Multicomponent reactive transport in multicontinuum media

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[1]   Multicomponent reactive transport in aquifers is a highly complex process, owing to a combination of variability in the processes involved and the inherent heterogeneity of nature. To date, the most common approach is to model reactive transport by incorporating reaction terms into advection-dispersion equations (ADEs). Over the last several years, a large body of literature has emerged criticizing the validity of the ADE for transport in real media, and alternative models have been presented. One such approach is that of multirate mass transfer (MRMT). In this work, we propose a model that introduces reactive terms into the MRMT governing equations for conservative species. This model conceptualizes the medium as a multiple continuum of one mobile region and multiple immobile regions, which are related by kinetic mass transfer processes. Reactants in both the mobile and immobile regions are assumed to always be in chemical equilibrium. However, the combination of local dispersion in the mobile region and the various mass transfer rates induce a global chemical nonequilibrium. Assuming this model properly accounts for transport of reactive species, we derive explicit expressions for the reaction rates in the mobile and immobile regions, and we study the impact of mass transfer on reactive transport. Within this framework, we observe that the resulting reaction rates can be very different from those that arise in a system governed by an ADE-type equation.

1.   Introduction

[2]   Reactive transport through natural permeable media is complex at various levels. Besides the complexities associated with flow and solute transport, accounting for reactions can require the incorporation of a potentially large number of aqueous and solid species as well as a variety of reaction types. At the local scale, multicomponent reactive transport has been traditionally modeled by starting from the corresponding governing equation for a conservative solute and adding additional terms that account for the influence of reactions [e.g., *Cederberg et al.*, 1985; *Rubin*, 1990; *Wang and VanCappellen*, 1996]. These additional terms aim to capture a range of different types of homogeneous and heterogeneous reactions (in terms of the number of phases involved). In some cases the reactions can lead to changes in the hydraulic properties of the medium (e.g., porosity or hydraulic conductivity).

[3]   While some analytical solutions for multicomponent reactive transport problems exist [e.g., *Sun et al.*, 1999, 2004; *Clement*, 2001; *Serrano*, 2003; *Quezada et al.*, 2004; *De Simoni et al.*, 2005, 2007; *Werth et al.*, 2006; *Sanchez-Vila et al.*, 2007; *Cirpka and Valocchi*, 2007], most are restricted to hydraulically and chemically homogeneous media. Furthermore, they are all based on the assumption that conservative transport is governed by the advection-dispersion equation (ADE). With the notable exception of adsorption and linear decay processes, few published articles address the use of analytical methods for solving reactive transport problems in heterogeneous media [*Miralles-Wilhelm et al.*, 1997; *Reichle et al.*, 1998; *Attinger et al.*, 1999; *Luo et al.*, 2008]. The ones that do exist rely primarily on perturbative methods.

[4]   Over the last two decades there has been a considerable amount of work addressing the appropriateness of the advection-dispersion equation in real media (see, e.g., the review by *Berkowitz et al.* [2006]). Processes such as intergranular or matrix diffusion add a complexity that must be accounted for in the governing transport equation [*Neretnieks*, 1980; *Wood et al.*, 1990]. Also, a number of authors have suggested using different models for the variability of the geochemical parameters [*Connaughton et al.*, 1993; *Chen and Wagenet*, 1995]. Among the models that have been used to represent these two very different processes, one that has proven quite successful is the multirate mass transfer (MRMT) model [e.g., *Haggerty and Gorelick*, 1995; *Carrera et al.*, 1998; *Haggerty et al.*, 2000]. In parallel, a number of other methods have been developed for modeling transport in heterogeneous media by means of effective dynamics formulations. These are based on semi-phenomenological approaches and include continuous time random walks (CTRW) [e.g., *Berkowitz and Scher*, 1998;

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Berkowitz et al., 2006] and fractional derivative models [e.g., *Benson et al.*, 2000]. All these methodologies share the common concept that if the medium is homogenized, there is a need to incorporate a term in the governing equation that accounts for the memory of the microscale heterogeneities that conservative solutes have sampled along their path. These memory effects, characterized by a memory function [see *Carrera et al.*, 1998, *Willmann et al.*, 2008], distinctly influence transport at the large scale, and are key for proper evaluation of remediation measures or in risk assessment [e.g., *Bolster et al.*, 2009]. All these nonlocal modeling approaches can be shown to be equivalent under some restrictive conditions [*Dentz and Berkowitz*, 2003].

[5] Equations based on such effective dynamics have been able to reproduce a number of field observations that cannot be modeled by any upscaled version of the ADE that is characterized by constant effective transport coefficients. Furthermore, ADE-type equations have been proven inadequate for simulating reactive transport [e.g., *Cirpka*, 2002]. As a result, thorough analyses of the effects of heterogeneity on reactive transport have been restricted to explicitly simulated variability of hydraulic conductivity and the use of local dispersion. Such is the case for *Molz and Widdowson* [1988] or *Fernàndez-Garcia et al.* [2008], who considered a stratified medium, or *MacQuarrie and Sudicky* [1990] and *Luo et al.* [2008], who looked at a random field. While such approaches yield valuable insight into the impact of heterogeneity on reactions, they are difficult to generalize and cumbersome in practice.

[6] One reason for the poor reproduction of reaction rates with an ADE equation is the improper characterization of mixing. On the other hand, effective dynamics models make an explicit attempt at representing the complexity of transport at the pore scale [*Lichtner*, 1985]. The fact that effective dynamics approximations incorporate pore-scale complexity and discriminate between mixing and spreading is hopeful, but not sufficient, for proper representation of reactive transport in real media. To be accurate, these approximations must correctly represent mixing, which to date has not yet been proven. Post calibration, what these approximations yield is a proper reproduction of the pdf of travel times [*Cirpka et al.*, 2008; *Sanchez-Vila et al.*, 2009]. Again, this is necessary for reproducing mixing, but not sufficient. One can envision cases where a given pdf is the result of mixing as well as the superposition of almost independent flow tubes. It is clear that further research is needed to ascertain the circumstances where mixing is properly reproduced. One way to do so would be to compare breakthrough curves of reacting and conservative tracers, a line of research that has recently been explored [*Edery et al.*, 2009; M. Willmann et al., Coupling of mass transfer and reactive transport for non-linear reactions in heterogeneous media, submitted to *Water Resources Research*, 2009].

[7] While the topic of properly representing mixing in effective equations for transport in heterogeneous porous media is by no means closed, the MRMT approach correctly reflects mixing caused by mass transfer processes between mobile and immobile regions (chromatographic mixing). In this work, we propose a reactive transport model that combines the MRMT approach to describe transport under linear mass transfer between mobile and immobile medium regions and multispecies chemical reaction. We present solutions for the reaction rates and probe the impact of mass transfer processes on the effective reactive transport dynamics.

2. Mathematical Model

[8] A multicomponent reactive transport problem is defined by (1) the chemical system, including the aqueous and mineral species involved and the reactions taking place amongst them, and (2) the transport model defined in terms of mass balance equations. In this work all reactions are assumed to be in chemical equilibrium; that is, the characteristic reaction time is much smaller than the characteristic diffusive time.

