A procedure for the solution of multicomponent reactive transport problems

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[1] Modeling transport of reactive solutes is a challenging problem, necessary for understanding the fate of pollutants and geochemical processes occurring in aquifers, rivers, estuaries, and oceans. Geochemical processes involving multiple reactive species are generally analyzed using advanced numerical codes. The resulting complexity has inhibited the development of analytical solutions for multicomponent heterogeneous reactions such as precipitation/dissolution. We present a procedure to solve groundwater reactive transport in the case of homogeneous and classical heterogeneous equilibrium reactions induced by mixing different waters. The methodology consists of four steps: (1) defining conservative components to decouple the solution of chemical equilibrium equations from species mass balances, (2) solving the transport equations for the conservative components, (3) performing speciation calculations to obtain concentrations of aqueous species, and (4) substituting the latter into the transport equations to evaluate reaction rates. We then obtain the space-time distribution of concentrations and reaction rates. The key result is that when the equilibrium constant does not vary in space or time, the reaction rate is proportional to the rate of mixing, $\nabla^T u \mathbf{D} \nabla u$, where $u$ is the vector of conservative components concentrations and $\mathbf{D}$ is the dispersion tensor. The methodology can be used to test numerical codes by setting benchmark problems but also to derive closed-form analytical solutions whenever steps 2 and 3 are simple, as illustrated by the application to a binary system. This application clearly elucidates that in a three-dimensional problem both chemical and transport parameters are equally important in controlling the process.

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1. Introduction

[2] Reactive transport modeling refers to the transport of a (possibly large) number of aqueous species that react among themselves and with the solid or gaseous phases. It is relevant because it helps in understanding the fate of pollutants in surface and groundwater bodies, the hydrochemistry of aquifers, and many geological processes [e.g., Gabrovšek and Dreybrodt, 2000; Freedman et al., 2003; Salas and Ayora, 2004; Emmanuel and Berkowitz, 2005]. Unfortunately, it is complex, both conceptually and mathematically. Modeling reactive transport involves two coupled ingredients: (1) the mass balance of all participating species, which is expressed by the solute transport equation for mobile species; and (2) a set of equations describing the reactions among species. The nature of participating species and reactions leads to a broad range of possible behaviors of the system [Rubin, 1983; Molins et al., 2004]. Moreover, reactions such as dissolution can also modify the aquifer properties (i.e., porosity and hydraulic conductivity) [e.g., Wood and Hewett, 1982; Philips, 1991; Kang et al., 2003; Singurindy and Berkowitz, 2003; Singurindy et al., 2004]. Therefore it is not surprising that numerous general mathematical formulations to solve reactive transport problems are available [e.g., Rubin, 1990, 1992; Yeh and Tripathi, 1991; Friedly and Rubin, 1992; Lichtner, 1996; Steefel and MacQuarrie, 1996; Clement et al., 1998; Saaltink et al., 1998, 2001; Tebes-Stevens et al., 1998; Robinson et al., 2000; Molins et al., 2004]. The resulting sets of governing equations have been included in a large number of reactive transport codes that can handle several species with different types of reactions (see Saaltink et al. [2004] for a list of codes).

[3] As opposed to numerical solutions, very few analytical results are available. These are of general interest, as they provide insights on the nature of the solution and allow evaluating the relative importance of the involved parame-
ters and processes. Analytical and semianalytical solutions are available in the case of linear and nonlinear equilibrium sorption reactions [e.g., Serrano, 2003, and references therein]. Analytical solutions are also available to solve reactive transport problems in case of (networks of) first-order kinetic reactions [Sun et al., 1999, 2004; Clement, 2001; Serrano, 2003; Quezada et al., 2004]. These methodologies are appropriate for radioactive decay chains and for many biochemical processes. However, they are difficult to extend to geochemical processes whose rates are nonlinear functions of the concentrations of the dissolved species, or to cases in which equilibrium conditions can be assumed and the reaction rates cannot be written explicitly.

[4] Because transport times are generally large in aquifers, most aqueous reactions and many dissolution/precipitation reactions can be modeled with the assumption of chemical equilibrium conditions at each point of the domain. As equilibrium is reached instantaneously, the amount of reactants evolving into products depends on the rate at which they mix, which is, in turn, governed by transport. To illustrate the concept, Figure 1a depicts a reaction of pure dissolution/precipitation in the mixing of two waters. The concentrations of the dissolved species, $c_1$ and $c_2$, in both mixing waters satisfy the equilibrium condition $c_1c_2 = K$, where $K$ is the equilibrium constant. For conservative species, concentrations of the mixture would be a linear function of the mixing waters concentrations, while equilibrium concentrations for reactive species are governed by a number of factors, including pH, salinity and temperature [e.g., Wigley and Plummer, 1976]. As a result, it is generally difficult to predict whether the mixture will precipitate or dissolve, and to estimate the amount of precipitated/dissolved mass.

