) in the following way. At the positions of the pore–grain interface where mass flux is taking place the solute flux and the species concentrations are continuous. The flux continuity is expressed in the solid grain boundary condition (3f) as an additional term. Continuity of concentration gives the boundary condition at the pore–grain interface for the equation describing transport within the grain (e.g., Lichtner and Kang, 2007).

In the following we will focus on the aqueous species. Approaches to model the change of the mineral volume fraction, for example, are discussed in e.g., Kang et al., 2006. Note that the fluid–solid interactions are directly dependent on the chemical heterogeneity in the pore space, that is, the mineral distribution on the fluid–solid interface as expressed by $\alpha_{\mathrm{m}}(\mathbf{x})$ and $\alpha_{\mathrm{ad}}(\mathbf{x})$, as well as the pore geometry.

There are a series of approaches to solve this reactive flow and transport problem including Lattice-Boltzmann (e.g., Kang et al., 2006; Acharya et al., 2007; Willingham et al., 2008), smoothed particle hydrodynamics (e.g., Tartakovsky et al., 2007; Tartakovsky et al., 2009a), computational fluid dynamics and pore network modeling (Meile and Tuncay, 2006; Li et al., 2006), see also the recent review by Meakin and Tartakovsky, 2009). Network models are computationally efficient, but are usually based on simplified models for the pore space. Lattice-Boltzmann models and smoothed particle hydrodynamics as well as computational fluid dynamics have a more solid physical basis, but are computationally very demanding. While pore-scale models have been used for modeling single and multiphase flow and transport phenomena, they have been used only recently for studying multispecies reactive transport (e.g., Steefel et al., 2005).

The reactive transport description (Eqs. (3a)–(3h)) is formulated within the Eulerian transport framework. Like conservative transport, reactive transport can be described within a Lagrangian framework (e.g., Gillespie, 1977; Stiles and Bartol, 2001; Delay et al., 2005).

The framework relies on the equivalence between the advection–diffusion equation and a formulation which is based on the concept that the solute plume can be decomposed into independent solute particles. In this approach the species concentration is defined as a superposition of the densities of the particles which constitute the plume

$$C_j(\mathbf{x},t) = \left\langle \delta\left[\mathbf{x}-\mathbf{x}_j(t)\right] \right\rangle. \tag{5}$$

The angular brackets denote the average over all particles, $\mathbf{x}_j(t)$ denotes the trajectory of a solute particle belonging to species $\mathcal{A}_j$. It is described by the following equation of motion

$$\frac{d\mathbf{x}_j(t)}{dt} = \mathbf{v}\left[\mathbf{x}_j(t)\right] + \sqrt{2D}\boldsymbol{\xi}(t), \tag{6}$$

where $\boldsymbol{\xi}(t)$ is a Gaussian white noise characterized by zero mean and the correlation $\langle \xi_i(t)\xi_j(t')\rangle = \delta_{ij}\delta(t-t')$. The reaction rates $r_i[\{c_n(\mathbf{x},t)\}]$ and the reactive flux $j_m[\{c_n(\mathbf{x},t)\}]$ at the solid–fluid boundary then have to be translated into probabilistic laws, which govern particle interactions and interactions between solute particles and the solid phase (e.g., Gillespie, 1977; Stiles and Bartol, 2001; Srinivasan et al., 2007). To illustrate this, let us consider the degradation of a single species $c(\mathbf{x},t)$ at the solid surface. The reaction flux $j_m[c(\mathbf{x},t)]$ in this case is given by

$$j_m[c(\mathbf{x},t)] = -\lambda c(\mathbf{x},t), \qquad \mathbf{x}\in\partial\Omega_s, \tag{7}$$

where λ is the degradation constant. Let us consider now the concentration in a thin layer of thickness δl at the solid–fluid boundary. The degradation law (7) implies that in a time step Δt

$$c(\mathbf{x},t+\Delta t)-c(\mathbf{x},t) = -\frac{\lambda\Delta t}{\delta l}c(\mathbf{x},t). \tag{8}$$

From this expression we can obtain the probability for a particle to react within the time interval Δt. It is given by

$$p_c = \frac{c(\mathbf{x},t)-c(\mathbf{x},t+\Delta t)}{c(\mathbf{x},t)} = \frac{\lambda\Delta t}{\delta l}. \tag{9}$$

Or in other words, if a particle hits the solid–fluid boundary, it survives with a probability $1-p_c$. The thickness δl of the layer is determined by the typical diffusion length within one time step, that is $\delta l = \sqrt{2D\Delta t}$. The degradation probability within a time step Δt close to the interface then becomes

$$p_c = \lambda\sqrt{\frac{\Delta t}{2D}}. \tag{10}$$

We presented here a simplified pore-scale reactive transport formulation. As pointed out in Steefel et al. (2005) many of the chemical, physical and biological processes occur at the pore scale. Thus, the proper understanding and modeling of these processes is important to understand reactive transport phenomena at the pore, but also at the continuum scale (Meile and Tuncay, 2006; Li et al., 2008; Battiato et al., 2009; Tartakovsky et al., 2008c). This is outlined in the following section.

2.2. Darcy scale

For practical applications of reactive transport modeling on the laboratory or field scale, the detailed characterization of the pore geometry and the solution of the pore-scale reactive flow and transport problems are not feasible. Thus, upscaled or coarse-grained flow and reactive transport equations are needed which depend only on a few effective flow, transport and reaction parameters. Mathematical upscaling methods include volume averaging (e.g., Whitaker, 1999) and homogenization theory (e.g., Hornung, 1997), moment methods (e.g., Brenner, 1980), numerical pore-scale models (e.g., Meile and Tuncay, 2006; Li et al., 2006; Meakin and Tartakovsky, 2009).

As pointed out above, fluid–fluid reactions are affected by pore-scale heterogeneity indirectly through the mixing properties of the species in the spatially fluctuating Stokes flow through the (complex) pore geometry. The impact of pore-scale heterogeneity on the effective mixing properties of a solute is classically quantified in terms of an effective hydrodynamic, or Taylor dispersion coefficient (e.g., Taylor, 1953; Aris, 1956; Brenner, 1980; Brenner and Adler, 1980; Koch and Brady, 1985).

Chemical heterogeneity such as a distributed relative mineral surface area as well as the complex pore geometry and the spatially varying Stokes flow act directly on heterogeneous reactions. These pore-scale fluctuations can be integrated into an effective reactive transport picture in terms of effective kinetic coefficients and effective specific reactive surfaces using, for example the volume-averaging approach (Edwards et al., 1993; Lichtner, 1993; Quintard and Whitaker, 1994; Kechagia et al., 2002; Lichtner and Tartakovsky, 2003; Lichtner and Kang, 2007), effective Langevin models (e.g., Tartakovsky et al., 2008b) and homogenization approaches (e.g., Hornung, 1997). Although the geometry of the pore space can be quite complex, in theoretical studies of pore-scale reactive transport, oftentimes a regular, periodic geometry is assumed (e.g., Edwards et al., 1993).

2.2.1. Continuum-scale flow and reactive transport

Upscaling the Stokes equation (Eq. (1)) as outlined in e.g., Whitaker (1986), Hornung (1997) gives the Darcy equation (e.g., Bear, 1972), which describes the specific discharge $\mathbf{q}(\mathbf{x}, t)$

$$\mathbf{q}(\mathbf{x},t) = -\frac{k(\mathbf{x})}{\nu\rho_f g}\nabla h(\mathbf{x},t), \tag{11}$$

where the permeability $k(\mathbf{x})$ reflects the medium geometry and composition. The hydraulic head is defined by $h(\mathbf{x}, t) = p(\mathbf{x}, t)/(\rho_f g) + z$. It is in general a function of space as the medium properties in geological media are spatially variable. Transient flow conditions (e.g., Bear, 1972) are common in subsurface systems and have some impact on solute spreading and mixing (e.g., Kinzelbach and Ackerer, 1986; Rehfeldt and Gelhar, 1992; Cirpka and Attinger, 2003; Dentz and Carrera, 2003) Mass conservation is expressed by

$$S_s\frac{\partial h(\mathbf{x},t)}{\partial t} + \nabla\cdot\mathbf{q}(\mathbf{x},t) = f(\mathbf{x},t), \tag{12}$$

where S_s is specific storage and $f(\mathbf{x}, t)$ represents the presence of sinks and sources.