[9] We first write the full multicomponent reactive transport problem in terms of chemical components. Then we extend it to multicontinuum media. The resulting system yields a suite of uncoupled conservative transport problems. Reaction rates can then be written explicitly in terms of the components and the prespecified memory function.

2.1. Chemical System

[10] The main assumption in this work is that all reactions are in chemical equilibrium. Thus, they can be represented by means of mass action laws. In matrix form [e.g., *Saaltink et al.*, 1998],

$$\mathbf{S} \log \mathbf{c} = \log \mathbf{K}, \tag{1}$$

$\mathbf{S}$ being the stoichiometric matrix, $\mathbf{c}$ being the vector of species concentrations (mass of species per unit volume of fluid), and $\mathbf{K}$ containing the equilibrium constants for all reactions involved. Mass action laws hold for both homogeneous (i.e., all reactants in the same phase) and heterogeneous (some reactants in aqueous and some in solid phases) reactions.

[11] Components are defined as linear combinations of species that remain unaffected by equilibrium reactions [*Saaltink et al.*, 1998]. This linear relation can be written as

$$\mathbf{u} = \mathbf{U}\mathbf{c}, \tag{2}$$

where $\mathbf{u}$ is the vector of components and $\mathbf{U}$ is termed the components matrix, satisfying

$$\mathbf{U}\mathbf{S}^T = 0. \tag{3}$$

Most methodologies to solve geochemical reactive transport problems are based on posing and solving the problem in the component space. Concentrations can then be obtained from speciation calculations. These consist of solving equations (1) and (2) for $\mathbf{c}$ given $\mathbf{u}$.

2.2. Reactive Transport in Single-Continuum Media

[12] The governing mass balance equations can be written in compact form as

$$\phi \frac{\partial}{\partial t} \mathbf{c}(\mathbf{x}, t) = \mathbf{M} L_t[\mathbf{c}(\mathbf{x}, t)] - \mathbf{f}'(\mathbf{x}, t), \tag{4}$$

where ϕ is porosity; $\mathbf{M}$ is a diagonal matrix with terms equal to either unity for aqueous species, or zero for minerals; and

$\mathbf{f}'$ is a sink/source term (mass of species per unit volume of aquifer and unit time). This last term accounts for the mass of a given species that is produced or lost owing to chemical reactions (e.g., precipitation will be a net loss of mass of each of the reacting species, and a gain in the mineral species). The linear operator $L_t(\mathbf{c})$ accounts for advection and diffusion/dispersion,

$$L_t[\mathbf{c}(\mathbf{x}, t)] = -\mathbf{q}\nabla\mathbf{c}(\mathbf{x}, t) + \nabla \cdot [\phi\mathbf{D}\nabla\mathbf{c}(\mathbf{x}, t)], \quad (5)$$

where $\mathbf{q}$ is Darcy's flux and $\mathbf{D}$ is the diffusion/dispersion tensor. The sink/source term $\mathbf{f}'$ in equation (4) is a linear combination of reaction rates, since a single species can be involved in more than one reaction with different stoichiometric coefficients. Defining $\mathbf{r}$ as the vector of reaction rates, it is possible to write [*Saaltink et al.*, 1998]

$$\mathbf{f}' = \mathbf{S}^T\mathbf{r}. \quad (6)$$

Notice that this formulation implicitly assumes that all species are subject to identical transport processes, which is true for advection and mechanical dispersion, but not necessarily for molecular diffusion and porosity.

2.3. Reactive Transport in Multicontinuum Media

[13] The transport of solutes through heterogeneous media is complicated since the exact spatial distribution of the solute flux is unknown. This implies that any solution of equation (4) will lead to uncertain $\mathbf{c}$ values. Several approaches, either analytical or numerical, are available in the literature to tackle this problem. Analytical approaches to conservative transport problems can be classified broadly into two groups: perturbation approaches and effective dynamics. In the former, the main idea is not to reproduce concentration values at the local scale, but rather to find their low-order statistical moments (typically, expected value and variance-covariance of concentrations). The process usually involves ensemble averaging, which smoothes out spatial fluctuations. As a result, transport parameters derived from conservative transport using these methods cannot be used for simulating mixing driven reactive transport. The goal of the effective dynamics approach is to find an effective equation to replace the ADE approach. Several nonlocal formulations can be used to model effective dynamics (FADE [*Benson et al.*, 2000; *Cushman and Ginn*, 2000]; CTRW [*Berkowitz and Scher*, 1998; *Berkowitz et al.*, 2006]; and MRMT [*Haggerty and Gorelick*, 1995; *Carrera et al.*, 1998; *Haggerty et al.*, 2001; *Lawrence et al.*, 2002; *Wang et al.*, 2005]). In the latter, concentrations can be localized, by viewing the medium as a multicontinuum. In essence, this implies viewing the medium as the superposition of a mobile and an ensemble of immobile continua. These regions interact so that solute mass is transferred between the mobile and each of the immobile regions. This model originated in the physical-chemistry literature where it was used to model photon trapping [e.g., *Schmidlin*, 1977] or noninstantaneous adsorption in batch reactors [e.g., *Connaughton et al.*, 1993] using a finite number of immobile phases. The MRMT model was later coupled to transport [*Haggerty and Gorelick*, 1995] and further extended to a continuous suite of immobile phases [*Haggerty and Gorelick*, 1998]. Effective dynamics models have success-

fully reproduced breakthrough curves analogous to those measured in the field (i.e., in physically heterogeneous media). *Dentz and Berkowitz* [2003] showed that MRMT is a subset of the more general CTRW model.

[14] Multicontinuum models for conservative species are fully defined by the distribution of α, first-order exchange rates between the mobile and the immobile continua. This distribution, $f(\alpha)$, can be seen as the fraction of immobile sites that transfer mass at a given rate α [T^{-1}]. This distribution is directly related to the memory function, g [*Carrera et al.*, 1998; *Haggerty et al.*, 2000], by

$$g(t) = \int_0^\infty \alpha f(\alpha) \exp(-\alpha t)\,d\alpha. \quad (7)$$

In the rest of the paper we will assume that the memory function corresponding to a conservative species has been well characterized (e.g., from breakthrough curves corresponding to a tracer experiment).

[15] Solute mass is distributed between mobile and immobile regions which concentrations $\mathbf{c}_m(\mathbf{x}, t)$ and $\mathbf{c}_{im}(\mathbf{x}, \alpha, t)$, respectively (all concentrations expressed as mass per unit volume of fluid; notice that both are local concentrations). Notice that the latter is an α-dependent distribution of concentrations because concentration in the immobile region depends on mass transfer from the mobile region. Thus, the total concentration at a given point in space $\mathbf{c}_t(\mathbf{x}, t)$ can be written as

$$\phi\,\mathbf{c}_t(\mathbf{x}, t) = \phi_m\mathbf{c}_m(\mathbf{x}, t) + \phi_{im}\int_0^\infty f(\alpha)\mathbf{c}_{im}(\mathbf{x}, \alpha, t)d\alpha, \quad (8)$$

where ϕ_m, ϕ_{im}, and $\phi(=\phi_m + \phi_{im})$ are mobile, immobile, and total porosities, respectively.

