A solution for multicomponent reactive transport under equilibrium and kinetic reactions

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[1]   Analysis of the space-time evolution of reactive solutes in porous systems is complex owing to the presence of different types of chemical reactions. The complete description of a reactive transport scenario entails calculating the spatial and temporal distribution of species concentrations and reaction rates. Here we develop an exact explicit expression for the space-time distribution of reaction rates for a scenario where the geochemical system can be described by an arbitrary number of equilibrium (fast) reactions and one kinetic (slow) reaction, in the absence of non-constant-activity immobile species. The key result is that the equilibrium reaction rate is the sum of two terms representing the availability of reactants. One term involves diffusion and dispersion and represents the contribution of mixing. The other term includes the contribution of the kinetic reaction. The approach also yields the local concentrations of all dissolved species. Yet the latter are not needed for the direct computation of equilibrium reaction rates. We illustrate the approach by means of a simple reactive transport scenario, involving a common ion effect in the presence of a kinetic and an equilibrium reaction leading to precipitation and dissolution processes within a one-dimensional fully saturated porous medium. The example highlights the highly nonlinear and nonmonotonic response of the system to the controlling input parameters.

1. Introduction

[2]   Chemical reactions may affect the fate of pollutants and the properties of the host porous medium. The conditions for the reactions to occur, their location, and often their rate are largely controlled by transport (see the discussion by *Rezaei et al.* [2005]), which is what motivates analyses of reactive transport. Modeling multicomponent reactive transport problems typically requires specifying (1) a set of mass balance equations (one for each species being transported) and (2) a second set of equations describing the reactions among species. The mass balance of each individual species is expressed by a solute transport equation with a source term to account for all the reactions undergone by each individual species. The transport equation itself can be written according to different conceptual models. These include the advection dispersion equation (ADE) [e.g., *Bear*, 1972], dual- or multiple-domain mass transfer (MRMT) models [e.g., *Cvetkovic et al.*, 1999; *Haggerty and Gorelick*, 1995; *Carrera et al.*, 1998], fractional derivatives depictions

of transport [e.g., *Benson et al.*, 2000; *Cushman and Ginn*, 2000], or continuous time random walks [e.g., *Berkowitz and Scher*, 1995; *Berkowitz et al.*, 2006].

[3]   From a pragmatic standpoint, chemical reactions can be subdivided into two broad groups, that is, "sufficiently fast" and "insufficiently fast" reactions [*Rubin*, 1983], depending on whether a characteristic reaction time is much smaller than the time scales associated with other mass-transfer processes (e.g., advection, diffusion, and dispersion). In the presence of sufficiently fast reactions the assumption of local chemical equilibrium can be considered appropriate. This is the case for most aqueous reactions. On the other hand, reactions involving minerals and aqueous species are often better described as kinetic, that is, insufficiently fast [e.g., *Steefel and Lasaga*, 1994]. Whenever reactions with different characteristic times occur simultaneously, the solution of the associated multicomponent system becomes mathematically complex due to the presence of nonlinearities [e.g., *Molins et al.*, 2004; *Steefel et al.*, 2005, and references therein].

[4]   A crucial element in the analysis of reactive transport scenarios is the assessment of the space-time patterns of reaction rates. This allows (1) identifying the position and magnitude of the maximum local rates, which may have significant impacts on the variation of hydraulic properties, including formation of wormholes in dissolution problems, or the occurrence of clogging and diagenetic phenomena in precipitation or biological problems [e.g., *Kielland*, 1937; *Steefel and MacQuarrie*, 1996; *Kräutle and Knabner*, 2005]; (2) assessing the extent of the domain contributing to the observed process [e.g., *Sanford and Konikov*, 1989;

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Rezaei et al., 2005; *Guadagnini et al.*, 2009]; and (3) providing information about the rate of evolution of the system toward equilibrium conditions [e.g., *Wood and Sanford*, 1990; *Sanchez-Vila and Bolster*, 2009].

[5] A series of mathematical formulations to solve multicomponent reactive transport problems are available in the literature and included in a variety of codes [e.g., *Kinzelbach et al.*, 1991; *Yeh and Tripathi*, 1991; *Lichtner*, 1996; *Steefel and MacQuarrie*, 1996; *Tebes-Stevens et al.*, 1998; *Clement et al.*, 1998; *Saaltink et al.*, 1998, 2001; *Bea et al.*, 2009]. All these methodologies are based on the idea that reactive transport problems can be reformulated as follows: (1) defining the chemical system in terms of components (i.e., linear combinations of reactive species concentrations), because some of these components are conservative so their associated transport equations can be decoupled from the full system, whereas other components (termed kinetic components) are associated with kinetic reactions and cannot be completely decoupled; (2) solving the transport equations for the conservative components; (3) calculating the kinetic components by solving a nonlinear algebraic system of equations; (4) performing speciation calculations to obtain the concentration of aqueous species from the space-time distribution of components; and (5) substituting the latter into the transport equations to evaluate reaction rates numerically. This approach can be applied when the concentrations of the reacting species stand in algebraic relationship to each other and transport parameters are identical for all compounds (e.g., if an ADE were used, that would mean that all species are subject to the same advective velocity and diffusion and dispersion coefficients). The former requirement is met by systems either in local chemical equilibrium or instantaneous, complete, irreversible reactions [e.g., *Ham et al.*, 2004; *Liedl et al.*, 2005] and can also be used for specific cases of kinetic reactions [*Molins et al.*, 2004; *Cirpka and Valocchi*, 2007]. The latter implies that all solutes sample the same velocity field (which does not happen, for example, in colloidal transport) and mostly assumes that the effects of mechanical dispersion are much larger than those of diffusion, which might be species-dependent.

[6] A methodology to compute homogeneous and heterogeneous reaction rates directly under instantaneous equilibrium was presented by *De Simoni et al.* [2005, 2007] assuming that a conservative quantity satisfies an ADE. This approach was extended by *Donado et al.* [2009] for the MRMT transport equation. Their general expression for the reaction rates illustrates that mixing processes control equilibrium reaction rates. Direct calculation of the equilibrium reaction rates according to the methodology of *De Simoni et al.* [2005, 2007] only requires solving two independent problems: (1) the transport of one or more conservative species and (2) chemical speciation. The approach was used by *Guadagnini et al.* [2009] in conjunction with laboratory-scale $CaCO_3$ dissolution experiments performed in a homogeneous flow cell and reported by *Singurindy et al.* [2004] to predict the global reaction rate of the system and describe the spatial distribution of equilibrium reactions rates within the cell. Deconstructing the complete reactive transport problem into two independent ones (transport of conservative species and speciation) has additional advantages. For instance, *Fernàndez-Garcia et al.* [2008] and *Sanchez-Vila et al.* [2009] employed this deconstruction

process to obtain explicit expressions for the reaction rates and the probability density function of aqueous species concentrations in a randomly heterogeneous stratified medium, respectively.

[7] Whenever reactions do not occur under equilibrium conditions it is not possible to explicitly evaluate reaction rates. Still, it is possible to pose the problem so that reaction rates are the dependent variables. *Sanchez-Vila et al.* [2007] found that reaction rates can be obtained by solving a nonlinear partial differential equation in the case of a bimolecular system where two aqueous species react to produce noninstantaneous precipitation and/or dissolution of a mineral. When the kinetic reaction is fast, the latter equation can be solved by means of a perturbation expansion in terms of the inverse of the Damköhler number, where the leading-order term corresponds to the expression already provided by *De Simoni et al.* [2005] for instantaneous equilibrium.

[8] The methods discussed in the preceding two paragraphs illustrate that chemical systems are driven by disequilibrium. The latter may be caused by mixing of two waters that are in equilibrium with minerals in the system (scenario discussed by *De Simoni et al.* [2005, 2007]) or by the addition of a water that is not in equilibrium with one (or several) minerals. This scenario leads (in general) to kinetic dissolution-precipitation (as discussed by *Sanchez-Vila et al.* [2007]). Disequilibrium may also occur, causing the concomitant fast reactions to take place, when any of the species resulting from the aforementioned kinetic reactions take part in any of the fast reactions (common-ion effect). No expression for the reaction rates is currently available for this case.