Volume averaging of the pore-scale reactive transport problem (Eqs. (3a)–(3h)) gives the continuum-scale reactive transport equations (e.g., Quintard and Whitaker, 1994; Lichtner, 1996; Lichtner and Kang, 2007)

$$\begin{aligned}\phi(\mathbf{x})\frac{\partial c_i(\mathbf{x},t)}{\partial t} &+ [1-\phi(\mathbf{x})]\frac{\partial s_i(\mathbf{x},t)}{\partial t} \\ &+ \nabla\cdot[\mathbf{q}(\mathbf{x},t)c_i(\mathbf{x},t) - \mathbf{D}(\mathbf{x},t)\nabla c_i(\mathbf{x},t)] \\ &= \phi(\mathbf{x})\sum_i \nu_{ij}r_j[\{c_n(\mathbf{x},t)\}] + r_i^{(s)}[\mathbf{x},\{c_n(\mathbf{x},t)\}],\end{aligned} \tag{13a}$$

see also Appendix A for a brief derivation by volume averaging. The porosity $\phi(\mathbf{x})$ denotes the ratio between the fluid volume $\Delta V_f(\mathbf{x})$ and the total averaging volume ΔV at a coarse-grained position $\mathbf{x}$; $c_j(\mathbf{x}, t)$ is the bulk concentration of the jth aqueous species, and $\mathbf{D}(\mathbf{x}, t)$ is the bulk dispersion tensor, which integrates the impact of the heterogeneous pore structure and pore velocity on the dispersive solute flux. The bulk reaction rate for the fluid–solid reactions $r_i^{(s)}(\mathbf{x}, t)$ is given by

$$r_i^{(s)}[\mathbf{x},\{c_n(\mathbf{x},t)\}] = \sum_m \nu_{im}a_m(\mathbf{x})k_m(1-\Omega_m[\{c_n(\mathbf{x},t)\}]). \tag{13b}$$

The specific reactive surface area $a_m(\mathbf{x})$ is defined by

$$a_m(\mathbf{x}) = \frac{1}{\Delta V}\int_{\Delta A_s(\mathbf{x})} df\alpha_m(\mathbf{x}), \tag{13c}$$

where $\Delta A_s(\mathbf{x})$ is the interfacial surface area within the averaging volume ΔV. In this upscaled reactive transport framework, heterogeneous reactions are represented, like homogeneous reactions, by an average source/sink term in the transport equation. The adsorbed concentration $s_j(\mathbf{x}, t)$ is now referred to the bulk solid volume,

$$s_j(\mathbf{x},t) = \frac{1}{\Delta V_s(\mathbf{x})}\int_{\Delta A_s(\mathbf{x})} df\alpha_{ad}S_j. \tag{13d}$$

The linear relation (Eq. (4)) between the dissolved and sorbed species concentrations now reads as

$$s_j(\mathbf{x},t) = k_d(\mathbf{x})c_j(\mathbf{x},t), \qquad k_d(\mathbf{x}) = \frac{k_{ad}}{\Delta V_s(\mathbf{x})}\int_{\Delta A_s(\mathbf{x})} df\alpha_{ad}, \tag{13e}$$

where $\Delta V_s(\mathbf{x})$ denotes the solid portion of the averaging volume. The distribution coefficient $k_d(\mathbf{x})$ in general varies in space. We are considering here a very simplified sorption model.

Note that the local equilibrium conditions (Eq. (3e)) and the saturation state Ω_m (Eq. (3h)) in this continuum-scale reactive transport description are expressed in terms of the volume averaged species concentrations. This assumes complete mixing on the support scale and excludes mass transfer limitations, see the discussions in Steefel et al. (2005), Li et al. (2006), Lichtner and Kang (2007), and Battiato et al. (2009).

The solution of the system of coupled partial differential equations (Eqs. (13a)–(13e)) is complex because it is highly non-linear. Numerical and analytical solution methods are outlined in Steefel and MacQuarrie (1996), Saaltink et al. (1998), Molins et al. (2004), De Simoni et al. (2005), Kräutle and Knabner (2005), and De Simoni et al. (2007), for example. Reviews of currently available computer codes for the numerical solution of the multispecies reactive transport problem can be found in, e.g., van der Lee and de Windt (2001) and Saaltink et al. (2004).

As in the pore-scale transport problems (3a)–(3h), also the Darcy-scale transport problems (13a)–(13e) can be solved by representing the solute distribution as an average over independent solute particles

$$c_i(\mathbf{x},t) = \langle\delta[\mathbf{x}-\mathbf{x}_i(t)]\rangle. \tag{14}$$

The coarse-grained particle trajectory is given by the Langevin equation (e.g., Kinzelbach, 1987; LaBolle et al., 1996; Salamon et al., 2006b; Delay et al., 2005),

$$\frac{d\mathbf{x}_i(t)}{dt} = \frac{\mathbf{q}[\mathbf{x}_i(t),t]-\nabla\cdot\mathbf{D}[\mathbf{x}_i(t),t]}{\phi[\mathbf{x}_i(t)]} + \sqrt{\frac{2\mathbf{D}[\mathbf{x}_i(t),t]}{\phi[\mathbf{x}_i(t)]}}\cdot\boldsymbol{\xi}(t), \tag{15}$$

where $\boldsymbol{\xi}(t)$ now is a Gaussian white noise characterized by zero mean and correlation $\xi_i(t)\xi_j(t') = \delta(t-t')$. The effective reaction rate laws need to be translated into probabilistic laws for the particle interactions (Kinzelbach, 1987; Valocchi and Quinodoz, 1989; Michalak and Kitanidis, 2000; Stiles and Bartol, 2001; Salamon et al., 2006a; Benson and Meerschaert, 2008; Edery et al., 2009). Note that the support scale of this description is the same as the one for Eqs. (13a)–(13e). That is, the fact that here transport is represented in terms of solute particles does not imply that this description resolves spatial scales that are smaller than the support scale of the continuum description.

2.2.2. Discussion

The continuum-scale reactive transport description (Eqs. (13a)–(13e)) is based on the assumption that on the pore scale well-mixed conditions prevail, and that changes in the species concentrations due to chemical reactions occur on time scales much larger than the mixing time, or in other words, that diffusion is much faster than reaction. This condition can be quantified by the microscopic Damköhler number

$$Da^{mic} = \frac{\tau_{\mathrm{D}}^{mic}}{\tau_{\mathrm{r}}}, \tag{16}$$

which compares a typical reaction time scale τ_{r} with the diffusion scale over the pore space $\tau_{\mathrm{D}}^{\mathrm{mic}} = l_{\mathrm{p}}^2/D$ with l_{p} a typical pore dimension. In realistic reactive transport scenarios these conditions are not always fulfilled.

Kechagia et al. (2002) studied the upscaling of reaction rates for reaction transport processes with fast or finite kinetics. They conclude that in general a non-local description for the reaction rate is required and the traditional volume-averaging approach is not valid. It is emphasized that a coupling between the macro and microscale (spatial non-locality) needs to be accounted for.

The impact of incomplete small-scale mixing on homogeneous and heterogeneous reaction rates and the validity of the continuum description (Eqs. (13a)–(13e)) was studied by Meile and Tuncay (2006) using a numerical pore-scale model. They compare the large-scale reaction rates determined from the mean concentrations, with the average small-scale reaction rates and determine the correction terms by Taylor expanding the latter about the mean species concentrations. They found that the difference between large-scale reaction rates and the average over the pore-scale rates is larger for heterogeneous then for homogeneous reactions. Li et al. (2006) employed a similar methodology to investigate the impact of pore-scale mass transfer limitations on the upscaling of chemical reaction rates. Oftentimes, kinetic rate laws determined in the laboratory are measured in well-mixed environments, either batch or flow through reactors, and thus frequently ignore mass transfer limitations and possible localization of geochemical reactions (e.g., Steefel et al., 2005; Li et al., 2006), which can lead to differences between laboratory results and in-situ measurements. Recently, Li et al. (2008) presented a comprehensive experimental and numerical study on the scale dependence of mineral dissolution rates due to concentration gradients in single pores and fractures, again challenging the well-mixed condition that is necessary for the Darcy-scale reactive transport description (Eqs. (13a)–(13e)) to be valid. Battiato et al. (2009) studied the breakdown of continuum reactive transport modeling as given by Eqs. (13a)–(13e) for mixing controlled heterogeneous reactions. They probe the conditions for which the continuum description is valid and identify the relevant Damköhler numbers to characterize the reactive transport phenomena. Kechagia et al. (2002), Steefel et al. (2005) and Tartakovsky et al. (2008c) stress the necessity of hybrid approaches for the adequate modeling of reactive transport that do not rely on the assumption of complete mixing on the pore scale.