[16] Mass balance of aqueous species needs to be defined both for the mobile (flowing) and immobile (no flowing) regions. The mobile region mass balance is analogous to equation (4) and reads

$$\phi_m\frac{\partial}{\partial t}\mathbf{c}_m(\mathbf{x}, t) + \phi_{im}\int_0^\infty \alpha[\mathbf{c}_m(\mathbf{x}, t) - \mathbf{c}_{im}(\mathbf{x}, \alpha, t)]f(\alpha)d\alpha$$
$$= L_t[\mathbf{c}_m(\mathbf{x}, t)] - \phi_m\mathbf{f}_m(\mathbf{x}, t). \quad (9)$$

The second term on the left hand side describes first-order mass transfer between the mobile and the immobile regions, $\mathbf{f}_m$ is a sink/source vector and corresponds to the mass removed by reactions from the mobile zone per unit volume of fluid in the mobile zone and unit time. Mass balance in the immobile regions is given by

$$\frac{\partial\mathbf{c}_{im}(\mathbf{x}, \alpha, t)}{\partial t} = \alpha[\mathbf{c}_m(\mathbf{x}, t) - \mathbf{c}_{im}(\mathbf{x}, \alpha, t)] - \mathbf{f}_{im}(\mathbf{x}, \alpha, t), \quad (10)$$

where the first term on the right-hand side expresses the mass exchanged with the mobile zone and $\mathbf{f}_{im}$ corresponds to the mass removed by reactions from that particular immobile zone (of volume $\phi_{im}f(\alpha)$) per unit volume of fluid (in the immobile zone) and unit time. This equation implies that water samples all the sites and species are always in chemical equilibrium in each site. The impact of the right-hand-side terms will be related to the availability of species

to transfer from the more mobile to the less mobile zones, and this will be directly related to the relationship between advective and dispersive characteristic times.

[17] Integrating equation (10) with the weight $f(\alpha)$, multiplying by ϕ_{im}, and adding the resulting equation and equation (9), yields the integrated mass balance equation

$$\phi_m \frac{\partial}{\partial t} \mathbf{c}_m(\mathbf{x}, t) + \phi_{im} \mathbf{\Gamma}(\mathbf{x}, t) = L_t[\mathbf{c}_m(\mathbf{x}, t)] - \mathbf{f}(\mathbf{x}, t), \qquad (11)$$

where $\mathbf{\Gamma}$ represents the time derivative of the total concentration in the immobile regions,

$$\mathbf{\Gamma}(\mathbf{x}, t) = \int_0^\infty f(\alpha) \frac{\partial \mathbf{c}_{im}}{\partial t} (\mathbf{x}, \alpha, t) d\alpha, \qquad (12)$$

and $\mathbf{f}$ integrates reactions in the mobile and immobile regions (i.e., the total mass removed from the system by reactions per unit volume of aquifer and unit time). It is equal to

$$\mathbf{f}(\mathbf{x}, t) = \underbrace{\phi_m \mathbf{f}_m(\mathbf{x}, t)}_{\mathbf{f}_{m,total}} + \underbrace{\phi_{im} \int_0^\infty f(\alpha)\, \mathbf{f}_{im}(\mathbf{x}, \alpha, t) d\alpha}_{\mathbf{f}_{im,total}}. \qquad (13)$$

In equation (13), $\mathbf{f}_{m,total}$ and $\mathbf{f}_{im,total}$ are the contributions to the total reaction rate taking place in the mobile and immobile domains, respectively.

[18] Up to this point, the system consists of N_s equations (11) and (10) (one for each α value if we use a discretized version of equation (11)) for mass balance, plus a number of equilibrium equations. This problem is nonlinear and must be solved for every $(\mathbf{x}, \alpha, t)$. Simplifications must be sought. To this end, we formulate the problem in terms of components in section 2.4.

2.4. Defining the System in Terms of Components

[19] Working with chemical components simplifies the mass balance equations system given by equations (10) and (11). Premultiplying equations (10) and (11) by $\mathbf{U}$, and using equations (3) and (6), we obtain

$$\phi_m \frac{\partial}{\partial t} \mathbf{u}_m(\mathbf{x}, t) + \phi_{im} \int_0^\infty f(\alpha) \frac{\partial \mathbf{u}_{im}}{\partial t} (\mathbf{x}, \alpha, t) d\alpha = L_t[\mathbf{u}_m(\mathbf{x}, t)], \qquad (14)$$

$$\frac{\partial \mathbf{u}_{im}(\mathbf{x}, \alpha, t)}{\partial t} = \alpha[\mathbf{u}_m(\mathbf{x}, t) - \mathbf{u}_{im}(\mathbf{x}, \alpha, t)], \qquad (15)$$

where $\mathbf{u}_m$ and $\mathbf{u}_{im}$ are the vectors of mobile and immobile component concentrations respectively, given by

$$\mathbf{u}_m = \mathbf{U}\mathbf{c}_m; \quad \text{and} \quad \mathbf{u}_{im} = \mathbf{U}\mathbf{c}_{im}. \qquad (16)$$

Solving equation (15) for $\mathbf{u}_{im}$, we obtain

$$\mathbf{u}_{im}(\mathbf{x}, \alpha, t) = \mathbf{u}_{im}^0 e^{-\alpha t} + \int_0^t \alpha e^{-\alpha(t-t')} \mathbf{u}_m(\mathbf{x}, t') dt'$$

$$\equiv \mathbf{u}_{im}^0 e^{-\alpha t} + (\alpha e^{-\alpha t}) * \mathbf{u}_m, \qquad (17)$$

where $\mathbf{u}_{im}^0(\mathbf{x}, \alpha)$ is the initial condition. Substituting equation (17) into equation (14), we obtain the governing equation for $\mathbf{u}_m$:

$$\phi_m \frac{\partial}{\partial t} \mathbf{u}_m(\mathbf{x}, t) + \phi_{im} \left[g_0 \mathbf{u}_m - g \mathbf{u}_{im}^0 + \frac{\partial g}{\partial t} * \mathbf{u}_m \right] = L_t[\mathbf{u}_m(\mathbf{x}, t)]. \qquad (18)$$

Concentrations of all species in either facies can be obtained via the flowing sequential approach: (1) Solve equation (18) to obtain $\mathbf{u}_m$. This is a linear partial differential equation and can be solved by means of any of the existing codes that can solve transport of conservative species with a multicontinuum approach. (2) Obtain $\mathbf{u}_{im}$ from equation (17). (3) Obtain $\mathbf{c}_m$ and $\mathbf{c}_{im}$ by speciation (inversion of equation (16)). Several numerical codes are available in the literature.