[9] Here we develop an exact analytical expression for the reaction rates associated with a multicomponent reactive transport problem in the presence of both kinetic and equilibrium chemical reactions. In a real geochemical setup, selecting whether a reaction can be considered instantaneous is not a trivial task. Whenever several reactions take place simultaneously, the reaction characteristic times $\tau_{r,i}$ ($i = 1$, ..., N_r, where N_r is the number of reactions) span several orders of magnitude. In a given subsurface transport problem, one is typically concerned with a range of times which can be related to some transport characteristic time, τ_t. All reactions characterized by $\tau_{r,i} \ll \tau_t$ can be treated mathematically as being instantaneous. On the other hand, reactions associated with $\tau_{r,i} \gg \tau_t$ can generally be neglected (and the corresponding species taking part only in these reactions can be seen as conservative for all practical purposes). Thus, only reactions associated with characteristic times comparable to τ_t need to be treated as kinetically driven. On the basis of this reasoning, we consider here a system where only one reaction is kinetically controlled while allowing for any number of equilibrium reactions to take place simultaneously. The methodology could be extended to include the presence of more than one kinetic reaction.

[10] We start from the work of *Molins et al.* [2004] and *De Simoni et al.* [2005] and develop expressions for the space-time distribution of reaction rates for a two-reaction system, when only one reaction occurs under instantaneous equilibrium. The equilibrium reaction rate is expressed as a function of a mixing-related term, the distribution of (conservative and kinetic) components and the kinetic reaction

rate. To illustrate the methodology, the resulting expressions are then solved numerically to simulate a simple reactive transport scenario, in the presence of a kinetic and an equilibrium reaction taking place within a one-dimensional fully saturated porous medium. We conclude by presenting the generalization of the formulation for a multicomponent system characterized by an arbitrary number of equilibrium reactions and one kinetic reaction.

2. Two-Reactions Model

[11] The general formulation for a system involving several equilibrium reactions is presented in section 4. Here we discuss the solution for a particular two-reaction system, which facilitates presenting the general ideas and the benefits of the methodology. The system involves the precipitation or dissolution of two minerals $B_4^{(s)}$ and $B_5^{(s)}$ in the presence of three aqueous species, B_1, B_2, and B_3, one of them participating in both reactions (common ion effect). The reactions considered are

$$B_1 + B_2 \rightleftharpoons B_4^{(s)}, \tag{1}$$

$$B_1 + B_3 \rightleftharpoons B_5^{(s)}. \tag{2}$$

[12] We treat both minerals as pure phases so that their activity is unity. We consider reaction (1) to occur at equilibrium at all points in the domain. On the contrary, reaction (2) is considered "slow." We explicitly exclude the possibility that the mineral in equilibrium dissolves completely (this would mean a drastic change in the chemical system).

[13] The system consists, then, of five reacting species. According to *Molins et al.* [2004], any chemical system can be represented by means of the stoichiometric matrix **S** that can be divided into two matrices, $\mathbf{S}_e$ and $\mathbf{S}_k$, containing the equilibrium and kinetic reactions, respectively. In this particular problem this leads to

$$\mathbf{S} = \begin{bmatrix} \mathbf{S}_e \\ \mathbf{S}_k \end{bmatrix} = \begin{bmatrix} \overset{B_2}{1} & \overset{B_3}{0} & \overset{B_1}{1} & \overset{B_5^{(s)}}{0} & \overset{B_4^{(s)}}{-1} \\ 0 & 1 & 1 & -1 & 0 \end{bmatrix}. \tag{3}$$

[14] We use the classification of *Molins et al.* [2004] to distinguish the different species involved in the chemical system, which leads to the particular ordering of columns (in principle, an arbitrary choice) adopted in (3): (i) secondary aqueous species involved in the equilibrium reaction, B_2; (ii) primary kinetic aqueous species, B_3; (iii) general primary aqueous species, B_1; (iv) kinetic mineral, $B_5^{(s)}$; and (v) constant-activity species, $B_4^{(s)}$.

[15] The mass action law associated with (1) can be expressed as

$$K_e^* = a_1 a_2, \tag{4}$$

where a_i ($i = 1, 2$) is the activity of aqueous species i, and K_e^* is the equilibrium constant. The kinetic reaction rate associated with (2) is described by the model [e.g., *Knapp*,

1989; *Langmuir*, 1997; *Lasaga et al.*, 1994; *Steefel and Lasaga*, 1994; *Steefel and Vancappellen*, 1990]

$$r_k = S_S k_0 \left(1 - \frac{a_1 a_3}{K_k^*} \right), \tag{5}$$

where K_k^* is the equilibrium constant of the kinetic reaction, r_k is the kinetic reaction rate (positive if the mineral dissolves), S_S is the specific reactive surface of the mineral, and k_0 is the rate constant. In the limit $k_0 \rightarrow \infty$, (5) reduces to $K_k^* = a_1 a_3$, indicating that the reaction occurs in equilibrium. Coefficients K_e^* and K_k^* usually depend on temperature and pressure. For simplicity, they are assumed constant in this work. Activities (a_i) and concentrations of the ith aqueous species (c_i) are related through the activity coefficient γ_i. For moderately saline solutions the latter can be approximated, for example, by the extended Debye-Hückel model (actually different models are available). For dilute solutions or whenever the ionic strength I does not vary much in space and time, the geochemical problem can be cast in terms of concentrations rather than activities. Thus, introducing the apparent equilibrium and kinetic constants, $K_e = K_e^*/(\gamma_1 \gamma_2)$ and $K_k = K_k^*/(\gamma_1 \gamma_3)$, respectively, leads to

$$K_e = c_1 c_2, \tag{6}$$

$$r_k = S_S k_0 \left(1 - \frac{c_1 c_3}{K_k} \right). \tag{7}$$

[16] We consider transport of the three aqueous species to be described by the following equations:

$$\phi \frac{\partial c_1}{\partial t} = L(c_1) + r_e + r_k(c_1, c_3), \tag{8}$$

$$\phi \frac{\partial c_2}{\partial t} = L(c_2) + r_e, \tag{9}$$

$$\phi \frac{\partial c_3}{\partial t} = L(c_3) + r_k(c_1, c_3), \tag{10}$$

where ϕ is the medium porosity, r_e is the sink/source term associated with the equilibrium reaction, and r_k is the corresponding sink/source term associated with the kinetic reaction, which depends on (c_1, c_3). Without loss of generality, we consider the transport operator $L(c_i)$ to be given by the advection-dispersion equation; that is,

$$L(c_i) = -\mathbf{q}\nabla c_i + \nabla \cdot (\mathbf{D}\nabla c_i), \tag{11}$$

where $\mathbf{q}$ and $\mathbf{D}$ are Darcy's flux and the diffusion/dispersion tensor, respectively.

[17] The solution of the problem then entails solving five coupled nonlinear equations, (6)–(10), in terms of the five unknowns (c_1, c_2, c_3, r_e, r_k). Following the approach of *Molins et al.* [2004], it is possible to partially decouple the system of equations upon introducing master species (also termed components). These are defined as linear combinations of the species concentrations that remain unaffected by

equilibrium reactions and allow full definition of the chemical state of the aqueous system. The idea of *Molins et al.* [2004] is to define a set of components, termed conservative, $\mathbf{u}_e$, that also remain unaffected by kinetic reactions. These are defined in terms of the component matrix $\mathbf{U}$ as

$$\mathbf{u}_e = \mathbf{U}\mathbf{c}, \qquad (12)$$

where $\mathbf{U}$ is chosen so that $\mathbf{U}\mathbf{S}^T = 0$. The details of the methodology are presented in the Appendix. In the two-reaction model, one can define a single conservative component,

$$u_e = c_2 + c_3 - c_1. \qquad (13)$$

[18] We note that simply adding equations (9) and (10) and subtracting (8) leads to the equation governing the transport of the conservative component; that is,

$$\phi \frac{\partial u_e}{\partial t} = -\mathbf{q}\nabla u_e + \nabla \cdot (\mathbf{D}\nabla u_e). \qquad (14)$$

In other words, dissolution or precipitation of two minerals $B_4^{(s)}$ and $B_5^{(s)}$ affects the individual concentrations of the three aqueous species, B_1, B_2, and B_3, but does not alter the space-time distribution of u_e. Equation (14) is fully decoupled from the five-dimensional complete coupled system and can be solved independently.