2.3. Field scale

The continuum-scale physical and chemical medium properties as quantified by the hydraulic conductivity, porosity and specific reactive surface in general vary on many scales. This spatial variability leads to large-scale flow and reactive transport behavior that is quantitatively different from its local-scale counterpart. Example manifestations of the latter are the increase of solute dispersion with increasing scale (e.g., Lallemand-Barres and Peaudecerf, 1978; Gelhar et al., 1992) as quantified by the macrodispersion coefficients (e.g., Gelhar and Axness, 1983; Dagan, 1984; Neuman et al., 1987), and the scale dependence of hydraulic conductivity (e.g., Sanchez-Vila et al., 2006). For the reaction rates measured on the large scale one often finds the opposite, namely effective rates that are smaller than the ones measured in the laboratory (e.g., Meile and Tuncay, 2006; Li et al., 2007; Lichtner and Kang, 2007). Furthermore, the feedback of physico-chemical heterogeneities and chemical reactions can lead to unexpected reactive transport behavior on the field scale (e.g., Englert et al., 2009; Li et al., 2010).

2.3.1. Upscaling

As outlined in the Introduction the detailed knowledge of the spatial variability of the physical and chemical medium properties and the (numerical) solution of the local-scale reactive flow and transport problems (11) and (13a)–(13e) in principle can quantify the observed flow and reactive transport behavior. However, the detailed characterization of the local-scale medium fluctuations is in many practical applications not possible and a numerical reactive transport simulator needs to operate on a coarse support scale due to limitations of computer power. Thus, coarse grained, averaged flow and reactive transport descriptions are required to quantify and explain observed large-scale phenomena and allow to make predictions.

Furthermore, the observed large-scale behavior is a collective phenomenon resulting from the interaction of medium heterogeneities and local-scale flow and transport processes. Upscaling is a way to understand and quantify such complexity and extract the relevant mechanisms. As for the transition from the pore to the continuum scale discussed in the previous section, coarse graining and upscaling implies averaging of the Darcy-scale flow and reactive transport equations (11) and (13a)–(13e). Upscaling approaches include stochastic averaging (e.g., Roberts, 1961; Kraichnan, 1970; Gelhar and Axness, 1983; Dagan, 1984; Neuman et al., 1987), volume averaging (e.g., Whitaker, 1999), homogenization theory (e.g., Auriault and Adler, 1995; Lunati et al., 2002) and renormalization techniques (e.g., Koch and Shaqfeh, 1992; Jaekel and Vereecken, 1997; Zhang, 1998).

2.3.1.1. Parameter upscaling. In the last three decades a significant effort was dedicated to the theoretical and experimental determination of effective transport and reaction parameters, which we call here parameter upscaling. The parameters typically investigated in the literature are macrodispersion coefficients (Gelhar and Axness, 1983; Dagan, 1988; Rajaram and Gelhar, 1993; Fiori, 1998; Attinger et al., 1999; Fiori and Dagan, 2002) as they allow for the quantification of the increase of the extent of a solute plume with time and travel distance. Furthermore, effective retardation coefficients (Chrysikopoulos et al., 1990; Bellin et al., 1993; Burr et al., 1994; Bellin and Rinaldo, 1995; Miralles-Wilhelm and Gelhar, 1996; Rajaram, 1997), and effective reactive surface areas and rate coefficients (e.g., Lichtner, 1993; Kechagia et al., 2002) integrate the impact of heterogeneity on effective reaction. It is consistently found that the macroscale effective transport and reaction parameters evolve with time until they eventually converge to a constant asymptotic value. This indicates that effective transport descriptions based on macroscale transport and reaction parameters are only of limited validity. Valocchi (1985) showed that the attainment of equilibrium conditions depends on the physical and chemical medium heterogeneity.

2.3.1.2. Process upscaling. In fact, averaging (stochastic or spatial averaging) of the local-scale transport equation (13a) reveals that the average concentrations are in general governed by non-Markovian dynamical equations (Roberts, 1961; Koch and Shaqfeh, 1992; Cushman and Ginn, 1993; Neuman, 1993; Whitaker, 1999; Morales-Casique et al., 2006). This non-Markovian property of average transport descriptions can be traced back to the loss of information due to the averaging process (Mori, 1958; Roberts, 1961; Zwanzig, 1961; Kubo et al., 1991).

In fact it has been shown (e.g., Espinoza and Valocchi, 1997; Dentz and Berkowitz, 2005; Dentz and Castro, 2009) that reactive transport under heterogeneous equilibrium adsorption properties on the large-scale results in a kinetic sorption process. Binning and Celia (2008) studied the pseudo reaction kinetics that arises from upscaling equilibrium reactions in heterogeneous media. Kechagia et al. (2002) and Tartakovsky et al. (2009b) studied the upscaling of sorption desorption reactions, to unravel under which conditions an effective reaction parameter is meaningful. Hu et al. (1997) studied non-local reactive transport in chemically, physically and biologically heterogeneous media.

2.3.2. Effective non-reactive transport models

It has been common practice in reactive transport modeling to combine a non-reactive transport model with a suitable reaction rate model to obtain a conservation equation for the concentrations of the reacting species (e.g., MacQuarrie and Sudicky, 1990; Kinzelbach et al., 1991; Ginn et al., 1995; Cirpka et al., 1999; Steefel et al., 2005). This principle is implemented in the pore-scale description (Eqs. (3a)–(3h)) and again in the continuum-scale description (Eqs. (13a)–(13e)). In the following we briefly review effective models for non reactive transport and discuss the issues arising when combining non-reactive transport and chemical reaction.

2.3.2.1. Macrodispersion approach. The macrodispersion approach (e.g., Gelhar and Axness, 1983) models effective transport by the same dynamical model as local-scale transport. The impact of spatial heterogeneities on large-scale transport is taken into account by a macrodispersion tensor. Similar to the hydrodynamic dispersion tensor, it quantifies the influence of local-scale fluctuations of the medium properties on large-scale solute spreading. The large-scale transport equation is given by

$$\overline{\phi}\frac{\partial \overline{c}(\mathbf{x},t)}{\partial t} + \overline{\mathbf{q}} \cdot \overline{c}(\mathbf{x},t) - \nabla \cdot \mathbf{D}^{\mathrm{m}} \nabla \overline{c}(\mathbf{x},t) = 0, \tag{17}$$

with $\overline{\phi}$ average porosity, $\overline{\mathbf{q}}$ the average Darcy velocity and $\mathbf{D}^{\mathrm{m}}$ the macrodispersion tensor.

Macroscale conservative transport descriptions in terms of the macroscale advection–dispersion equation (Eq. (17)) are in general not able to qualitatively and quantitatively describe so called anomalous or non-Fickian transport behavior, which is frequently observed, specifically at short transport distances. Such behavior is characterized by non-linear growth of the spatial variance of the solute distribution (non-Fickian dispersion) and early or late solute arrival times.

2.3.2.2. Non-local transport approaches. Due to these shortcomings alternative effective transport descriptions for the average solute distribution have been suggested. They are based on spatially and temporally non-local transport equations, which are characterized by memory functions that depend on the heterogeneity statistics. This means such transport models are generally non-Markovian, i.e., the system state at a given time depends not only on the system state at one previous time but on the full system history. Non-local models that have been used for the description of effective transport in heterogeneous media include the multirate mass transfer (MRMT) or multicontinuum approach (Haggerty and Gorelick, 1995; Harvey and Gorelick, 1995; Carrera et al., 1998; Haggerty et al., 2000), the continuous time random walk approach (e.g., Montroll and Weiss, 1965; Scher and Lax, 1973; Berkowitz and Scher, 1998; Metzler and Klafter, 2000; Cortis et al., 2004b; Dentz et al., 2004; Berkowitz et al., 2006), the moment equation approach (Neuman, 1993; Morales-Casique et al., 2006; Jarman and Tartakovsky, 2008; Neuman and Tartakovsky, 2008), projector formalism approaches (Zwanzig, 1961; Kubo et al., 1991; Cushman and Ginn, 1993; Cushman et al., 1994; Cushman et al., 2002), the fractional advection–dispersion equation approach (e.g., Meerschaert et al., 1999; Benson et al., 2000) as well as the stochastic-convective transport approach (Dagan and Bressler, 1979; Dagan and Cvetkovic, 1996; Cvetkovic and Dagan, 1996; Ginn et al., 1995; Cvetkovic et al., 1996; Cirpka and Kitanidis, 2000;Gin, 2001). In the following, we briefly summarize these approaches. More extensive reviews on these approaches can be found in Berkowitz et al. (2006) and Neuman and Tartakovsky (2008).