2.5. Evaluation of Reaction Rates

[20] Total reaction rates may be obtained by means of mass balance considerations from equations (9) and (10). Alternatively, it is possible to derive an explicit expression for the direct evaluation of the total reaction taking place in the system. The resulting expression (see Appendix A) is

$$\mathbf{f} = \phi_m \mathbf{H} \nabla^T \mathbf{u}_m \mathbf{D} \nabla \mathbf{u}_m + \phi_{im} \mathbf{J}_m \left[g_0 \mathbf{u}_m + \frac{\partial g}{\partial t} * \mathbf{u}_m \right]$$

$$- \phi_{im} \int_0^\infty f(\alpha) \mathbf{J}_{im} \frac{\partial \mathbf{u}_{im}}{\partial t} d\alpha, \qquad (19)$$

where $\mathbf{H}$ is the Hessian matrix of the species concentration with respect to the components in the mobile phase (the components of the kth reaction Hessian matrix are given by $\mathrm{H}_{ij}^k = \partial^2 c_m^k / \partial u_{m,i} \partial u_{m,j}$, $i, j = 1, \ldots, N_s - N_r$ where c_m^k is the secondary species associated to the kth reaction (see *De Simoni et al.* [2005] for details). In a similar way, $\mathbf{J}_{im}$ and $\mathbf{J}_m$ represent the Jacobian matrix of the species concentration with respect to the components either in the immobile phase ($\mathrm{J}_{im,ij} = \partial c_{im,i} / \partial u_{im,j}$) or in the mobile phase ($\mathrm{J}_{m,ij} = \partial c_{m,i} / \partial u_{m,j}$). The total reaction rate is the sum of three terms on the right-hand side of equation (19): (1) the first term quantifies the impact of dispersion induced mixing in the mobile region, and (2) the second and third terms together account for the enhanced mixing of the reacting species due to mass transfer between the mobile and immobile zones, incorporating memory effects through $g(t)$ and the impact of the reactions taking place in the immobile regions. Actually, the first term is identical to the one derived by *De Simoni et al.* [2005] for reactive transport in homogeneous media.

3. Particularization for a Binary System

3.1. Problem Statement

[21] We consider a system consisting of an instantaneous bimolecular precipitation/dissolution reaction of two solutes (B_1 and B_2) in equilibrium with a solid mineral (species M_3):

$$aB_1 + bB_2 \rightleftarrows M_{3(s)}. \qquad (20)$$

For simplicity, but without any loss of generality, we consider $a = b = 1$, so that we have the following stoichiometric matrix:

$$\mathbf{S}^T = \begin{pmatrix} 1 \\ 1 \end{pmatrix}. \qquad (21)$$

The law of mass action is expressed for both the mobile and the immobile concentrations. Assuming a diluted system,

$$\log c_{m_1} + \log c_{m_2} = \log K \quad \text{and}$$
$$\log c_{im_1}(\alpha) + \log c_{im_2}(\alpha) = \log K \quad \forall \alpha. \qquad (22)$$

The mass balance equations for the two aqueous species are

$$\phi_m \frac{\partial c_{m_i}(\mathbf{x},t)}{\partial t} + \phi_{im}\Gamma_i(\mathbf{x},t) = -\mathbf{q}\nabla c_{m_i}(\mathbf{x},t) + \nabla \cdot [\phi_m \mathbf{D}\nabla c_{m_i}(\mathbf{x},t)]$$
$$- r, \quad i = 1,2, \qquad (23)$$

with

$$\Gamma_i(\mathbf{x},t) = \int_0^\infty f(\alpha)\frac{\partial c_{im_i}(\mathbf{x},\alpha,t)}{\partial t}d\alpha. \qquad (24)$$

3.2. Solution

[22] Following the general methodology of section 2, it is necessary to define the mobile conservative components of the system to satisfy equation (3). Among various possibilities, the simplest one is to select

$$\mathbf{U} = \begin{pmatrix} 1 & -1 \end{pmatrix}. \qquad (25)$$

This implies that the system can be fully defined in terms of a single conservative component for the mobile domain, and another one for each mass transfer rate in the immobile one:

$$u_m = c_{m_1} - c_{m_2} \quad \text{and} \quad u_{im}(\alpha) = c_{im_1}(\alpha) - c_{im_2}(\alpha). \qquad (26)$$

The governing equation for u_m (now the individual term in vector $\mathbf{u}_m$) is equation (18). If an analytical or numerical solution for u_m to a given transport problem is obtained, then u_{im} can be obtained explicitly from equation (17).

[23] If the equilibrium constant does not depend on the concentrations of the species, the mass action law equations (equation (22)) in either phase can be combined with equation (26) to explicitly obtain the species concentrations in terms of the components concentrations:

$$c_{m,j} = \frac{(-1)^{j-1}u_m + \sqrt{u_m^2 + 4K}}{2} \quad \text{and}$$
$$c_{im,j} = \frac{(-1)^{j-1}u_{im} + \sqrt{u_{im}^2 + 4K}}{2} \quad j = 1,2. \qquad (27)$$

Finally, the total reaction rates in the system can be obtained from

$$r_{im}(\mathbf{x},t) = \phi_{im}\int_0^\infty f(\alpha)r_{im}(\mathbf{x},\alpha,t)d\alpha$$
$$= \phi_{im}\int_0^\infty f(\alpha)\left\{\alpha[c_{m_2}(\mathbf{x},t) - c_{im}(\mathbf{x},\alpha,t)] - \frac{\partial c_{im}(\mathbf{x},\alpha,t)}{\partial t(\mathbf{x},\alpha,t)}\right\}d\alpha, \qquad (28)$$

$$r_m(\mathbf{x},t) = \phi_m \frac{\partial^2 c_{m_2}(\mathbf{x},t)}{\partial u_m^2(\mathbf{x},t)}\nabla^T u_m(\mathbf{x},t)\mathbf{D}\nabla u_m(\mathbf{x},t)$$
$$+ \phi_{im}\frac{\partial c_m(\mathbf{x},t)}{\partial u_m(\mathbf{x},t)}\left[g_0 u_m + \frac{\partial g}{\partial t} * u_m\right]$$
$$- \phi_{im}\int_0^\infty f(\alpha)\frac{\partial c_{im}(\mathbf{x},\alpha,t)}{\partial u_{im}(\mathbf{x},\alpha,t)}\frac{\partial u_{im}}{\partial t}d\alpha - r_{im}(\mathbf{x},t). \qquad (29)$$

In this particular chemical configuration the derivatives of species concentrations with respect to components used in equations (28) and (29) are explicitly given by

$$\frac{\partial c_{m,j}}{\partial u_m} = \frac{1}{2}\left((-1)^{j-1} + \frac{u_m}{\sqrt{u_m^2 + 4K}}\right) \text{ and } \frac{\partial^2 c_{m,j}}{\partial u_m^2} = \frac{2K}{(u_m^2 + 4K)^{3/2}}$$
$$j = 1,2, \qquad (30)$$

$$\frac{\partial c_{im,j}}{\partial u_{im}} = \frac{1}{2}\left((-1)^{j-1} + \frac{u_{im}}{\sqrt{u_{im}^2 + 4K}}\right) \text{ and } \frac{\partial^2 c_{im,j}}{\partial u_{im}^2} = \frac{2K}{(u_{im}^2 + 4K)^{3/2}}$$
$$j = 1,2. \qquad (31)$$

4. Application Example: 1-D Fixed-Step Function

[24] A significant feature of the methodology proposed is that, whenever the transport of conservative species is solvable analytically, so too is the multicomponent reactive transport problem. This is illustrated by means of an example of a 1-D column with constant input concentration.