[19] The introduction of a kinetic component u_k, defined as (see Appendix)

$$u_k = c_3 - u_e = c_1 - c_2, \qquad (15)$$

allows further reduction of the dimensionality of the coupled problem. Subtracting (9) from (8) yields the governing equation for this component:

$$\phi \frac{\partial}{\partial t} u_k = L(u_k) + r_k(u_k, u_e). \qquad (16)$$

Here we have written r_k as a function of u_k and u_e because components fully describe the aqueous system and concentrations can be derived from them. In fact, using (6) and (15) leads to the following relationships between the aqueous species concentrations c_1 and c_2 and u_k:

$$c_1 \equiv f_1(u_k) = \frac{u_k}{2} + \frac{\sqrt{u_k^2 + 4K_e}}{2},$$
$$c_2 \equiv f_2(u_k) = -\frac{u_k}{2} + \frac{\sqrt{u_k^2 + 4K_e}}{2}. \qquad (17)$$

[20] Using (17) for c_1 and expressing $c_3 = u_k + u_e$ and substituting in (7) allows the kinetic reaction rate to be expressed in terms of the two components u_e and u_k as

$$r_k = S_s k_0 \left[1 - \frac{u_k + u_e}{2K_k} \left(u_k + \sqrt{u_k^2 + 4K_e} \right) \right]. \qquad (18)$$

[21] Finally, using the mass balance equation of c_2 (9) together with (16) leads, after some algebraic manipulations performed along the lines of the work of *De Simoni*

et al. [2005], to the following expression relating the equilibrium and kinetic reaction rates:

$$r_e(\mathbf{x}, t) = \frac{\partial c_2}{\partial u_k} r_k(u_e, u_k) - \frac{\partial^2 c_2}{\partial u_k^2} \nabla^T u_k \mathbf{D}\nabla u_k. \qquad (19)$$

[22] We note that the derivatives of concentrations with respect to the kinetic component can be written explicitly as

$$\frac{\partial c_2}{\partial u_k} \equiv \frac{\partial c_1}{\partial u_k} - 1 = -\frac{1}{2} + \frac{u_k}{2\sqrt{u_k^2 + 4K_e}},$$
$$\frac{\partial^2 c_2}{\partial u_k^2} \equiv \frac{\partial^2 c_1}{\partial u_k^2} = \frac{2K_e}{\left(u_k^2 + 4K_e\right)^{3/2}}. \qquad (20)$$

[23] The equilibrium reaction rate (19) incorporates two terms: the first one accounts for the influence of the reactants being released noninstantaneously to the system by the kinetic reaction, and the second one accounts for mixing of the kinetic component.

[24] In essence, the complete analysis of these types of precipitation/dissolution processes in the presence of an instantaneous equilibrium and a kinetic reaction entails deconstructing the problem according to the following steps:

[25] 1. Solve equation (14) for the conservative component u_e.

[26] 2. Solve equation (16) for u_k, using (18) for r_k.

[27] 3. Perform chemical speciation using (17) to obtain c_1 and c_2.

[28] 4. Compute $c_3 = u_e + u_k$.

[29] 5. Finally, the reaction rates r_k and r_e can be obtained by either of the following alternative ways: (a) explicit calculation from (18) and (19) or (b) by mass balance arguments from (9) and (10).

[30] The critical point in the procedure is then step 2, i.e., the computation of u_k by means of (16). The latter equation is nonlinear and in general should be solved numerically. It follows that the methodology we present replaces the problem of solving a coupled problem involving the simultaneous solution of three partial differential equations (PDEs) plus two nonlinear equations [equations (6)–(10)], with the successive (and thus decoupled) solution of a linear conservative PDE, a nonlinear PDE, and a set of explicit algebraic expressions. The advantage of using this decoupled option with respect to the coupled one should be further explored in practical applications.

[31] Finally, we note that direct calculation of reaction rates according to step 5a by means of our equations (18) and (19) does not require calculation of the actual species concentrations. Therefore, if one is only interested in assessing reaction rates, there is no need to compute aqueous species concentrations. The choice of steps 5a or 5b in general depends on the solution scheme. Following option 5a is better suited for analytical approaches, whereas option 5b may be preferred in the context of numerical approaches.

[32] A final comment involves the possibility of the chemical system changing in space or time, related for example to the complete dissolution of one of the minerals. If it actually occurred, one would need to redefine the chemical system at any given time, which would become spatially dependent (the problem domain would become divided in subdomains with different chemical systems). In

Table 1. Ion Size Parameters and Activity Coefficients of the Solutes for Ionic Strength $I = 0.1$ mol kg^{-1}

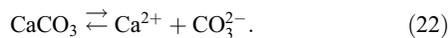| Species	Ca^{2+}	SO$_4^{2-}$	CO$_3^{2-}$
Ionic radius, $\overset{\circ}{a_i}$ (Å)	6	4	5
Activity coefficient, γ_i	0.68	0.90	0.67

this case, the system of components is different for every subdomain (as discussed by *Rubin* [1983]).

3. Application Example

3.1. Description of the Chemical System

[33] This section is devoted to illustrating the methodology presented in section 2 by way of a simplified example, patterned according to the two-reaction system described in (1) and (2). The system we consider is inspired by the calcite-gypsum system. The actual calcite-gypsum system is geochemically complex and involves a large number of aqueous species and minerals. In this context, we emphasize that our aim is not to solve the complete calcite-gypsum system but rather to convey the key functional dependences encapsulated in (19) through a simple scenario. Section 4 is then devoted to a more general derivation and discussion of a general geochemical system involving a large number of reactions.

[34] Typically, the presence of aqueous concentrations of calcium [Ca^{2+}] and sulphate [SO$_4^{2-}$] ions under saturated conditions causes gypsum to precipitate. This precipitation reaction is faster than calcite dissolution, and it is usually a good approximation to consider local equilibrium conditions for Ca^{2+} and SO$_4^{2-}$ [*Skoulikidis and Beloyannis*, 1984] at all times. In this spirit, we note that under high-pH conditions some key characteristics of the calcite-gypsum precipitation/dissolution can be grasped by analyzing the following two reactions:

$$CaSO_4 \cdot 2H_2O \underset{\rightharpoonup}{\leftharpoonup} Ca^{2+} + SO_4^{2-} + 2H_2O, \qquad (21)$$

$$CaCO_3 \underset{\rightharpoonup}{\leftharpoonup} Ca^{2+} + CO_3^{2-}. \qquad (22)$$

[35] Here we consider reaction (21) to occur at equilibrium, while (22) is modeled as a kinetic (slow) process. On the basis of (3), the system can be characterized by the following stoichiometric matrix:

$$
\mathbf{S} = \left(\frac{\mathbf{S}_e}{\mathbf{S}_k} \right) = \begin{pmatrix} \overset{SO_4^{2-}}{1} & \overset{CO_3^{2-}}{0} & \overset{Ca^{2+}}{1} & \overset{CaCO_3^{(s)}}{0} & \overset{CaSO_4 \cdot 2H_2O^{(s)}}{-1} \\ 0 & 1 & 1 & -1 & 0 \end{pmatrix} . \qquad (23)
$$

[36] Activity coefficients of the aqueous species involved in the system can be calculated, for example, on the basis of the Debye-Hückel equation. Table 1 reports the values adopted for the ionic radius, $\overset{\circ}{a_i}$, of the *i*th species appearing in (21) and (22) and the resulting activity coefficients. Albeit not required by our methodology, and because our interest lies in illustrating the key features of (19), we consider a

constant ionic strength at all points, i.e., $I = 0.1$ mol kg$^{-1}_{[H_2O]}$. It is also worth noting that changes in ionic strength are limited under the conditions of our example.