2.3.2.3. Multicontinuum approach. The MRMT approach is based on the observation that non-Fickian transport in heterogeneous medium can be caused by the contrast of fast transport in regions of high transport velocity and slow transport in regions characterized by small velocities. In the MRMT approach this phenomenon is modeled by dividing the medium into a mobile region, in which transport is due to advection and dispersion, and a set of immobile regions where transport can be due to diffusion and slow advection. The mobile and immobile regions are connected through linear mass transfer mechanisms, see below. The medium heterogeneity is mapped onto the distribution of typical mass transfer times (e.g., Cunningham et al., 1997; Gouze et al., 2008; Willmann et al., 2008).

2.3.2.4. Continuous time random walk (CTRW) approach. The CTRW approach generalizes the classical random walk (RW) approach, see Eqs. (6) and (15). The RW approach models solute transport in terms of random particle transitions in space during a constant time increment, that is, the particle trajectory is a stochastic process. The CTRW approach generalizes the RW approach in modeling slow and fast solute transport by a random time increment. That is, not only the spatial but also the time increment is modeled as a stochastic process. Heterogeneity is mapped on the joint distribution of transition length and times (e.g., Berkowitz and Scher, 1997; Cortis et al., 2004a; Dentz and Berkowitz, 2005; Dentz and Castro, 2009). The particle density (solute concentration) in this modeling framework satisfies a temporally non-local advection–dispersion equation (e.g., Berkowitz, 2002; Dentz et al., 2004). The MRMT and CTRW approaches are equivalent under some conditions (e.g., Dentz and Berkowitz, 2003).

2.3.2.5. Moment equations and projector formalism approach. The moment equation approach is based on the stochastic averaging of the Darcy-scale advection–dispersion equation (Eq. (13a)). This yields spatio-temporally non-local equations for the mean concentration, the concentration variance, and in principle also for the higher order ensemble moments of the state variables (e.g., Morales-Casique et al., 2006). These moment equations include memory functions, which in principle can be related to the statistics of the underlying heterogeneity. In general this is quite a complex task. A similar approach is the projector formalism approach (e.g., Cushman and Ginn, 1993; Cushman et al., 2002) which is based on the stochastic averaging of the concentration distribution given by (Eq. (14)) in terms of the particle trajectories given by Eq. (15). Like the moment equation approach, the projector formalism approach yields a spatio-temporally non-local transport equation for the mean concentration.

2.3.2.6. Fractional advection–dispersion equations. The fractional advection–dispersion equation approach (e.g., Benson et al., 2000; Cushman and Ginn, 2000) models the spatial and temporal memory kernels in a non-local advection–dispersion equation as power-law functions. It can be related to random walk models characterized by broad distributions of spatial and temporal random increments such as Levy flights and Levy walks (Meerschaert et al., 2001; Metzler and Klafter, 2000).

2.3.2.7. Stochastic-convective approach. The stochastic streamtube approach considers transport to take place in a set of individual streamtubes that is characterized statistically by an ensemble of streamtubes with (constant) effective velocities. Mixing occurs within the streamtubes while mass transfer between them is not taken into account. In this way, advective spreading can be separated from actual solute mixing. Thus, transport in a single streamtube is given by the one-dimensional advection–dispersion equation. The average concentration is then obtained by the sum of the partial concentrations weighted by the distribution of travel times in the individual streamtubes (Dagan and Bressler, 1979; Ginn et al., 1995; Cvetkovic et al., 1996; Cirpka and Kitanidis, 2000; Ginn, 2001).

2.3.3. Effective reactive transport models

The modeling of reactive transport requires the knowledge not only of the average concentrations but also of the multipoint moments of the species concentrations because the advection–dispersion reaction equation (Eq. (13a)) is in general non-linear in the concentrations (Lichtner and Tartakovsky, 2003; Cirpka et al., 2008b; Luo et al., 2008; Tartakovsky et al., 2009b). This is an important difference to non-reactive transport upscaling. The average species concentrations, which are typically described by the effective non-reactive transport models discussed above, cannot be used directly to model reactive transport. The simplest effective model, namely, the macrodispersion approach, for example, overpredicts solute mixing (Kitanidis, 1988; Molz and Widdowson, 1988; MacQuarrie and Sudicky, 1990; Kitanidis, 1994; Ginn et al., 1995) and thus is not suited to quantify reactive transport. The shortcomings of using average concentrations for reactive transport modeling were studied experimentally and theoretically in, e.g., Kapoor et al. (1997), Kapoor and Kitanidis (1998), Raje and Kapoor (2000), Gramling et al. (2002), Meile and Tuncay (2006), Cirpka et al. (2008a), and Luo et al. (2008).

Thus, so called ‘hybrid’ models are required that deliver the mean behavior of the species concentration on the one hand and information on the local concentrations on the other hand. Both the multicontinuum approach (e.g., Lichtner and Kang, 2007; Liu et al., 2008; Donado et al., 2009) and the stochastic-convective approach (e.g., Ginn, 2001) have these attributes and therefore are used for the modeling of multispecies reactive transport.

The multicontinuum approach relies on the identification of subdomains with similar properties and their modeling as secondary continua, which communicate with the primary connected flow domain by first-order and diffusive mass transfer. The set of secondary continua is characterized statistically by the distribution of its physical and chemical characteristics, as for example typical mass transfer times, porosity, reactive surface areas, sorption coefficients. Thus, the multicontinuum approach represents a hybrid model that models large-scale behavior and simultaneously allows for the quantification of the local-scale concentrations in the immobile domains and thus reflects the small-scale structure with (localized) chemical reactions. Reactive transport is solved for the mobile and each immobile subdomain separately. The average concentrations and reaction rates are determined in terms of the local species concentrations (e.g., Donado et al., 2009; Willmann et al., 2010). Thus, the impact of correlations of the local concentrations on reaction rates is taken into account.

The stochastic-convective approach is similar in that the average species concentrations are given explicitly by the weighted sum of the partial concentrations in individual streamtubes (Cirpka and Kitanidis, 2000; Ginn, 2001; Seeboonruang and Ginn, 2006a; Seeboonruang and Ginn, 2006b). Reactive transport is solved for each streamtube. Thus, local-scale concentration fluctuations can be quantified in the average reaction behavior. Due to the lack of mass exchange between streamtubes, mixing at large times may actually be underestimated because concentration gradients between streamtubes cannot be accommodated. This however, is a phenomenon that leads to actual heterogeneity-induced mixing (e.g., Kitanidis, 1994). In this sense, the stochastic-convective approach can be considered as a ‘minimal mixing’ model (Robinson and Viswanathan, 2003; Seeboonruang and Ginn, 2006a,b) as opposed to the macrodispersion approach as a ‘maximum mixing model’.

3. Quantification of spreading and mixing in the context of reactive transport

As outlined in the previous sections, the correct quantification of mixing and spreading of the reacting species plays an important role for the effective modeling of reactive transport in heterogeneous media. For transport in homogeneous media, mixing and spreading are the same and can both be characterized in terms of diffusion and dispersion coefficients. In heterogeneous media this is different. Medium heterogeneities and spatial fluctuations of the flow field lead to a distortion of the solute plume. At times that are smaller than the mass transfer time over a typical heterogeneity scale, these mechanisms increase the solute spread but not the mixing of the solute (e.g., Kitanidis, 1994). Thus, for heterogeneous media, the processes of spreading and mixing need to be separated. Nevertheless, both processes are coupled. The concentration contrasts that are generated by the spread of the solute enhance mass transfer due to diffusion and local dispersion and thus lead to enhanced mixing. In the following we will review measures for these processes in terms of dispersion coefficients and their quantification in the context of reactive transport.

3.1. Dispersion coefficients

The quantification of dispersion in fluctuating flow fields has been extensively studied in the past in a series of fields ranging from turbulent transport to solute dispersion in geological media (Taylor, 1953; Aris, 1956; Roberts, 1961; Kraichnan, 1970; Kraichnan, 1976; Brenner, 1980; Gelhar and Axness, 1983; Koch and Brady, 1987; Neuman et al., 1987; Dagan, 1988; Young and Jones, 1991).