4.1. Problem Statement

[25] The column is completely saturated with water in chemical equilibrium with the crushed mineral acting as porous media. We assume initial concentrations of components $u_m^0 = u_{im}^0 = 0$ (i.e., $c_{1,m}^0 = c_{1,im}^0 = c_{2,m}^0 = c_{2,im}^0 = \sqrt{K}$). At the inlet, a solution with a different chemical signature (though still in equilibrium with the mineral) is injected. Despite this setup leads to mineral precipitation along the column (preferentially at the inlet), we consider that the total mineral precipitated is not sufficient to change porosity or permeability in the medium. Accounting for variations in hydraulic parameters is not a limitation if the solutions of the species concentrations are sought numerically, but significantly complicates analytical solutions. The flow applied, q_x, is steady state and uniform. The system is best presented in dimensionless terms:

$$\frac{\partial u_m'}{\partial t'} + \beta\left(g_0 u_m' + \frac{\partial g}{\partial t} * u_m'\right) = \frac{1}{Pe}\frac{\partial^2 u_m'}{\partial x'^2} - \frac{\partial u_m'}{\partial x'}, \qquad (32)$$

$$t_{adv} = \phi_m\frac{L}{q_x}, \quad Pe = \frac{q_x L}{\phi_m D}, \quad \beta = \frac{\phi_{im}}{\phi_m}, \quad t' = \frac{t}{t_{adv}}, \quad x' = \frac{x}{L},$$
$$u_m' = \frac{u_m}{\sqrt{K}}, \qquad (33)$$

Table 1. Normalized Reaction Rates and Corresponding Probabilities Used in the Two Models Defined in Section 4.2

ω_j	p_j
Model $\widehat{\omega}0$	
0.1	0.4097
0.2	0.1771
0.3	0.0916
0.4	0.0601
0.5	0.0485
0.6	0.0443
0.7	0.0427
0.8	0.0421
0.9	0.0420
1.0	0.0419
Model $\widehat{\omega}1$	
0.4	0.0397
0.7	0.3043
1.0	0.3754
1.3	0.1982
1.6	0.0640
1.9	0.0150
2.2	0.0028
2.5	0.0005
2.8	0.0001

where L is the characteristic length of the column. Additional dimensionless variables are

$$\omega = t_{adv}\alpha, \quad c'_m = \frac{c_m}{\sqrt{K}}, \quad c'_{im} = \frac{c_{im}}{\sqrt{K}}, \quad u'_{im} = \frac{u_{im}}{\sqrt{K}}, \quad (34)$$

[26] The initial and boundary conditions are

$$u'_m(x', t' = 0) = 0 \qquad x' \geq 0,$$
$$u'_m(x' = 0, t') = u_0; \quad u'_m(x' = \infty, t') = 0 \quad t' > 0. \qquad (35)$$

The solution to this system is obtained in Laplace space (see Appendix A):

$$\widehat{u'_m}(x', s) = \frac{u_0}{s} \exp\left[\frac{Pe}{2}x'\right] \exp\left\{-\frac{Pe}{2}x'\sqrt{1 + \frac{4}{Pe}s[1 + \beta\widehat{g}(s)]}\right\}, \qquad (36)$$

where P_e is the Peclet number, the dimensionless memory function in Laplace space is given by $\widehat{g}(s) = \int_0^\infty \frac{\omega f(\omega)}{s + \omega}d\omega$, and ω corresponds to the dimensionless mass transfer rate. Equation (36) cannot be back-transformed analytically, but can be presented in terms of the corresponding solution for homogeneous media:

$$\widehat{u'_m}(x', s) = \widehat{u'_{m1}}(x', s)\widehat{u'_{m2}}(x', s)$$
$$\widehat{u'_{m1}}(x', s) = \frac{u_0}{s} \exp\left[\frac{Pe}{2}x'\right] \exp\left\{-\frac{Pe}{2}x'\sqrt{1 + \frac{4s}{Pe}}\right\} \qquad (37)$$
$$\widehat{u'_{m2}}(x', s) = \exp\left\{-\frac{Pe}{2}x'\sqrt{1 + \frac{4s}{Pe}}\left(\sqrt{1 + \frac{4\beta s\widehat{g}}{Pe + 4s}} - 1\right)\right\}.$$

[27] From the properties of Laplace transforms, the final solution is given by

$$u'_m(x', t') = \mathcal{L}^{-1}\left\{\widehat{u'_{m1}}(x', s)\right\} * \mathcal{L}^{-1}\left\{\widehat{u'_{m2}}(x', s)\right\}. \qquad (38)$$

It should also be noted that $\mathcal{L}^{-1}\left\{\widehat{u'_{m1}}(x', s)\right\}$ corresponds to the well-known solution provided by Ogata and Banks [1961], for a pulse injection in a homogeneous media, given by

$$u'_{m1}(x', t') = \frac{u_0}{2}\left[\exp(Pe\, x')\text{erfc}\left(\frac{Pe}{2}\frac{x' + t'}{\sqrt{Pe\, t'}}\right) + \text{erfc}\left(\frac{Pe}{2}\frac{x' - t'}{\sqrt{Pe\, t'}}\right)\right]. \qquad (39)$$

In short, equation (38) is the convolution of the Ogata-Banks solution with a function incorporating the effects of heterogeneity by the inclusion of the memory function. From equation (37), when β tends to zero (homogeneous problem), then $u'_m(x', t')$ reduces to the Ogata-Banks solution.

4.2. Reaction Rate

[28] Heterogeneity within the 1-D column is modeled by a multiple sites mass transfer probability density function (pdf) described by $f(\omega) = \sum_{j=1}^{N} p_j\delta(\omega - \omega_j)$, where ω is defined by a discretized version of a gamma function. We selected two functions in order to analyze ω values ranging from very small to intermediate (denoted as models $\widehat{\omega}0$ and $\widehat{\omega}1$, respectively). The actual (ω_j, p_j) values used are displayed in Table 1. In the first of these cases (model $\widehat{\omega}0$) the ω values are all less than one with the largest value of p corresponding to $\omega = 0.1$. In the second case the largest p value corresponds to $\omega = 1.0$.

[29] The total reaction rate in the immobile zone is obtained from a discretized version of equation (28) written in dimensionless form

$$\frac{t_{adv}}{\phi_{im}\sqrt{K}}r_{im} \equiv r'_{im} = \sum_{j=1}^{N} p_j\left(\omega_j\left(c'_{m,2} - c'_{im,2,j}\right) - \frac{\partial c'_{im,2,j}}{\partial t'}\right). \qquad (40)$$

The corresponding total reaction rate in the mobile zone (extension of equation (29)) is

$$\frac{t_{adv}}{\phi_m\sqrt{K}}r_m \equiv r'_m$$
$$= \underbrace{\frac{1}{Pe}\frac{\partial^2 c'_{m,2}}{\partial u'^2_m}\left(\frac{\partial u'_m}{\partial x'}\right)^2}_{\text{mixing}}$$
$$+ \underbrace{\beta\left[g_0 u'_m + \frac{\partial g'}{\partial t} * u'_m\right]\sum_{j=1}^{N} p_j\frac{\partial c'_{m,2}}{\partial u'_m} - \beta\sum_{j=1}^{N} p_j\frac{\partial c'_{im,2,j}}{\partial t} - r'_{im}}_{\text{mass transfer}}, \qquad (41)$$

where the memory function is $g(t') = \sum_{j=1}^{N} p_j\omega_j e^{-\omega_j t'}$.