[37] The apparent equilibrium constants we selected are $\log K_e = -4.62$ for gypsum and $\log K_k = -8.35$ for calcite [*Morel and Hering*, 1993]. We adopted a value of $S_S k_0 = 4.64 \times 10^{-7}$ mol g^{-1} s^{-1} [*Steefel and Lasaga*, 1994]. The porosity of the host porous medium is set to 0.12. In our application we assume that modification in the solid mass due to transport involves very thin layers of the matrix [*Rubin*, 1983] and no significant variations of the pore system occur. If porosity variations occurred, the methodology could still be applied by just incorporating the variations in flow with time caused by the progressive changes in porosity induced by precipitation.

3.2. Transport Problem and Dimensional Analysis

[38] We model transport within a one-dimensional column packed with a combination of calcite and gypsum so that both minerals are available for dissolution at all points. The analysis is performed upon introducing dimensionless space-time coordinates and state variables. Table 2 reports the key dimensionless variables of interest, indicated as primed quantities. Dimensionless components are then defined as

$$u_e' = c'_{[SO_4^{2-}]} + c'_{[CO_3^{2-}]} - c'_{[Ca^{2+}]}, \quad u_k' = c'_{[CO_3^{2-}]} - u'. \qquad (24)$$

[39] Rewriting (24) using dimensionless quantities introduced in Table 2 leads to

$$\phi \frac{\partial u'_e}{\partial t'} = -Pe \frac{\partial u'_e}{\partial x'} + \frac{\partial^2 u'_e}{\partial x'^2}, \qquad (25)$$

Table 2. Characteristic Time Scales and Dimensionless Variables Used in the Computational Example of the Two-Reaction Model[a]

Characteristic time scales	
Diffusive time	$\tau_d = L^2/D$
Advective time	$\tau_a = L/q$
Reactive time	$\tau_r = \sqrt{K_k}/(S_S k_0)$
Dimensionless variables	
Péclet number	$P_e = \tau_d/\tau_a = qL/D$
Damköhler number	$Da = \tau_d/\tau_r = Pe\,\tau_d/\tau_r$
Dimensionless time	$t' = t/\tau_d$
Dimensionless distance	$x' = x/L$
Relative equilibrium reaction constant	$K^*_{12} = K_e/(\gamma_1\gamma_2)$
Relative kinetic reaction constant	$K^*_{13} = K_k/(\gamma_1\gamma_3)$
Dimensionless equilibrium reaction constant	$K_{12} = K^*_{12}/K_G$
Dimensionless kinetic reaction constant	$K_{13} = K^*_{13}/K_G$
Relative equilibrium constant	$K_r = K^*_{12}/K^*_{13}$
Dimensionless concentration (species i)	$c'_i = c_i/\sqrt{K_G}$
Dimensionless reaction rate ($j = e, k$)	$r'_j = r_j\tau_d/\sqrt{K_G}$

[a]L is the length of the column, x is the space coordinate, $c_1 = c_{[Ca^{2+}]}$, $c_2 = c_{[SO_4^{2-}]}$, $c_3 = c_{[CO_3^{2-}]}$, and $K_G = \sqrt{K^*_{12}K^*_{13}}$.
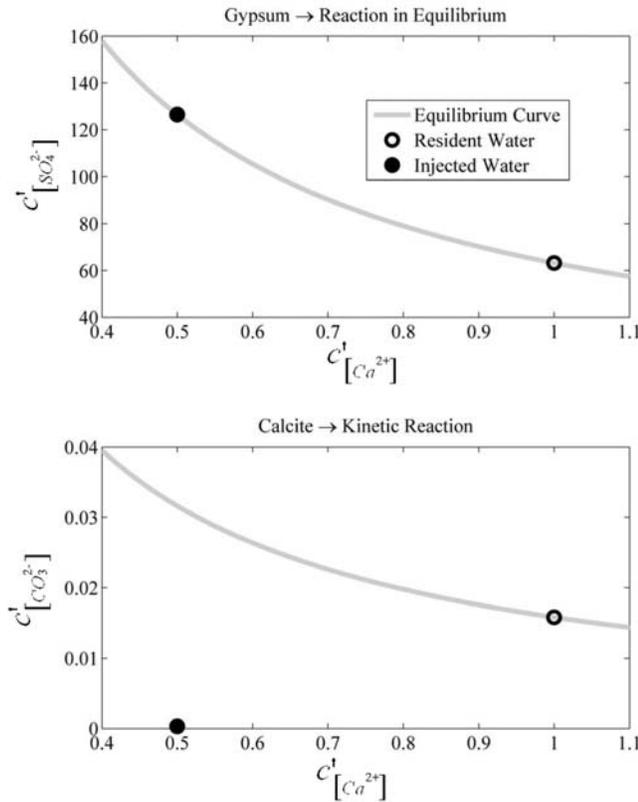
Figure 1. Chemical signatures of the waters involved in the example presented. Equilibrium curves in (dimensionless) concentration space are also included. The resident water is in equilibrium with respect to both minerals; the injected water is in equilibrium with respect to gypsum and undersaturated with respect to calcite. Notice the different scales used in the axes.

which is solved for given initial and boundary conditions in section 3.3. By the same token, the equation satisfied by the kinetic component can be written as

$$\phi \frac{\partial u'_k}{\partial t'} = -Pe \frac{\partial u'_k}{\partial x'} + \frac{\partial^2 u'_k}{\partial x'^2} + r'_k. \qquad (26)$$

[40] The expressions for $c'_{[\text{Ca}^{2+}]}$, $c'_{[\text{SO}_4^{2-}]}$, and r'_k are

$$c'_{[\text{Ca}^{2+}]} = \frac{u'_k + \sqrt{u'^2_k + 4K_{12}}}{2},$$

$$c'_{[\text{SO}_4^{2-}]} = \frac{-u'_k + \sqrt{u'^2_k + 4K_{12}}}{2}, \qquad (27)$$

$$r'_k = Da \, K_r^{1/4} \left(\frac{1}{K_r^{1/2}} - c'_{[\text{Ca}^{2+}]} c'_{[\text{CO}_3^{2-}]} \right). \qquad (28)$$

[41] Once r'_k is estimated, r'_e can be computed as

$$r_e'(x,t) = \left(\frac{\partial^2 c'_{[\text{Ca}^{2+}]}}{\partial u_k'} - 1 \right) r_k' - \frac{\partial^2 c'_{[\text{Ca}^{2+}]}}{\partial u_k'^2} \left(\frac{\partial u_k'}{\partial x} \right)^2, \qquad (29)$$

and the derivatives appearing in (29) can be computed explicitly from (27).

3.3. Numerical Solution

[42] The numerical solution of a particular problem is presented here to illustrate the methodology. For the purpose of our illustration we consider a highly diffusive system ($Pe = 0.1$) to enhance the relevance of reaction rates.

[43] Water is initially in equilibrium with respect to calcite and gypsum. The values for initial (resident) normalized concentrations are $c'_{[\text{Ca}^{2+}]}|^{t=0} = 1$, $c'_{[\text{SO}_4^{2-}]}|^{t=0} = 63.229$, and $c'_{[\text{CO}_3^{2-}]}|^{t=0} = 0.0158$. With these values the initial concentrations of the conservative and kinetic components are then $u'_e|^{t=0} = 62.2448$ and $u'_k|^{t=0} = -62.229$.

[44] Water undersaturated with respect to calcite and saturated with respect to gypsum is continuously introduced in the system at the inlet ($x' = 0$) starting at time $t = 0$. Concentration values for the injected water are taken as $c'_{[\text{Ca}^{2+}]}|_{x=0} = 0.5$, $c'_{[\text{SO}_4^{2-}]}|_{x=0} = 126.458$, and $c'_{[\text{CO}_3^{2-}]}|_{x=0} = 0.00031631$. With these concentrations, the boundary conditions are $u'_e|_{x=0} = 125.9583$ and $u'_k|_{x=0} = -125.958$ for the conservative and kinetic components, respectively. Figure 1 (top) juxtaposes the initial and boundary conditions to the corresponding equilibrium curves in ($c'_{[\text{Ca}^{2+}]}$, $c'_{[\text{SO}_4^{2-}]}$) space. The corresponding depiction in the ($c'_{[\text{Ca}^{2+}]}$, $c'_{[\text{CO}_3^{2-}]}$) space is also reported in Figure 1. The setup thus corresponds to a water that is initially in chemical equilibrium with the two minerals and is displaced by water that is undersaturated with respect to calcite and saturated with gypsum.