Macroscopic dispersion coefficients can be defined by the method of moments (e.g., Aris, 1956) in terms of the rate of growth of the average width of the spatial solute distribution. Average here is understood to be a stochastic average. Nevertheless, it has been shown (e.g., Kitanidis, 1992; Wang and Kitanids, 1999) that volume averaging and stochastic averaging lead to the same results for the macrodispersion coefficients. The average width is quantified by the second centered moment of the average concentration

$$\kappa^{\mathrm{a}}_{ij}(t) = \left[\int d\mathbf{x} x_i x_j \bar{c}(\mathbf{x},t) - \int d\mathbf{x} x_i \bar{c}(\mathbf{x},t) \int d\mathbf{x} x_j \bar{c}(\mathbf{x},t)\right], \qquad (18)$$

and its temporal change is defined as the apparent dispersion coefficients

$$D^{\mathrm{a}}_{ij}(t) = \frac{1}{2}\frac{d\kappa^{\mathrm{a}}_{ij}(t)}{dt}. \qquad (19)$$

The macrodispersion coefficients in Eq. (17) are given by the long time limits $D^{\mathrm{m}}_{ij} = \lim_{t\to\infty} D^{a}_{ij}(t)$ if they exist. For transport in stratified media with infinite transverse extension, this is not the case (e.g., Matheron and de Marsily, 1980) for example.

3.1.1. From pore to continuum scale

Pore-scale heterogeneity and the resulting fluctuations of the Stokes velocity in the pore space lead to enhanced spreading and mixing. The latter has been quantified in terms of hydrodynamics dispersion coefficients (Brenner, 1980; Brenner and Adler, 1980; Plumb and Whitaker, 1988; Mauri, 1990; Auriault and Adler, 1995; Luo et al., 2008; Bolster et al., 2009). Here we will focus on the behavior of the longitudinal asymptotic dispersion coefficient $D^{\mathrm{m}}_{\mathrm{L}}$ as a function of Peclet number (e.g., Pfannkuch, 1963; Sahimi, 1995).

Recent results obtained by pore-scale modeling (Bijeljic et al., 2004) have confirmed the existence of four dispersion regimes in laminar flow that are dependent on Peclet number. The Peclet number compares diffusive to advective mass transport and here is defined by $Pe = \overline{u}l/D$, where $\overline{u}$ is a typical flow velocity, l a characteristic length scale and D a dispersion coefficient.

The longitudinal dispersion coefficient, $D^{\mathrm{m}}_{\mathrm{L}}$, is lower than the molecular diffusion coefficient D for $Pe \leq 1$ due to restricted diffusion imposed by the solid phase. With both diffusion and advection present ($Pe > 1$), there is a transition region to a power-law regime where $D^{\mathrm{m}}_{\mathrm{L}} \propto Pe^{\delta}$ with $\delta \approx 1.2$, which is found in experiments in beadpacks, sandpacks and homogeneous sandstones. For $Pe > 400$ there is a cross-over to a purely advective, mechanical dispersion regime with $D^{\mathrm{m}}_{\mathrm{L}} \propto Pe$.

By combining CTRW theory, pore-scale modeling and experiment, the exponent $\delta = 1.2$ for intermediate Pe and the transition to a linear regime at higher Pe has been explained in (Bijeljic and Blunt, 2006). The heterogeneity of the pore space causes a variation in typical flow speeds, leading, when advection dominates at the pore scale, that is, $Pe \gg 1$, to an approximately power-law distribution of pore-to-pore travel times with an exponent β that is directly related to the structural heterogeneity of the medium. The two exponents $\delta = 1.2$ (obtained independently from experiment and pore-scale modeling) and β (obtained independently from CTRW and pore-scale modeling) have been shown to be related in both asymptotic and pre-asymptotic regime.

Solute must be transported throughout the porous medium for a time or length sufficiently large to allow for a full sampling of the flow field heterogeneity before the dispersion coefficient can reach an asymptotic value and the spreading becomes purely Gaussian. If these conditions are not satisfied, solute undergoes spreading in a pre-asymptotic regime for which the dispersion coefficient increases with time and the average distance traveled (Han et al., 1985; Koch and Brady, 1987; Dagan, 1988; Salles et al., 1993; Gelhar et al., 1992; Berkowitz et al., 2000) and the apparent dispersion coefficient can vary spatially and temporally. This is particularly important in large-scale geological porous media where large structural and flow heterogeneities may result in the asymptotic behavior being reached only after very long travel distances or never being reached.

3.1.2. From Darcy to field scale

As pointed out in Section 2.3 Darcy-scale spatial variability leads to enhanced spreading and mixing of a transported solute, which can be measured in terms of macroscopic dispersion coefficients. Using stochastic modeling, Gelhar and Axness (1983) obtained for the longitudinal dispersion coefficient

$$D^{\mathrm{m}}_{\mathrm{L}} = \sigma^2_{\mathrm{f}}\overline{u}l, \qquad (20)$$

where σ_f^2 is the variance of the log-permeability field and l its correlation length. This result was obtained using a second order perturbation expansion in the fluctuations of the flow velocity in a log-conductivity field, which is characterized by an exponential variogram. In this approximation, the transverse dispersion coefficient turns out to be of the order of the diffusion coefficient.

The apparent dispersion coefficients (Eq. (19)) evolve in time on a scale that is given by the typical advection time over a fluctuation scale of the spatially varying flow field, $\tau_u = l/\overline{u}$ (Dagan, 1988). As pointed out above, they measure the increase of the extension of the mean concentration distribution and not the increase of the mean extension of the plume. The mean, or effective plume width is quantified by the average over the width of the local-scale plume

$$\kappa_{ij}^{e}(t) = \left[\int d\mathbf{x} x_i x_j \overline{c}(\mathbf{x},t) - \int d\mathbf{x} \int d\mathbf{x}' x_i x_j' \overline{c(\mathbf{x},t)c(\mathbf{x}',t)}\right]. \tag{21}$$

The effective dispersion coefficients then are defined as half the temporal rate of change of the effective width

$$D_{ij}^{e}(t) = \frac{1}{2}\frac{d\kappa^{e}(t)}{dt}. \tag{22}$$

The difference between the apparent and effective dispersion coefficients as first pointed out by Batchelor (1949, 1952) in the context of turbulent diffusion, measure the average square fluctuations of the center of mass of the solute plume,

$$D_{ij}^{a}(t) - D_{ij}^{e}(t) = \frac{1}{2}\frac{d}{dt}\int d\mathbf{x}\int d\mathbf{x}' x_i x_j' \left[\overline{c(\mathbf{x},t)c(\mathbf{x}',t)} - \overline{c(\mathbf{x},t)}\;\overline{c(\mathbf{x}',t)}\right]. \tag{23}$$

A quantitative analysis of the difference between the apparent and effective dispersion coefficient in a stochastic context can be found in (e.g., Attinger et al., 1999; Dentz et al., 2000; Cirpka and Attinger, 2003; Dentz and Carrera, 2003). In the context of volume averaging this was studied in (e.g., Dentz and Carrera, 2007; Zavala-Sanchez et al., 2009).

As pointed out above, the apparent dispersion evolves on the advection time scale τ_u. This expresses the fact that the evolution of the apparent dispersion coefficient is determined by purely advective fluctuations. Actual solute mixing, however, is produced by the interaction of advectively created concentration contrasts and mass transfer due to diffusion. The evolution of the effective dispersion coefficient (Eq. (22)) reflects these mechanisms and evolves on the diffusion time scale $\tau_D = l^2/D$, that is the typical time that is needed by a solute to diffuse over typical heterogeneity scale, that is the time needed to smooth out a heterogeneity-induced concentration contrast. Dentz et al. (2000) derived an approximate expression for the effective dispersion coefficient for a point-like initial condition in an infinite aquifer. For an exponentially correlated log-conductivity field it reads as

$$D_L^{e} = \sigma_f^2 \overline{u} l \left[1 - \frac{1}{(1 + 2t/\tau_D)^{-(d-1)/2}}\right], \tag{24}$$

which is valid for large *Pe* and times larger than the advection time scale τ_u; d is the spatial dimension.