[30] In equation (32) we have separated the contributions from the mixing part (i.e., the corresponding reaction if β is equal to zero) from that of the presence of the immobile zones in the MRMT model.

[31] The specific chemical problem considered is precipitation of siderite ($FeCO_3 = Fe^{2+} + CO_3^{2-}$) with an equilibrium constant $\log K(25°C) = -10.7$ [*Coudrainribstein and Morel*, 1987]. The porosity ratio was fixed at a constant value of 5/7, following the indications of *Sanchez-Vila and Carrera* [2004]. The reaction rate is computed by the inverse Laplace transform of equation (37) using the de Hoog algorithm (K. J. Hollenbeck, INVLAP.M: A
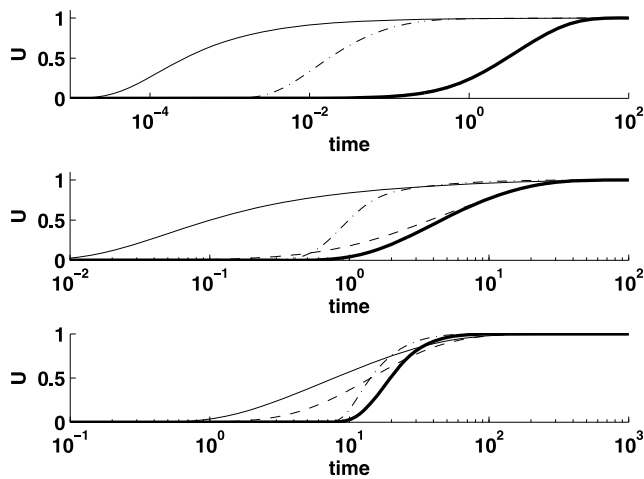
Figure 1. Values of u'_m and u'_{im} (weighted averaged) over time at three points in space and for two Peclet numbers: (top) $x = 0.1$, (middle) $x = 1$, and (bottom) $x = 10$: u'_m, $Pe = 0.1$ (solid line); u'_{im}, $Pe = 0.1$ (dashed line); u'_m, $Pe = 10$ (dash-dotted line); and u'_{im}, $Pe = 10$ (solid bold line).

MATLAB function for numerical inversion of Laplace transforms by the de Hoog algorithm, unpublished manuscript, 1998). Results are discussed in section 5.

5. Evaluation of Concentrations and Rates

[32] The dimensionless mass transfer rate (ω) represents the ratio between mass transfer rate and advection rate. It has a strong influence on the behavior of breakthrough curves (BTCs) of the dimensionless immobile concentration. In the $\widehat{\omega}0$ model, mass transfer is very slow. Correspondingly, solute transfers back to the mobile zone with difficulty, causing significant tailing in BTCs. In the $\widehat{\omega}1$ model the characteristic times of mass transfer and dispersion are similar. Finally it should be noted that if all ω values were very large (i.e., mass transfer between the
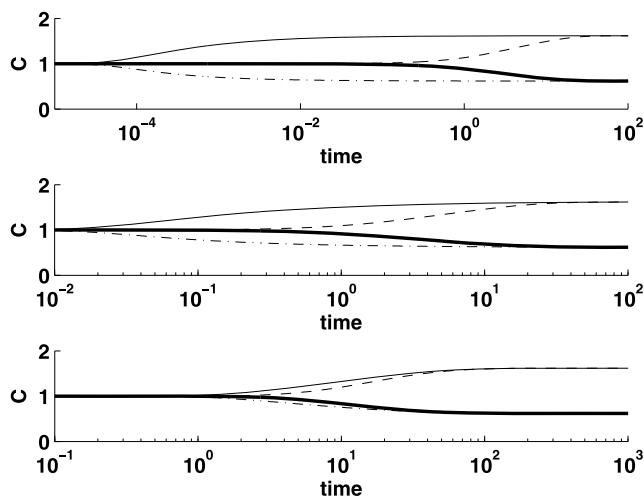

Figure 2. Concentration of the two aqueous species in the mobile and immobile zones (weighted average) and for the case $Pe = 0.1$: (top) $x = 0.1$, (middle) $x = 1$, and (bottom) $x = 10$: c'_{1m} (solid line); c'_{1im} (dashed line); c'_{2m} (dash-dotted line); and c'_{2im} (solid bold line).

mobile and immobile phases is instantaneous), the system would respond as that of a homogeneous media with a retardation factor equal to $1 + \beta$, and consequently reactions could be obtained from the results of *De Simoni et al.* [2005].