[45] The solution of the reactive transport problem involves solving the nonlinear PDE (29). We solve it by means of an implicit predictor-corrector approach relying on a forward finite difference for time and a central finite difference scheme for space.

3.4. Analysis of the Results

[46] We start by examining the evolution of the aqueous concentrations of the species taking part in the kinetic reaction in the ($c'_{[\text{Ca}^{2+}]}$, $c'_{[\text{CO}_3^{2-}]}$) plane. Figure 2 depicts the pathlines characterizing the temporal evolution of the state of the chemical system for three selected locations along the column and three values of the Damköhler number, Da. As a reference, the equilibrium curve is reported, together with the compositions of the initial (resident) and injected water. Pathlines are defined here as the collection of concentration (pair) values that a given point in the column samples with time. In our example, all of them originate from the point corresponding to the chemical signature of the resident water and move leftward with time (time increases along the direction of the arrows in Figure 2). We note that for small values of Da, i.e., $Da = 10^{-2}$, the kinetic reaction is very slow, and all pathlines (corresponding to $x' = 0.05, 0.5, 0.95$) tend toward the point corresponding to the injected (boundary) water. This indicates that advection processes dominate with respect to chemical reaction. Notice that the final point (which corresponds to infinite time) of the pathlines does not correspond exactly to that of the injected water, because some amount of reaction still takes place in the system.

[47] The picture changes as Da increases. For intermediate values of Da, the final point of a pathline lies somewhere in between the one corresponding to the injected water and the equilibrium curve. We note that pathlines tend to lie closer
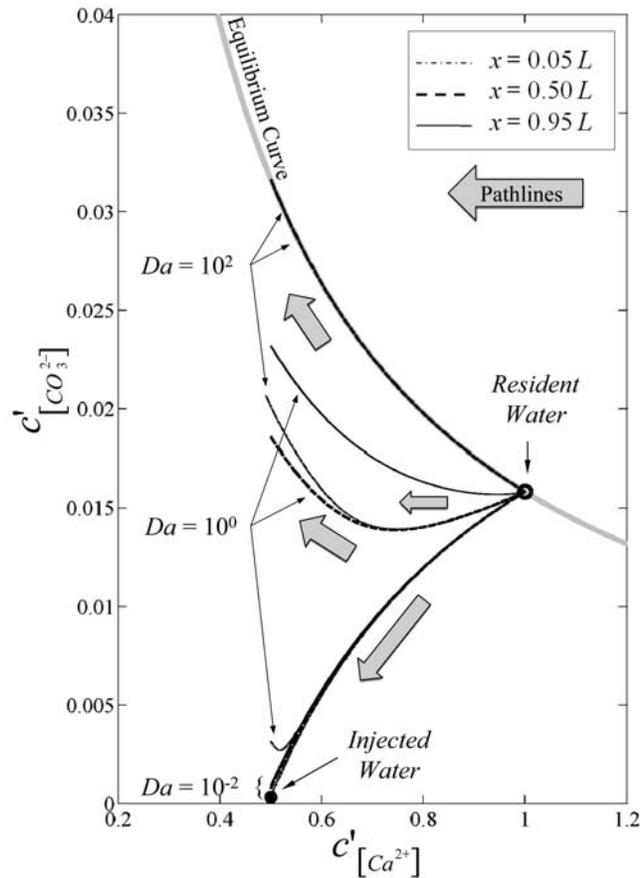
Figure 2. Pathlines characterizing the temporal evolution of the state of the chemical system in the ($c'_{[Ca^{2+}]}$, $c'_{[CO_3^{2-}]}$) plane and for three selected locations along the column and three values of the Damköhler number, Da. As a reference, the equilibrium curve is reported, together with the compositions of the initial (resident) and injected water. Time increases along the direction of the arrow along each pathline. For small Da values, water eventually reaches a chemical signature very close to that of the injected water. For large Da values and at some distance from the inlet, the resulting water is close to chemical equilibrium.

to the equilibrium curve as the distance between the observation point and the inlet boundary increases. This is associated with the fact that the system has more time to equilibrate. It is interesting to observe that some of the pathlines in Figure 2 are associated with a nonmonotonic distribution of values of $c'_{[CO_3^{2-}]}$ sampled with time. This indicates an initial decrease in $c'_{[CO_3^{2-}]}$, followed by an increase at a later time. Obviously, the system is close to equilibrium at all times for very large values of Da, except very close to the inlet point, and pathlines at all points lie near the equilibrium curve. Moreover, all curves end at a similar (albeit not exactly equal) value of $c'_{[Ca^{2+}]}$. This result is a particular consequence of the equilibrium constants ratio we adopted in the example, $K_e \gg K_k$. In general, the pattern of the results may change according to the relative strength of K_e and K_k.

[48] Figure 3 depicts the time evolution of the equilibrium and kinetic components (u'_e and u'_k) at three different locations within the column for $Da = 1$. Figure 4 depicts the details of

the large (dimensionless) time behavior of u'_k. Notice that the asymptotic value tends to increase with Da and travel distance.

[49] Once the components have been calculated, the concentrations of the different species can be obtained as outlined in section 2. Figure 5 depicts the temporal variation of the normalized concentrations of the aqueous species at different points along the column.

[50] It can be seen that although the impact of the Damköhler number on $c'_{[Ca^{2+}]}$ and $c'_{[SO_4^{2-}]}$ is negligible (relative differences between different curves are very small and cannot be discerned because of the scale of representation), the concentration of carbonate ($c'_{[CO_3^{2-}]}$) depends strongly on Da and relative differences between the calculated curves are very large.

[51] We note that the arrival of the inflow water, which is undersaturated with respect to calcite, can cause in some cases a drop in the concentrations of both Ca^{2+} and CO_3^{2-} concentrations. Dissolution of calcite can then cause a rebound in carbonate concentration, which displays a tendency to increase in time, depending on location and Da (which is seen particularly for short distances from the inlet and for moderate to large Da, i.e., $Da = 10^0$, 10^2). The observed rebound does not occur for Ca^{2+}, which is consumed by gypsum precipitation. We observe that the extraction of Ca^{2+} causes further dissolution of calcite, to the point that for high Da or short travel distances the asymptotic concentration of CO_3^{2-} is higher than that of either input or resident waters.

[52] The temporal behavior of normalized kinetic and equilibrium reaction rates is shown in Figure 6. Gypsum precipitation rate r'_e, despite occurring at equilibrium, is (nonmonotonically) affected by Da because it depends on the interplay between transport and reaction characteristic times, which ultimately govern the evolution of the system. In the limit for large Damköhler numbers the equilibrium reaction rate tends to the solution presented by De Simoni et al. [2005] for a bimolecular reaction system. An important feature of the system is that r'_e tends to (negative) nonzero (albeit in some cases very close to zero) asymptotic values for large times. This is particularly clear for intermediate values of Da at $x = 0.5$ (Figure 6e). Likewise, the kinetic reaction rate depends on Da and tends to a positive asymptotic value (Figures 6a–6c). This is equivalent to stating that the system is always active also in the limit for large times, because a kinetic reaction always takes place in order to preserve local equilibrium conditions. As a consequence, the late-time concentrations $c'_{[Ca^{2+}]}$ and $c'_{[SO_4^{2-}]}$ are generally different (albeit only slightly, in the analyzed scenario) from those of the input (external) water.