[5] In this paper we propose a concise methodology to analyze groundwater reactive transport in the presence of general homogeneous and classical heterogeneous equilibrium reactions (according to the classification of Rubin [1983]) caused by mixing of different waters. We analyze situations where all reactions in the system can be assumed at equilibrium conditions at all times. Emphasis is placed on evaluating not only concentrations, but also reaction rates. The method is first applied to a binary system, providing an original analytical expression for the reaction rate in the case of mixing-driven precipitation. The methodology is then extended to deal with all kinds of classical heterogeneous and homogeneous equilibrium reactions. The complete methodology allows the mathematical decoupling of the problem into four steps: (1) definition of mobile conservative components of the system, (2) transport of these components, (3) speciation, and (4) evaluation of reaction rates and mass change of constant activity species. The method is proposed as a useful tool in deriving further analytical solutions describing reactive transport processes. It can also be of practical use in developing, adapting, or testing numerical codes to solve solute transport problems involving multiple reactions.

[6] The outline of the paper is as follows. In section 2 we present the mathematical formulation of the problem. Section 3 is focused on the reactive transport problem in the presence of a pure dissolution/precipitation reaction. Specifically, we analyze in detail a three-dimensional porous medium with uniform flow carrying two dissolved constituents at equilibrium with a solid mineral. We derive a closed-form solution for the mixing-driven precipitation process induced by an instantaneous point-like injection of water containing the same constituents of the resident water, but at a different equilibrium state. Finally, in
section 4 we generalize the formulation to solute transport problems involving multiple reactions.

2. Preliminary Concepts

2.1. Chemical Equilibrium

[7] Equilibrium reactions are described by mass action laws, which in the case of multiple species can be written in a compact form as [Saalink et al., 1998]

\[ S_a \log a = \log K', \] (1)

where \( S_a \) is the stoichiometric matrix, that is a \( N_r \times N_s \) matrix \((N_r \text{ and } N_s \text{ being the number of reactions and the total number of chemical species, respectively})\) containing the stoichiometric coefficients of the reactions, \( a \) is the vector of activities of all species and \( K' \) is the vector of equilibrium constants. In general, the activity of aqueous species, \( a_{aq} \), is a mildly nonlinear function of aqueous concentrations, \( c_{aq} \), which can be written as

\[ \log a_{aq} = \log c_{aq} + \log \gamma(c_{aq}). \] (2)

where the activity coefficient, \( \gamma \), may be a function of all aqueous concentrations and can be computed in several ways, the Debye-Hückel equation being a frequent choice for moderate salinities [Helgeson and Kirkham, 1974]. For dilute solutions, which are frequently observed in many real groundwater problems, the activity coefficients can be assumed as unitary. If some reactions involve pure phases or, in general, mixtures with fixed proportions of constituents or minerals or gas phases, the activities of the corresponding species can be assumed to be fixed and constant (e.g., activity is unity for pure minerals and water).

[8] Let \( N_c \) be the number of constant activity species. We split vector \( a \) (equation (1)) into two parts, \( a_c \) and \( a_{aq} \), containing the constant activity and the remaining aqueous species, respectively. Here and in the following, subscripts \( c \) and \( a \) are used to identify the constant activity and the remaining aqueous species, respectively. Matrix \( S_a \) is also divided into two parts, that is, \( S_a = (S_{aq} | S_{c}), \) where \( S_{aq} \) and \( S_{c} \) contain the stoichiometric coefficients of constant activity species and of the aqueous species, respectively. Since \( N_r \) activities are fixed and (1) can be used to eliminate \( N_r \) activities, we can now pose the problem in terms of \( N_s - N_c - N_r \) independent activities (conforming with Gibbs phase rule). Once these are calculated, we would obtain the remaining \( N_r \) activities on the basis of the chemical equilibrium relations (equation (1)). We call as primary those species corresponding to the independent \( N_s - N_c - N_r \) activities; the remaining \( N_r \) species are called secondary. We then split \( S_{cq} \) into two parts, that is, \( S_{cq} = (S_{cq}^p | S_{cq}^s), \) where \( S_{cq}^p \) and \( S_{cq}^s \) contain the stoichiometric coefficients of the primary and secondary species, respectively.