[33] We start by looking at the reactive transport problem presented in section 4 in terms of normalized concentrations. Owing to the particular choice of boundary conditions (step-input function), the initial water will eventually be substituted by the input water. This effect takes place faster in the mobile phase and eventually transmits to the different immobile phases (according to the corresponding ω values). In Figure 1 we see the evolution of the concentrations of the components with time for two particular values of Pe ($= 0.1$, i.e., diffusion-dominated problem, or 10, i.e., advection-dominated problem) and for three different distances ($x = 0.1$, 1, and 10). Unless stated otherwise, Figures 1–6 include
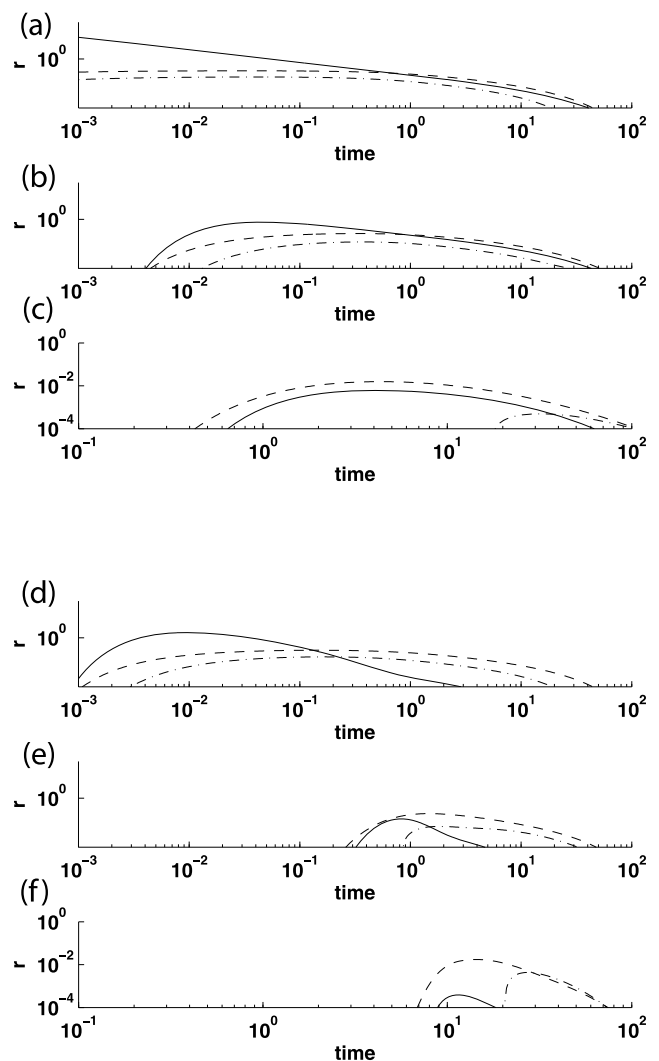
**Figure 3.** Reaction rates with time at three points in space: (a, d) $x = 0.1$, (b, e) $x = 1$, and (c, f) $x = 10$. Figures 3a–3c correspond to $Pe = 0.1$, and Figures 3d–3f correspond to $Pe = 10$. The total reaction rate is the sum of the three individual contributions presented in equations (40) and (41): mixing term (solid line), mass transfer term (dashed line), and total reaction in the immobile zone (dash-dotted line).
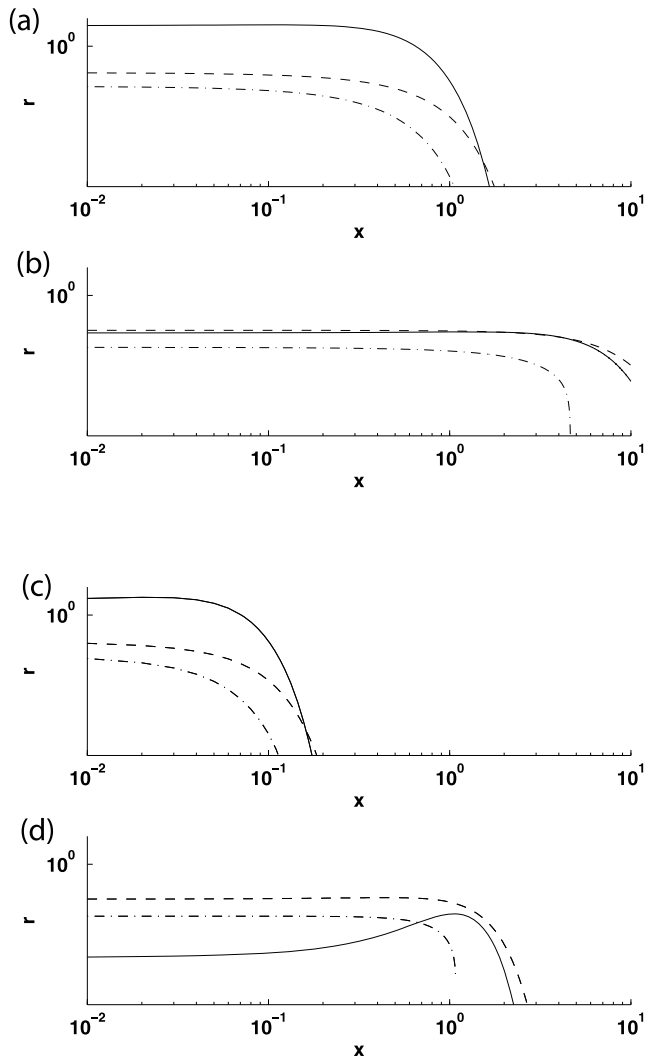
Figure 4. Reaction rates versus distance at two points in time: (a, c) $t = 0.01$ and (b, d) $t = 1$. Figures 4a and 4b correspond to $Pe = 0.1$, and Figures 4c and 4d correspond to $Pe = 10$. The total reaction rate is the sum of the three contributions presented in equations (40) and (41): mixing term (solid line), mass transfer term (dashed line), and total reaction in the immobile zone (dash-dotted line).

only the results corresponding to model $\widehat{\omega}0$. In Figure 1 we observe a clear separation between the curves corresponding to the mobile and the immobile zones (the latter is actually the weighted arithmetic average of the component concentrations). For the diffusive case (smaller Peclet number) the changes in the mobile zone occur earlier, which is a reflection of the diffusive front that propagates through the system. For completeness, Figure 2 displays the corresponding concentration of aqueous species obtained from the normalized expressions of the actual concentrations (equation (27)).

[34] The distribution of reaction rates in space and time is presented next. Figure 3 displays the various contributions to the total reaction rates over time at three points in space. For the point closest to the inlet the mixing driven contribution (see equation (41)) is largest, and it is only at late times that the mass transfer contribution dominates and becomes the main contributor to the total reaction rate.
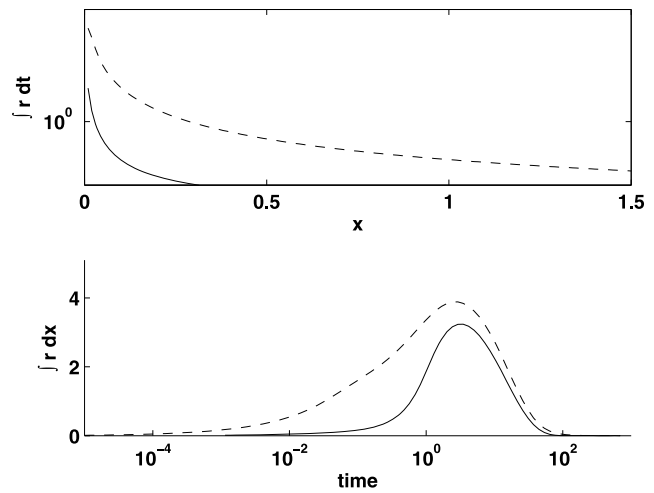
Figure 5. Reaction rate (top) integrated over time against spatial coordinate and (bottom) integrated over space against time. The two curves correspond to two different Pe values: $Pe = 0.01$ (dashed line) and $Pe = 10$ (solid line).

For large travel distances almost all of the reaction is driven by the mass transfer term. While this holds true for both Peclet numbers, it is clearly visible that the mass transfer term is more important in the higher Peclet number case. At short times, the concentration gradients are large and the reactions are driven by mixing due to local dispersion. With increasing time, gradients are smoothed out and mass transfer dominates over local dispersion as a mixing mechanism and becomes the dominating driving force of chemical reaction. This effect is more pronounced for advection-dominated transport ($Pe = 10$). After the smoothing out of the large initial gradients, local dispersion plays only a subordinate role.