4. General Formulation

[53] We now extend the methodology illustrated in section 2 to describe multispecies transport processes in the presence of generic homogeneous and classical heterogeneous reactions. Chemical equilibrium is defined in terms of the mass action law, relating reactants and products. Following the notation introduced in section 2, one can write

$$\log \mathbf{K}^* = \log \mathbf{K} - \mathbf{S}_{ea} \log \gamma(\mathbf{c}_a), \tag{30}$$

where $\mathbf{S}_{ea}$ is an $N_e \times N_{sa}$ matrix (N_e and N_{sa} being the number of equilibrium reactions and the number of aqueous
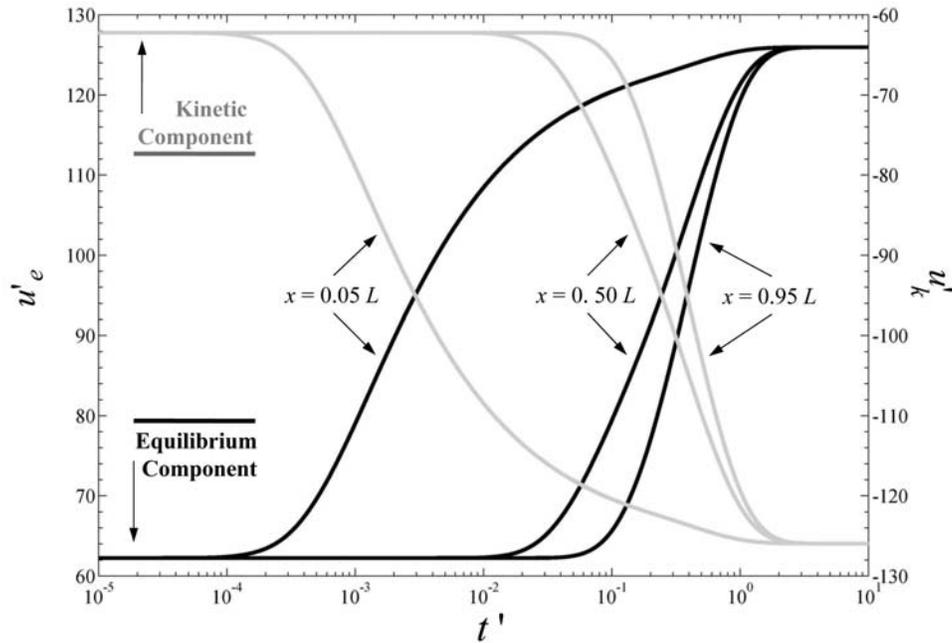
Figure 3. Evolution of equilibrium and kinetic components with (dimensionless) time at three different locations along the column and $Da = 1$.

species in the system, respectively) containing the stoichiometric coefficient of equilibrium reactions; c_a is the vector of concentrations of aqueous species; K and K^* are the vectors of equilibrium and equivalent equilibrium constants, respectively; and γ is the vector of activity coeffi-

cients. The stoichiometry of kinetic reactions is typically included in the kinetic stoichiometric matrix, S_k of size $N_k \times N_s$, where N_k and N_s are the number of kinetic reactions and the total number of species, respectively, including aqueous and constant activity (in our formulation we have not
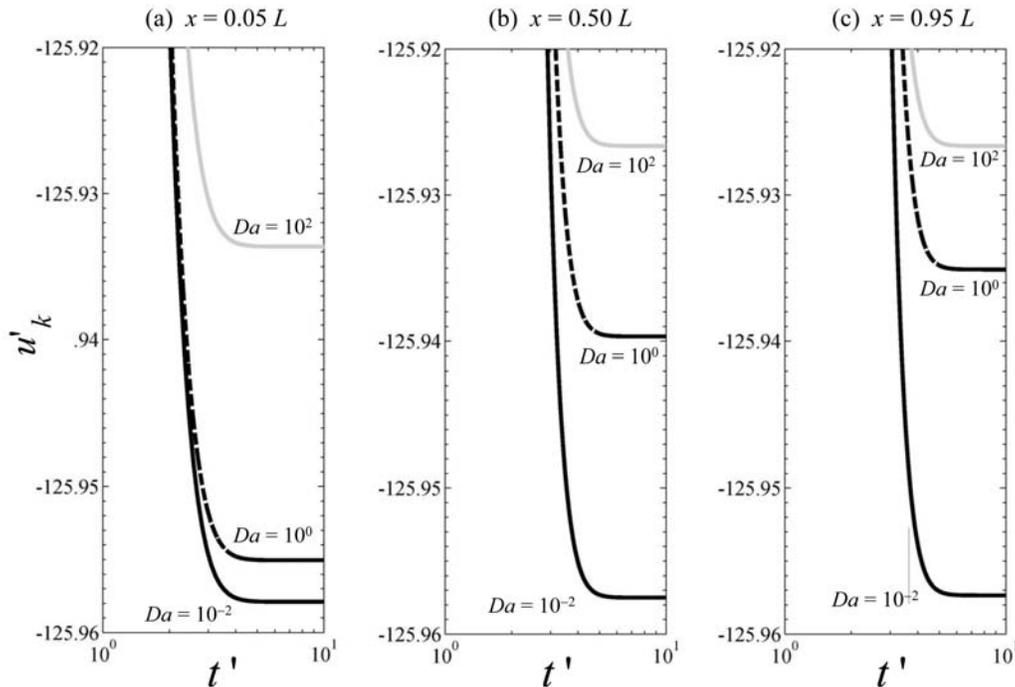

Figure 4. Details of the large time evolution of the kinetic component at three different locations along the column and for three values of Da. Notice (vertical scale) that even though the quantitative variations are not very large, they result in relevant detectable differences in reaction rates (see Figure 6).
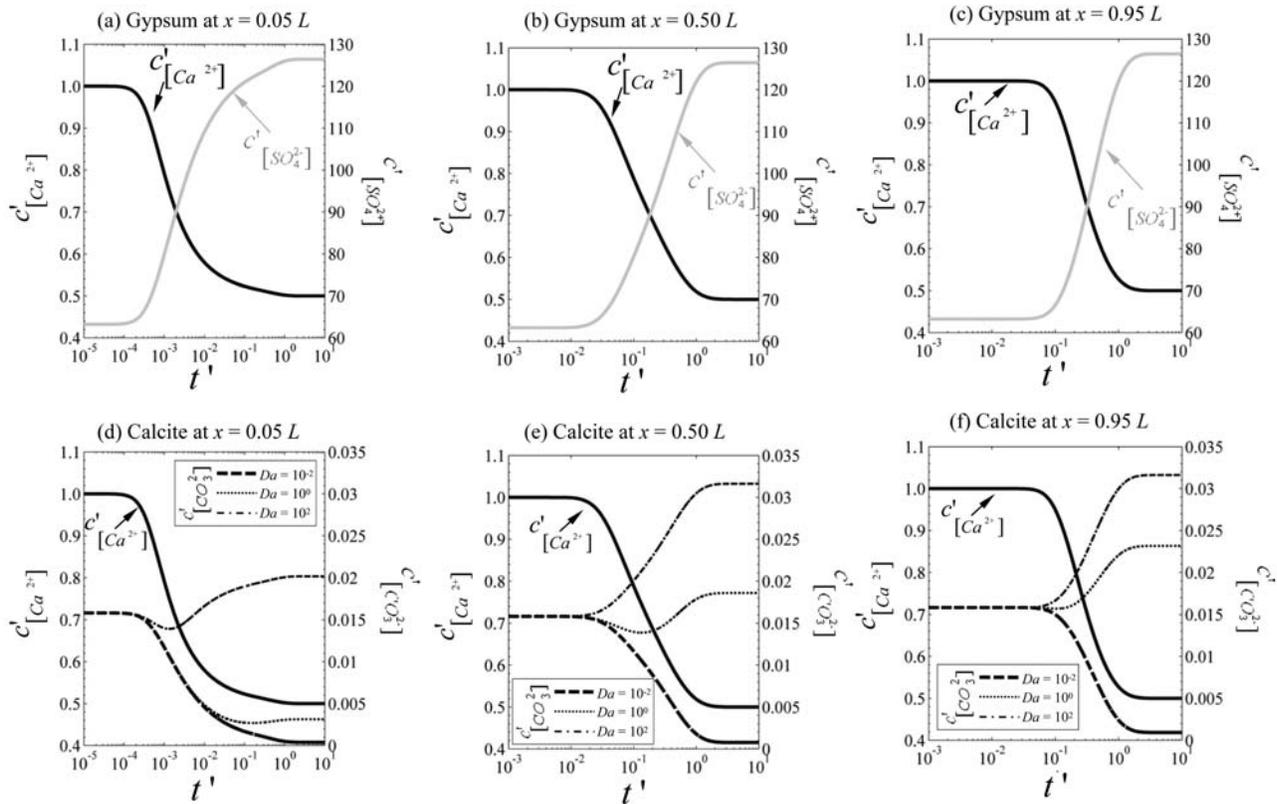
Figure 5. Temporal evolution of the normalized aqueous concentrations for three different locations along the column and three values of Da.