It has been found that macroscale models of reactive transport that use the macrodispersion coefficients to quantify solute mixing significantly overestimate reaction rates observed in the field (Kitanidis, 1988; Molz and Widdowson, 1988; MacQuarrie and Sudicky, 1990; Kitanidis, 1994; Ginn et al., 1995; Kapoor et al., 1997; Raje and Kapoor, 2000; Gramling et al., 2002). In fact, as outlined above the asymptotic macrodispersion coefficient overestimates solute dispersion at intermediate times. The effective coefficient is a better measure for solute dispersion. This insight was used by Cirpka (2002) and Janssen et al. (2006), who employed effective dispersion coefficients for reactive transport modeling on smoothed hydraulic conductivity fields.

3.2. Mixing and reactive transport

The difference between mixing and spreading is particularly important in the context of effective reactive transport (De Simoni et al., 2005; De Simoni et al., 2007; Sanchez-Vila et al., 2007; Cirpka et al., 2008b; Fernandez-Garcia et al., 2008; Luo et al., 2008; Tartakovsky et al., 2008a), as mixing controls the probability of reactants to meet in a moving fluid.

To illustrate this, we consider the following bimolecular heterogeneous reaction

$$\mathcal{A}_1 + \mathcal{A}_2 \rightleftharpoons \mathcal{M} \tag{25}$$

in the continuum description discussed in Section 2.2. Here, transport is described by Eqs. (13a)–(13e) for the two aqueous species ($j = 1, 2$)

$$\phi \frac{\partial c_j(\mathbf{x},t)}{\partial t} + \nabla \cdot [\mathbf{q}(\mathbf{x}) - \mathbf{D}\nabla] c_j(\mathbf{x},t) = r(\mathbf{x},t), \tag{26}$$

and reaction rate $r(\mathbf{x}, t)$ is given by

$$r(\mathbf{x},t) = k_r[1 - \Omega], \qquad \Omega = \frac{c_1(\mathbf{x},t)c_2(\mathbf{x},t)}{K}, \tag{27}$$

where k_r is the kinetic rate constant. The reaction time scale here is defined by $\tau_r = \sqrt{K}/k_r$.

For this continuum description to hold, the two waters must mix very fast in the support volume compared to the τ_r. This requires that the microscopic Damköhler number $Da_{mic} = \tau_D^{mic}/\tau_r \ll 1$ with $\tau_D^{mic} = l_p^2/D_{mic}$. This means that the reaction is very slow compared to the microscopic transport scale. On the continuum scale, we assume that the typical time τ_t for concentration changes due to bulk transport is large compared to the reaction time. This requires that the bulk Damköhler number $Da = \tau_t/\tau_r \gg 1$. For large *Da*, the system is close to equilibrium, which is expressed by $\Omega = 1$, that is, the mass action law for the bulk species concentrations $c_1(\mathbf{x}, t)c_2(\mathbf{x}, t) = K$. In this limit, the reaction (Eq. (25)) is purely mixing controlled.

Note that the local equilibrium condition does not imply that $r(\mathbf{x}, t)$ is zero. In dimensionless terms the reaction rate is given by

$$\hat{r}(\mathbf{x}, t) = Da\left[1 - \hat{\Omega}\right], \tag{28}$$

where $\hat{r}(\mathbf{x}, t)$ and $\hat{\Omega}$ are the dimensionless reaction rate and saturation. The equilibrium limit implies that $Da \to \infty$. In this limit, the term $[1-\Omega]$ tends to zero, but at the same time Da goes to infinity. Thus, the limit $Da \to \infty$ has to be taken carefully for $r(\mathbf{x}, t)$, see below. The physical explanation for the finiteness of the reaction rate is that as soon as two waters in different equilibria mix, the resulting water does not satisfy the chemical equilibrium condition and a fast (compared to the bulk transport scale) reaction will take place that brings the system back to chemical equilibrium. These mechanisms are illustrated in Fig. 1.

In the limit of large Da, it can be shown (Sanchez-Vila et al., 2007) that the reaction rate (27) converges to (De Simoni et al., 2005)

$$r^{\mathrm{eq}}(\mathbf{x}, t) = \lim_{Da \to \infty} r(\mathbf{x}, t) = -\left.\frac{dc_2^2(c)}{dc^2}\right|_{c = c(\mathbf{x}, t)} [\nabla c(\mathbf{x}, t)\mathbf{D}\nabla c(\mathbf{x}, t)] \tag{29}$$

where the conservative component $c(\mathbf{x}, t) = c_1(\mathbf{x}, t) - c_2(\mathbf{x}, t)$ satisfies Eq. (26) for $r(\mathbf{x}, t) = 0$.

The term in the square brackets in Eq. (29) expresses the fact that mixing is driven by concentration gradients and subsequent dispersive mass transfer. The average over this mixing factor is also called scalar dissipation in the literature, see, e.g., the textbook by Pope (2000). Its correct modeling lies at the heart of any mixing model, see below.

While in homogeneous media, mixing is entirely driven by diffusion and local dispersion, in heterogeneous media this is different. The medium heterogeneity creates concentration contrasts, which, through local dispersion, can lead to increased mixing. Fig. 2 illustrates the distribution of a solute in a highly heterogeneous porous medium. In order to assess the mixing potential in such a system, one considers suitable averages of the mixing factor.

Kitanidis (1994) studied a similar mixing measure in terms of entropy to characterize mixing. The entropy of a continuous distribution $c(x, t)$ can be defined by

$$H(t) = -\int d^d x c(\mathbf{x}, t) ln c(\mathbf{x}, t). \tag{30}$$

It quantifies the degree of disorder of the transport system. The exponential of the entropy $H(t)$ is defined as the dilution index

$$E(t) = exp[-H(t)]. \tag{31}$$

It has the dimensions of volume and is a measure for the volume occupied by solute. Thus, it measures the dilution of a

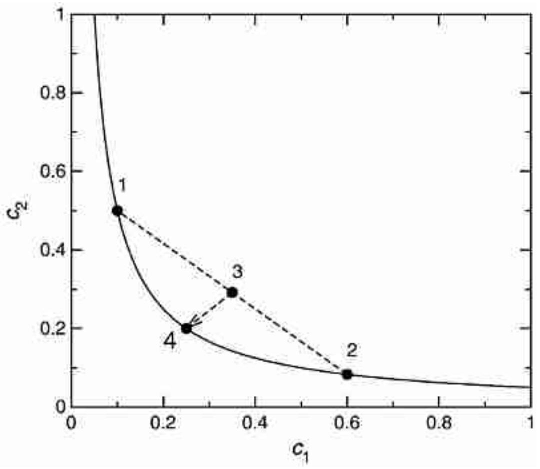

Fig. 1. Illustration of mixing induced precipitation for the simple bi-molecular reaction (25). The hyperbola $c_1 = K/c_2$ describes the subset of possible chemical compositions at equilibrium. At points 1 and 2 the two waters have different equilibrium compositions, $c_1^{(i)}$ and $c_2^{(i)}, i = 1, 2$. Algebraic mixing leads to the new water composition at point 3, $[c_1^{(3)} = \alpha c_1^{(1)} + (1-\alpha)c_1^{(2)};\ c_2^{(3)} = \alpha c_2^{(1)} + (1-\alpha)c_2^{(2)}]$, where α denotes the mixing ratio (for the illustration, we choose $\alpha = 0.5$). The dashed line, describes the set of possible concentrations due to algebraic mixing. The arrow describes the reaction path towards the new equilibrium position at point 4. As a consequence, M precipitates (after De Simoni et al., 2005).