[35] The presence of mass transfer between mobile and immobile zones leads to a broader temporal distribution of the reaction rates, which indicates that the system relaxes to
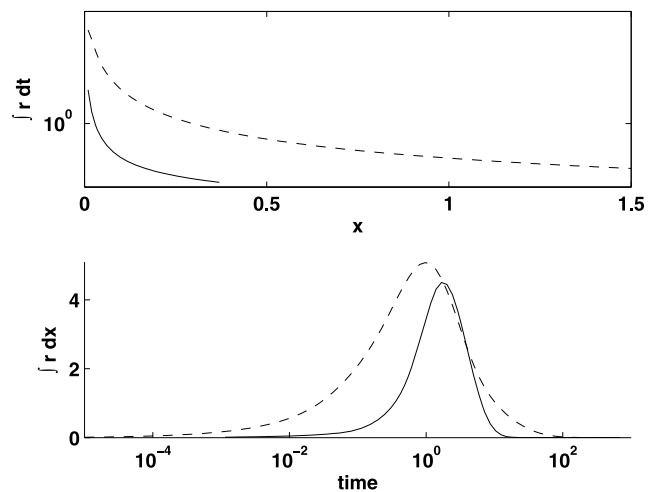
Figure 6. Integrated reaction rates for the $\widehat{\omega}1$ model: (top) reaction rate integrated over time against spatial coordinate and (bottom) reaction rate integrated over time against time. The two curves correspond to two different Pe values: $Pe = 0.01$ (dashed line) and $Pe = 10$ (solid line).

global equilibrium at later times than for a homogeneous medium, for which mixing is exclusively due to local dispersion. These features are also reflected in the spatial distributions of the reaction rates, illustrated in Figure 4 (for two different times, $t = 0.01$ and $t = 1$). Close to the inlet, the different contributions to the total reaction rate are basically constant and decrease fast in the vicinity of the diffusive front. At small dimensionless times ($t = 0.01$) the mixing term dominates over the mass transfer term everywhere both for the $Pe = 0.1$ and $Pe = 10$ cases. For $t = 1$, the mass transfer term is of increasing importance. In the diffusion dominated case ($Pe = 0.1$), the mass transfer and mixing terms are almost equal. For the advection-dominated case ($Pe = 10$), the mass transfer term clearly dominates over the mixing term everywhere. The mixing term is small close to the inlet and increases toward a maximum close to the diffusive front, which reflects the spatial distribution of the gradient of the mobile component. In absolute terms, the largest reaction rates occur close to the inlet (see Figure 5), as concentration gradients are largest. Total reaction rates are heavily affected by Pe. The more diffusive the problem, the larger the total rate. Another effect of the choice of Pe is visible when the rate is integrated in space. For the more diffusive case reactions are measurable over a larger time span. This effect is independent of the choice of the distribution of ω values (see Figure 6 for the results corresponding to the $\widehat{\omega}1$ model, which are qualitatively similar to those of Figure 5).

6. Conclusions

[36] We study reactive transport in an effective medium that is composed by a mobile region and a suite of immobile regions which are characterized by a distribution of solute retention times. The mobile and immobile regions communicate by linear kinetic mass transfer. The retention properties are the same at each point in space; that is, the solute can encounter the full spectrum of retention zones at any point and can be derived from observations corresponding to a conservative tracer. Such an effective medium can be visualized as consisting of multiple overlapping continua. The resulting transport model is termed reactive multirate mass transfer (R-MRMT) model.

[37] Under the assumption that species are subject to the same advective velocity and diffusion coefficient, we set the geochemical problem in term of chemical components. Then, we derive explicit expressions for the reaction rates in both the mobile and the immobile zones. We identify three contributions to the total reaction rate: (1) a term that is identical in form to the one derived by *De Simoni et al.* [2005], which quantifies local dispersive mixing in the mobile region, (2) a term that quantifies reaction due to the chemical disequilibrium caused locally by mass transfer between the mobile and immobile regions, and (3) a term that quantifies the total reaction in the immobile regions. The latter term is relatively small compared with the contributions from the mobile region. Nevertheless, the mass exchange between the mobile and immobile zones has an important effect on the reaction dynamics.

[38] For advective-dispersive transport in a system characterized by an ADE, the only mechanism driving reactions is local dispersion. In the presence of immobile regions,

advective transport and mass transfer between the mobile and immobile zones leads to mixing of the mobile water and water that has been released from the immobile regions. This induces nonequilibrium and thus additional reaction. In the latter model, the characteristic reaction time is given by the typical retention time scale, which can be very large. Thus, for reactive transport in a medium characterized by a broad distribution of retention times, the time for the system to reach global equilibrium can be significantly increased.

Appendix A

A1. General Reaction Rate

[39] The starting point is equation (14). Also, note that species concentrations can be written in terms of components concentrations and the equilibrium constants; that is, $\mathbf{c}_m = \mathbf{c}_m(\mathbf{u}_m, \mathbf{K})$, and $\mathbf{c}_{im} = \mathbf{c}_{im}(\mathbf{u}_{im}, \mathbf{K})$. $\mathbf{K}$ values can vary with salinity and temperature. Assuming $\mathbf{K}$ is constant in space and time, we can apply the chain rule ($d\mathbf{c}_m = \frac{\partial \mathbf{c}_m}{\partial \mathbf{u}_m} d\mathbf{u}_m$, similar for $d\mathbf{c}_{im}$) to equation (11):

$$\mathbf{f}(\mathbf{x}, t) = \frac{\partial \mathbf{c}_m}{\partial \mathbf{u}_m} \left\{ -\phi_m \frac{\partial \mathbf{u}_m}{\partial t} - \mathbf{q} \nabla \mathbf{u}_m + \nabla \cdot [\phi_m \mathbf{D} \nabla \mathbf{u}_m] \right\}$$
$$- \phi_{im} \int_0^\infty f(\alpha) \frac{\partial \mathbf{c}_{im}}{\partial t}(\mathbf{x}, \alpha, t) d\alpha + \phi \mathbf{H} \nabla \mathbf{u}_m \mathbf{D} \nabla \mathbf{u}_m. \quad \text{(A1)}$$

Finally, incorporating equation (15), we obtain equation (19). Additional terms would appear in equation (A1) if one were to consider variability of $\mathbf{K}$ values.

A2. General Solution in Laplace Space of the Total Mobile Concentration

[40] Writing equation (32) in Laplace space, we get

$$s\widehat{u'_m} - u^0 + \beta \left[g_0 \widehat{u'_m} + (s\widehat{g} - g_0)\widehat{u'_m} \right] = \frac{1}{Pe} \frac{d^2 \widehat{u'_m}}{dx'^2} - \frac{d\widehat{u'_m}}{dx'}, \quad \text{(A2)}$$

With the superscript $\widehat{\ }$ indicating a variable in Laplace space. Reordering equation (A2), we get

$$\frac{1}{Pe} \frac{d^2 \widehat{u'_m}}{dx'^2} - \frac{d\widehat{u'_m}}{dx'} - [1 + \beta\widetilde{g}]s\widehat{u'_m} = -u^0. \quad \text{(A3)}$$

[41] A particular solution of equation (A3) is given by $\widehat{u'_m} = \frac{u^0}{s}$. The general solution is given by

$$\widehat{u'_m} = A_1 \exp\left[\left(1 + \sqrt{1 + \frac{4}{Pe}s(1 + \beta\widehat{g})} \right) \frac{Pe \, x'}{2} \right]$$
$$+ A_2 \exp\left[\left(1 - \sqrt{1 + \frac{4}{Pe}s(1 + \beta\widehat{g})} \right) \frac{Pe \, x'}{2} \right]. \quad \text{(A4)}$$

From the boundary conditions, $A_1 = 0$, as the solution must remain finite for $x' \to \infty$. To obtain the second integration constant, let us notice that for $x' = 0$, it is $\widehat{u'_m} = \frac{u_0}{s}$. Thus, $A_2 = \frac{u_0}{s}$, and the specific solution for this problem becomes equation (36).

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