included the presence of immobile species with nonconstant activity). Mass balances for all species are expressed as

$$\phi \frac{\partial \mathbf{c}}{\partial t} = \mathbf{M}L(\mathbf{c}) + \mathbf{S}_e^T \mathbf{r}_e + \mathbf{S}_k^T \mathbf{r}_k(\mathbf{c}), \qquad (31)$$

where $\mathbf{c}$ is the vector of species concentrations (size N_s); ϕ is the porosity of the medium; $\mathbf{M}$ is a diagonal matrix, with diagonal terms equal to unity for mobile species and zero otherwise; $\mathbf{r}_e$ and $\mathbf{r}_k$ are the equilibrium and kinetic reaction rates vectors, respectively; and superscript T denotes transpose. Upon considering transport in a single aqueous phase and that all species are subject to the same transport parameters, the linear operator $L(\ )$ is defined as in (11).

[54] In the following we assume that the geochemical system can be described by N_e reactions occurring at equilibrium in the presence of one kinetic reaction; that is, $N_k = 1$. This situation is frequently encountered in natural aquatic systems, where the evolution of the whole system is controlled by the rate of one reaction which is notably slower than the rest. Examples include systems where a particular biogeochemical reaction is dominant and slower than precipitation/dissolution [e.g., *Cirpka et al.*, 1999; *Cirpka and Valocchi*, 2007]. Our aim is to evaluate the expressions for rates of the equlibrium and kinetic reactions, generalizing the results presented in section 2 to take into account an arbitrary number of equilibrium reactions. The resulting expressions can alternatively be seen as a generalization of the work by *De Simoni et al.* [2005], with an arbitrary number of equilibrium reactions, in order to

include a kinetic reaction. As we did for the two-reaction model, we adopt sequentially the chemical paradigms of *Molins et al.* (2004), as described in the following (see the Appendix).

[55] 1. Equilibrium reaction rates are eliminated, and the number of unknowns in (31) is reduced (in the notation of *Molins et al.* [2004], this step is called the Tank Paradigm).

[56] 2. After step 1, the presence of the kinetic reaction rate still preserves the fully coupled nature of the system. Application of the Canal Paradigm [*Molins et al.*, 2004] procedure allows decoupling the $N_c = N_s - N_e - N_k$ equations satisfied by conservative components from the N_k transport equations governed by the kinetic reaction rate. This allows calculating the conservative components upon solving N_c independent conservative transport equations. Still, this step would involve solving the N_k reactive transport equations (where the kinetic rate is a function of species concentrations) together with the N_e chemical expressions (30) and the N_c definitions of conservative components.

[57] 3. By applying the River and Aquifer Paradigms procedure, it is possible to eliminate both the kinetic and constant-activity species from the system. This leads to a fully decoupled problem that can be solved in steps similar to those proposed in section 2 for the two-reaction model. This procedure yields the space-time distribution of equilibrium and kinetic reaction rates from the numerical solution of (31) once the vector $\mathbf{c}$ is known.

[58] As shown by *Molins et al.* [2004], the chemical system can always be written in such a way that one secondary species is associated with an equilibrium reaction. For
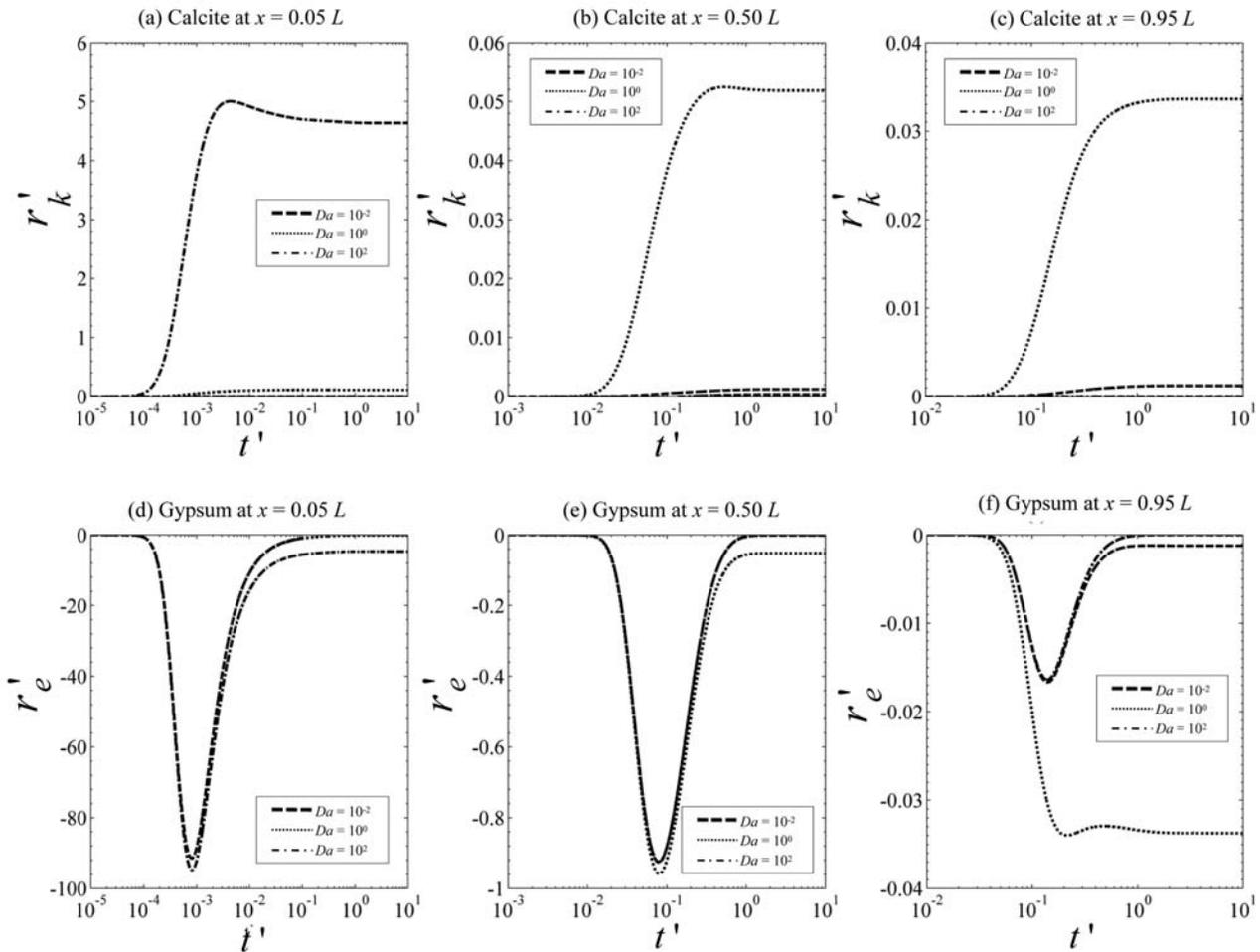
Figure 6. Temporal evolution of the normalized kinetic and equilibrium reaction rates at three different locations along the column and three values of Da. Notice the significant differences in vertical scales for each plot.

simplicity, we take the equilibrium and kinetic constants independent of temperature and pressure. We further assume that S_s and k_0 are constant in space and time [e.g., *Lasaga*, 1984; *Steefel and Lasaga*, 1994; *Lichtner*, 1996; *Mayer et al.*, 2002; *Giovangigli and Massot*, 2004]. This allows writing the transport equation for the secondary species, $\mathbf{c}_e$, as

$$\phi \frac{\partial \mathbf{c}_e}{\partial t} = L(\mathbf{c}_e) + \mathbf{r}_e. \qquad (32)$$