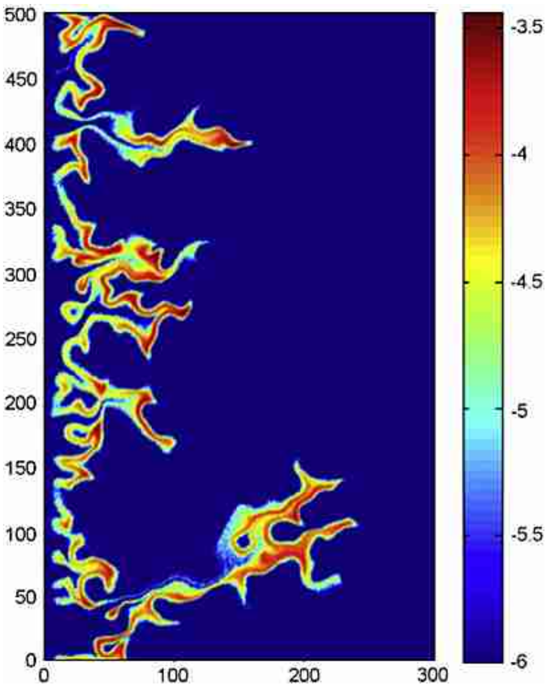

Fig. 2. Spatial distribution of the conservative component $c(\mathbf{x}, t)$ for an initial line injection at $x_1 = 0$ after $t = 2.7\tau_u$. Transport is simulated by particle tracking for 10^6 particles in a two-dimensional highly heterogeneous hydraulic conductivity field characterized by a log-conductivity variance of 9 and correlation length of 10 m (e.g., Le Borgne et al., 2008). The axes are given in the units of meters. Spreading represents the spatial extent of the plume, while mixing quantifies the degree of homogeneity inside the plume.

system. Kitanidis (1994) shows that the temporal change of the system entropy is given by

$$\frac{dH(t)}{dt} = \int \frac{d^d x}{c(\mathbf{x},t)}[\nabla c(\mathbf{x},t)\mathbf{D}\nabla c(\mathbf{x},t)]. \tag{32}$$

We identify the same factor as above as a measure for the mixing of a system. In the absence of dispersion and diffusion, that is, in the absence of local-scale mixing mechanisms, the entropy is given by the one of the initial system, $H(t)=H_0$ and the dilution index accordingly, $E(t)=E_0$. This means that in the absence of dispersion, there is no mixing, that is, the entropy of the system is not increasing. The increase of disorder in a system implies, as outlined above, the increase of volume occupied by the solute. This means that the maximum concentration decreases and in general the concentration contrasts are smoothed out. Thus, mixing is a mechanism that leads to the decrease of concentration variability. The mixing potential of a system can be measured by its ability to decrease concentration contrasts (e.g., Kapoor and Kitanidis, 1998).

The latter can be measured in terms of the evolution of the global concentration variance σ_c^2, which is defined by

$$\sigma_c^2(t) = \int d^d x \overline{c'(\mathbf{x},t)^2}. \tag{33}$$

The concentration fluctuations are $c'(\mathbf{x},t)=c(\mathbf{x},t)-\overline{c}(\mathbf{x},t)$, and the overbar denotes the ensemble average over the stochastic process, which models the underlying spatio-temporal heterogeneity. This quantity has been investigated by e.g., Kapoor and Kitanidis, 1998. They derive the following relationship between the time derivative of $\sigma_c^2(t)$ and the mixing factor

$$\frac{d\sigma_c^2(t)}{dt} = -2\int d^d x\left[\overline{\nabla c'(\mathbf{x},t)\mathbf{D}\nabla c'(\mathbf{x},t)} + \overline{\mathbf{q}'(\mathbf{x})c(\mathbf{x},t)}\cdot\nabla\overline{c}(\mathbf{x},t)\right], \tag{34}$$

where $\mathbf{q}'(\mathbf{x})$ denotes the local-scale velocity fluctuations. This relation is not closed as it still depends on the local concentration fluctuations. The most popular closure approximations are the macrodispersion closure for $\overline{\mathbf{q}'(\mathbf{x})c(\mathbf{x},t)}$ and the interaction by exchange with the mean (IEM) model (e.g., Villermaux and Devillon, 1972; Pope, 2000), which here reduces to (Kapoor and Kitanidis, 1998)

$$\int d^d x \overline{\nabla c'(\mathbf{x},t)\mathbf{D}\nabla c'(\mathbf{x},t)} = \chi\sigma_c^2(t), \tag{35}$$

where χ is a modeling constant that is related to the characteristic dissipation time. Models for the effect of microdiffusion/dispersion, that is, closure models for the average mixing factor, are called mixing models, see, e.g., the textbook by Pope (2000) and references therein. One requirement for a mixing model is that it should reduce the concentration variance, that is, in some sense the impact of microdiffusion is modeled by a proxy, namely its impact on mixing.

Many authors have pointed out that the quantification of incomplete mixing requires the quantification of the statistics of the concentration values of the reactants (Kapoor et al., 1997; Kapoor and Kitanidis, 1998; Lichtner and Tartakovsky, 2003; Meile and Tuncay, 2006; Lichtner and Kang, 2007; Cirpka et al., 2008a; Luo et al., 2008), because pore or local-scale reaction rates are in general non-linear functions of the species concentration, see Section 2. Thus, in order to evaluate the effect of incomplete mixing, the probability density function (PDF) of concentration needs to be known, which can be defined as follows (e.g., Pope, 2000)

$$p(c;\mathbf{x},t) = \overline{\delta[c-c(\mathbf{x},t)]}, \tag{36}$$

where the overbar denotes a suitable average. Concentration PDFs can be determined using Monte-Carlo method or closure assumptions such as the IEM model. For some systems they can be determined analytically. Examples for the exact determination of the concentration PDF can be found in e.g., Lichtner and Tartakovsky (2003), Shvidler and Karasaki (2003), and Tartakovsky et al. (2009b). Another method is to assume a PDF (e.g., Girimaji, 1991) and model its parameters. Applications of this approach to solute transport in the subsurface can be found in e.g., Caroni and Fiorotto, 2005; Bellin and Tonina, 2007; Cirpka et al., 2008a.

4. Summary and outlook

In this paper, we reviewed briefly the state of the art on mixing, spreading and reaction in heterogeneous media. Starting from a pore-scale description, we have presented different methods used for upscaling reactive transport to the scales of interest. In the process of upscaling reactive transport, it is of special importance to differentiate spreading, that describes the spatial extent of the dispersed plume, and mixing, that describes the probability of chemical species to mix and react in a moving fluid. It is now widely recognized that the existence of heterogeneities at different scales imply that the reactive transport laws and parameters at large scale are different from their local counterparts. Quantifying this large-scale reaction and transport behavior for heterogeneous media is a major challenge.

A fundamental need for progressing in this field is to obtain detailed experimental characterizations and images at pore scale, which is the place where the complex interaction between diffusion, advection and reactions occur (e.g., Steefel et al., 2005; Meakin and Tartakovsky, 2009). Promising experimental techniques have been proposed recently for reactive (Fridjonsson et al., 2010-this issue; Gouze and Luquot, 2010-this issue; Katz et al., 2010-this issue) and non-reactive flow and transport (Bouquain et al., 2010-this issue; Alkindi et al., 2010-this issue; Planeta et al., 2010-this issue). The progress of pore-scale numerical models towards detailed realistic representation of the local-scale processes (e.g., Kang et al., 2006; Meakin and Tartakovsky, 2009; Tartakovsky et al., 2007; Bijeljic et al., 2010-this issue; Ryan et al., 2010-this issue), also opens new perspectives for understanding these local-scale interactions. The development of efficient numerical methods is an essential need for investigating the effect of heterogeneity on upscaled transport and reaction. Important progresses are currently achieved in this domain using Lagrangian methods (e.g., Benson and Meerschaert, 2008; Edery et al., 2009; Besnard et al., 2010-this issue; Fernandez-Garcia and Sanchez-Vila, 2010-this issue).

New experimental and theoretical upscaling strategies are proposed for the quantification of the impact of heterogeneity on effective flow, transport and reaction (e.g., Meile and Tuncay, 2006; Lichtner and Kang, 2007; Li et al., 2008; Battiato et al., 2009; Hammond et al., 2010-this issue; Battiato and Tartakovsky, 2010-this issue; Neuweiler et al., 2010-this issue; Planeta et al., 2010-this issue; Bijeljic et al., 2010-this issue; Dentz et al., 2010-this issue) and for quantifying the uncertainty related to effective reactive transport models (e.g., Srinivasan et al., 2007; Tartakovsky and Broyda, 2010-this issue). The heterogeneity impact on spreading can be represented by non-Fickian effective models (e.g., Neuman and Tartakovsky, 2008; Le Borgne et al., 2008). The heterogeneity impact on mixing, due to the interaction between diffusion and the velocity field heterogeneity, is still elusive and has received a particular attention recently, since it is expected to represent the main influence of heterogeneity on reactive transport (e.g., Dentz and Carrera, 2007; De Simoni et al., 2007; Cirpka et al., 2008a; Luo et al., 2008; Dentz et al., 2009; Tartakovsky et al., 2009a; Willingham et al., 2008; Bolster et al., 2010-this issue). A major challenge is to couple effective transport formulations with reactive transport and to develop upscaling approaches for the (non-linearly) coupled transport and reaction processes.