Expanding $\mathbf{c}_e$ as a function of $\mathbf{u}$, where $\mathbf{u}^T = (\mathbf{u}_e^T, u_k)$ is the vector including all (conservative and kinetic) components, yields

$$\frac{\partial \mathbf{c}_e}{\partial \mathbf{u}} \cdot \left[\phi \frac{\partial \mathbf{u}}{\partial t} - L(\mathbf{u}) \right] = \frac{\partial^2 \mathbf{c}_e}{\partial \mathbf{u}^2} \nabla^T \mathbf{u}\, \mathbf{D}\, \nabla \mathbf{u} + \mathbf{r}_e. \qquad (33)$$

We note the left-hand side of (33) vanishes for all components but u_k, which satisfies equation (16). Substituting (16) into (33) yields

$$\mathbf{r}_e = \frac{\partial \mathbf{c}_e}{\partial u_k} r_k - \frac{\partial^2 \mathbf{c}_e}{\partial \mathbf{u}^2} \nabla^T \mathbf{u}\, \mathbf{D}\, \nabla \mathbf{u}. \qquad (34)$$

[59] This equation generalizes (19) and is interesting for several reasons. The first term represents the contribution of reactants from the kinetic reaction to the equilibrium (fast) reaction. The second one represents the contribution of mixing. Both terms are quite straightforward to compute. The only factors that are potentially hard to evaluate are the derivatives of the secondary species with respect to the components. Computing these might require speciation codes that allow any kind of components. These include, for example, RETRASO [*Saaltink et al.*, 2001] or CHEPROO [*Bea et al.*, 2009]. Regardless of the way one evaluates it, equation (34) explicitly recognizes that fast reactions are driven not only by mixing but also by the contribution of kinetic reactions. In the absence of the latter, one immediately recovers from (34) the expression of *De Simoni et al.* [2005], where the reaction is solely driven by mixing. This situation may occur, for example, when a slowly reacting mineral is exhausted in the system. In such a case r_k would become zero, and u_k would become conservative in the portions of the system where the mineral has been exhausted.

[60] The formulation provided by (34) is quite general. It can be used in cases where high-ionic-strength gradients are

present in the system, provided that salinity is treated as an additional component that obeys the same transport equation as the remaining ones. The equation may need modification (along the lines discussed by *De Simoni et al.* [2005]) in the presence of temperature gradients, because temperature in general does not obey the same transport equation as chemical species. Equation (34) is locally valid even in the case where the domain is divided into zones characterized by the occurrence of different chemical systems, controlled by different equilibrium mineral assemblages [*Rubin*, 1983]. In this case, however, it would not be possible to solve analytically for the equilibrium components, which would be different in each mineral zone, and numerical methods would be required.

5. Conclusions

[61] Our work leads to the following major conclusions:

[62] 1. The methodology we propose allows exact explicit expressions of the space-time distribution of reaction rates to be obtained when the geochemical system can be described by N_e reactions occurring at equilibrium in the presence of one kinetic reaction. The equilibrium reaction rate is then expressed as a function of a mixing-related term, the distribution of (conservative and kinetic) components, and the kinetic reaction rate.

[63] 2. The complete analysis of the analyzed reactive transport problem entails deconstructing it according to a sequence of decoupled steps. A key point of the procedure is that it eliminates the need to compute aqueous concentrations if one is only interested in assessing reaction rates. Our formulation explicitly recognizes that equilibrium reactions are in general driven not only by mixing but also by the contribution of kinetic reactions.

[64] 3. From a computational standpoint, the critical point in the procedure leading to (34) is the computation of the reactive component, u_k, which satisfies a highly nonlinear PDE. In general, the latter should be solved numerically. It follows that the numerical accuracy associated with the direct evaluation of reaction rates for a complex geochemical system should be further explored. Furthermore, the functional dependencies embedded in (34) might change in the presence of temperature gradients, because temperature in general does not obey the same transport equation as chemical species. Notwithstanding the aforementioned drawbacks, (34) is quite general.

[65] 4. The methodology is illustrated upon considering a simplified example, which is inspired by the calcite-gypsum system. For illustration purposes, we simplify the otherwise complex system by means of a two-reaction model. The transport of reactive species is then solved to simulate the kinetic dissolution of one mineral (calcite) in the presence of water geochemically equilibrated with a second mineral (gypsum) within a one-dimensional column. The solution is offered in terms of relevant dimensionless parameters controlling the system, highlighting the role of the heavily nonlinear interplay between characteristic transport and reaction times. A key finding is that the system is always active in the limit for large times, because the reactants kinetically interact in order to preserve local equilibrium conditions.

Appendix A: Decoupling of the Two-Reaction Model

[66] Following the methodology and terminology of *Molins et al.* [2004], the problem can be decoupled by the sequential application of four paradigms.

A1. Tank Paradigm

[67] In this part of the methodology, the conservative components (only one in our problem) are defined, and the kinetic constant activity species is left only in the kinetic reaction. At this stage it is necessary to write a matrix such that $\mathbf{U}_e \mathbf{S}_e^T = \mathbf{0}$ (where $\mathbf{0}$ indicates a vector where all components are null). While this choice is nonunique, it has no influence on the final result. Thus, it is advisable to write the simplest possible matrix. For our two-reaction example, we choose the following:

$$\mathbf{U}_e = \begin{array}{c} \begin{matrix} B_2 & B_3 & B_1 & B_5^{(s)} & B_4^{(s)} \end{matrix} \\ \begin{bmatrix} 1 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} \end{array}. \tag{A1}$$

Since from (8) $\mathbf{S}_e = [1\ 0\ 1\ 0\ -1]$, it directly follows that $\mathbf{U}_e \mathbf{S}_e^T = \mathbf{0}$.

A2. Canal Paradigm

[68] In this stage the system is decoupled in components without kinetic reaction rate and one with kinetics. By row operations in the matrix, adding row 4 to both rows 2 and 3, we get

$$\mathbf{U}_{canal} = \begin{pmatrix} \mathbf{U}_c \\ \mathbf{U}_r \end{pmatrix} = \begin{array}{c} \begin{matrix} B_2 & B_3 & B_1 & B_5^{(s)} & B_4^{(s)} \end{matrix} \\ \begin{bmatrix} 1 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 1 & 1 \\ \hline 0 & 0 & 0 & 1 & 0 \end{bmatrix} \end{array}. \tag{A2}$$

A3. River Paradigm

[69] The main idea is to eliminate the kinetic constant-activity species of the system and also to reduce the number of components. Substituting row 2 minus row 3 into row 2, and deleting the (now unnecessary) row 3, leads to

$$\mathbf{U}_{river} = \begin{pmatrix} \mathbf{U}_c \\ \mathbf{U}_r \end{pmatrix} = \begin{array}{c} \begin{matrix} B_2 & B_3 & B_1 & B_5^{(s)} & B_4^{(s)} \end{matrix} \\ \begin{bmatrix} 1 & 0 & 0 & 0 & 1 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 0 & 1 & 0 & 1 \end{bmatrix} \end{array}. \tag{A3}$$

A4. Aquifer Paradigm

[70] Here the constant-activity species in equilibrium is eliminated from the system. Now row 1 is added to row 2, also subtracted from row 3, and then removed from the system:

$$\mathbf{U}_{aquifer} \equiv \mathbf{U} = \begin{pmatrix} \mathbf{U}_c \\ \mathbf{U}_r \end{pmatrix} = \begin{array}{c} \begin{matrix} B_2 & B_3 & B_1 & B_5^{(s)} & B_4^{(s)} \end{matrix} \\ \begin{bmatrix} 1 & 1 & -1 & 0 & 0 \\ \hline -1 & 0 & 1 & 0 & 0 \end{bmatrix} \end{array}. \tag{A4}$$

[71] From (A4) we directly read the two components. In the top row we have the (only) conservative component, $u_e = c_2 + c_3 - c_1$; in the bottom row, we read the kinetic component, $u_k = c_1 - c_2$. Notice that by combining both components an alternative expression for the kinetic component can be obtained; that is, $u_k = c_3 - u_e$.

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