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Appendix A. Volume averaging

The continuum-scale reactive transport equation (Eq. (13a)) can be obtained from the pore-scale transport formulation by volume averaging (e.g., Whitaker, 1999). In the following, we provide a brief derivation of the continuum-scale reactive transport equations using volume averaging. A more complete and rigorous account on volume averaging and scale analyses is given in the textbook by Whitaker (1999).

We consider a representative averaging volume ΔV whose dimensions are much larger than the typical pore scale. The volume ΔV is the sum of the fluid volume ΔV_f and the solid volume ΔV_s,

$$\Delta V = \Delta V_\mathrm{f}(\mathbf{x}) + \Delta V_\mathrm{s}(\mathbf{x}). \tag{A.1}$$

The interfacial area between the fluid and solid phases is denoted by ΔA_s. The unit vector on the solid–fluid boundary pointing from the fluid into the solid is denoted by $\mathbf{n}_\mathrm{fs}$. We now define the volume-averaging operator as

$$E_\mathrm{v}[\varphi(\mathbf{x})] = \frac{1}{\Delta V} \int\limits_{\Delta V_\mathrm{f}(\mathbf{x})} d^d x \varphi(\mathbf{x}), \tag{A.2}$$

with $\varphi(\mathbf{x})$ a test function. The average Eq. (A.2) is termed superficial average. In order to represent a quantity in the fluid, the so-called intrinsic average is of more interest. Thus, we define the intrinsic species concentration $c_i(\mathbf{x}, t)$ as

$$c_i(\mathbf{x}, t) = \phi(\mathbf{x})^{-1} E_\mathrm{v}[C_i(\mathbf{x}, t)]. \tag{A.3}$$

It refers to the liquid volume ΔV_l. The superficial and intrinsic averages are related by the porosity, which is defined as the ratio of fluid to total averaging volume $\phi(\mathbf{x}) = \Delta V_\mathrm{f}(\mathbf{x})/\Delta V$. In order to average Eqs. (3a)–(3h), we make use of the spatial averaging theorem, which states that (e.g., Whitaker, 1999)

$$E_\mathrm{v}[\nabla\varphi(\mathbf{x})] = \nabla E_\mathrm{v}[\varphi(\mathbf{x})] + \frac{1}{\Delta V} \int\limits_{\Delta A_\mathrm{s}} df \mathbf{n}_\mathrm{fs}(\mathbf{x})\varphi(\mathbf{x}), \tag{A.4}$$

where ΔA_s is the area of the solid–fluid interface. Averaging of Eqs (3a)–(3h) and using Eq. (A.4) gives

$$\begin{aligned} &\phi(\mathbf{x}) \frac{\partial c_i(\mathbf{x}, t)}{\partial t} + \nabla \cdot \mathbf{q}(\mathbf{x}) c_i(\mathbf{x}, t) + \nabla \cdot E_\mathrm{v}\left[\mathbf{v}'(\mathbf{x}) C_i'(\mathbf{x}, t)\right] \\ &-\nabla D E_\mathrm{v}[\nabla C_i(\mathbf{x}, t)] = \sum_j \nu_{ij} E_\mathrm{v}\left\{r_j[\{C_n(\mathbf{x}, t)\}]\right\} \\ &+ \frac{1}{\Delta V} \int\limits_{\Delta A_\mathrm{s}} df \mathbf{n}_\mathrm{fs}(\mathbf{x}) \cdot D \nabla C_i(\mathbf{x}, t), \end{aligned} \tag{A.5}$$

where the Darcy velocity $\mathbf{q}(\mathbf{x})$ is given by

$$\mathbf{q}(\mathbf{x}) = \phi(\mathbf{x}) E_\mathrm{v}[\mathbf{v}(\mathbf{x})]. \tag{A.6}$$

Furthermore, we divided the flow velocity $\mathbf{v}(\mathbf{x})$ and the concentration $C_i(\mathbf{x}, t)$ into their volumetric mean and fluctuations about it

$$\mathbf{v}(\mathbf{x}) = E_\mathrm{v}[\mathbf{v}(\mathbf{x})] + \mathbf{v}'(\mathbf{x}), \quad C_i(\mathbf{x}, t) = E_\mathrm{v}[C_i(\mathbf{x}, t)] + C_i'(\mathbf{x}, t). \tag{A.7}$$

Using the boundary conditions (Eq. (3f)) at the fluid–solid interface gives

$$\begin{aligned} &\phi(\mathbf{x}) \frac{\partial c_i(\mathbf{x}, t)}{\partial t} + \nabla \cdot \mathbf{q}(\mathbf{x}) c_i(\mathbf{x}, t) + \nabla \cdot E_\mathrm{v}\left[\mathbf{v}'(\mathbf{x}) C_i'(\mathbf{x}, t)\right] \\ &-\nabla D E_\mathrm{v}[\nabla C_i(\mathbf{x}, t)] = \sum_j \nu_{ij} E_\mathrm{v}\left\{r_j[\{C_n(\mathbf{x}, t)\}]\right\} \\ &+ \frac{1}{\Delta V} \int\limits_{\Delta A_\mathrm{s}} df \sum_m \nu_{im} \alpha_\mathrm{m}(\mathbf{x}) k_m (1 - \Omega_m) - \frac{1}{\Delta V} \int\limits_{\Delta A_\mathrm{s}} df \alpha_\mathrm{ad}(\mathbf{x}) \frac{\partial S_i(\mathbf{x}, t)}{\partial t}. \end{aligned} \tag{A.8}$$

The latter equation poses a series of closure problems. The third term on the left represents dispersion of the solute due to velocity fluctuations and can be closed by using the concept of mechanical dispersion

$$E_\mathrm{v}\left[\mathbf{v}'(\mathbf{x}) C_i'(\mathbf{x}, t)\right] \approx -\overline{\mathbf{D}}(\mathbf{x}) \nabla c_i(\mathbf{x}, t), \tag{A.9}$$

where the dispersion tensor $\overline{\mathbf{D}}(\mathbf{x})$ represents the impact of pore scale velocity fluctuations and geometry on the continuum-scale solute spreading. Such dispersion closures have been studied frequently in the literature (e.g., Brenner, 1980; Brenner and Adler, 1980; Edwards et al., 1993; Koch and Brady, 1985).

In the fourth term on the left one obtains (Whitaker, 1999)

$$E_\mathrm{v}[\nabla C_i(\mathbf{x},t)] \approx \phi(\mathbf{x})\nabla c_i(\mathbf{x}). \tag{A.10}$$

In order to close the first reaction term on the right side, we approximate the point-concentrations $C_n(\mathbf{x}, t)$ by their intrinsic averages $c_n(\mathbf{x}, t)$. This results for the homogeneous reaction term in

$$E_\mathrm{v}\Big\{r_j[\{C_n(\mathbf{x},t)\}]\Big\} \approx \phi(\mathbf{x})\ r_j[\{c_n(\mathbf{x},t)\}]. \tag{A.11}$$

The quality of this approximation was studied by e.g., Battiato et al. (2009) for a bi-molecular equilibrium reaction.

In order to close the second reaction term stemming from fluid–solid interactions, we assume that the point concentrations at the interface can be approximated by the average concentration in the fluid phase and so

$$\begin{aligned}\frac{1}{\Delta V}\int\limits_{\Delta A_s} df \sum_m \nu_{im}\alpha_\mathrm{m}(\mathbf{x})k_m(1-\Omega_m[\{C_n(\mathbf{x},t)\}]) \\ \approx \sum_m \nu_{im}a_\mathrm{m}(\mathbf{x})k_m(1-\Omega_m[\{c_n(\mathbf{x},t)\}]),\end{aligned} \tag{A.12}$$

where the specific reactive surface is defined by Eq. (13c). This approximation implies that the fluid phase is completely mixed.

The last term on the right side is written as

$$\frac{1}{\Delta V}\int\limits_{\Delta A_s} df \alpha_\mathrm{ad}(\mathbf{x})\frac{\partial S_i(\mathbf{x},t)}{\partial t} = [1-\phi(\mathbf{x})]\frac{\partial s_i(\mathbf{x},t)}{\partial t}, \tag{A.13}$$

where $s_i(\mathbf{x}, t)$ is defined by Eq. (13d). Using these approximations and defining the dispersion tensor $\mathbf{D}(\mathbf{x})$ as

$$D_{ij}(\mathbf{x}) = \overline{D}_{ij}(\mathbf{x}) + \delta_{ij}\phi(\mathbf{x})D \tag{A.14}$$

gives Eq. (13a).

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