[9] It is convenient to redefine the chemical system so that the matrix of the stoichiometric coefficients of the secondary species coincides with the opposite of the identity matrix, \( I. \) Mathematically, this is equivalent to multiplying equation (1) by \( (S_{cq}^p)^{-1} \) (a proper choice of primary and secondary species leads to \( S_{cq}^p \) invertible). As activities \( a \) are fixed and known, we can rewrite the mass action law (1) as

\[ \log a_{aq}^p = S_{aq}^p \log a_{aq}^p - \log K, \] (3)

where \( a_{aq}^p \) and \( a_{aq}^p \) are the activities of primary and secondary species, respectively; \( S_{cq}^p = -I \) and \( S_{cq}^s \) are the redefined matrices of stoichiometric coefficients of secondary and primary species, respectively; \( K \) is the redefined vector of equilibrium constants, \( \log K = (S_{cq}^p)^{-1} (\log K' - S_{aq} \log a_{aq}). \) With these definitions and upon assuming unitary activity coefficients, the mass action law (1) reduces to

\[ S_{cq} \log c_{aq} = \log K. \] (4)

When the assumption of unitary activity coefficients is not justified, one needs (2) to relate activities and concentrations. However, it is still possible to write the mass action law in terms of concentrations. This is accomplished by substituting \( K \) with an equivalent equilibrium constant, \( K^e, \) defined as

\[ \log K^e = \log K - S_{cq} \log \gamma(c_{aq}). \] (5)

where \( K^e \) is a function of \( c_{aq} \), besides other possible independent state variables, such as temperature.

[10] In the following we present all chemical equations in terms of concentrations, using (4). Appendix A is devoted to the discussion of an example to facilitate understanding of the meaning of the vectors and matrices appearing in the mass action law.

2.2. Mass Balances

[11] Mass balance of each species can be written in a concise vector notation as

\[ \frac{\partial (m)}{\partial t} = MLt(c) + f. \] (6)

Here, vector \( m \) contains the mass of species per unit volume of porous medium; it can be split into two parts, \( m_c \) and \( m_{aq} \), of porous medium, respectively related to the constant activity species and to the remaining species. Vector \( c \) contains the concentrations of species \( (m_i = nc, \) for mobile species, where \( n \) is porosity). Matrix \( M \) is diagonal and its diagonal terms are unity when a given species is mobile and zero otherwise; \( f \) is a general source/sink term. The linear operator \( L(c) \) appearing in (6) is defined as

\[ L(c) = -\nabla \cdot (D \nabla c) + \nabla \cdot (aD \nabla c). \] (7)

where \( D \) is the dispersion tensor and \( q \) is Darcy’s flux.

[12] Assuming that the source/sink terms are only due to chemical reactions and that the system is always at chemical equilibrium, we can express \( f \) as

\[ f = S^r f. \] (8)

where \( f \) is the vector of reaction rates (expressed per unit volume of medium) and \( S \) is defined after (1). We notice that reactive transport processes also affect immobile species. For instance, while a mineral at equilibrium with the solution is not transported, its mass is changed in order to allow the system to attain equilibrium.

[13] A reactive transport process is completely described by the concentrations of the \( N_r \) species, together with the definition of the \( N_r \) (unknown) reactions rates, including the \( N_r \) rates of mass change of the constant activity species. To
this end, one has to solve the $N_s$ mass balance equations (6) together with the $N_r$ equilibrium equations (4). While the problem is very complex because of the nonlinearity of the governing system, it can be significantly simplified upon introducing the concept of components [e.g., Rubin, 1990, 1992; Friedly and Rubin, 1992; Steefel and MacQuarrie, 1996; Saaltink et al., 1998, 2001; Molins et al., 2004], as described below.

2.3. Components

Components are linear combinations of species whose mass is not affected by equilibrium reactions. Their introduction is convenient since it allows eliminating the chemical reactions source term in the transport equations. Most of the solution methods for reactive transport problems mentioned in the introduction are based on this concept. We introduce the components matrix, $\mathbf{U}$, defined such that

$$\mathbf{U} \mathbf{S}_{\text{eq}}^{m} = 0. \tag{9}$$

Recalling that the system was defined so that $\mathbf{S}_{\text{eq}} = (\mathbf{S}_{\text{eq}}^{m}) - 1$, a widely used expression for $\mathbf{U}$ is

$$\mathbf{U} = (\mathbf{I}_{N_u} \mid \mathbf{S}_{\text{eq}}^{m}), \tag{10}$$

where $N_u = N_s - N_c - N_r$. The expression for the components matrix is not unique. The motivation of expressing $\mathbf{U}$ by (9) is that multiplying (6) by $\mathbf{U}$, yields the equation

$$\frac{\partial (\mathbf{m})}{\partial t} = L_r(\mathbf{u}). \tag{11}$$

For this system, $\mathbf{S}_{eq}$ can be split as

$$\mathbf{S}_{eq} = (1) \tag{14a}$$

$$\mathbf{S}_{eq} = (\mathbf{S}_{eq}^{m} \mid \mathbf{S}_{eq}^{g}) = (-1 \mid -1). \tag{14b}$$

Matrices $\mathbf{S}_{eq}$ and $\mathbf{S}_{eq}^{m}$ contain the stoichiometric coefficients related to the constant activity species and to the remaining aqueous species, respectively. Equation (14b) implicitly identifies $B_1$ as primary species and $B_2$ as secondary.

The equilibrium constant, $K$, is strictly related to solubility of the solid phase, $S_{3s}$, and usually depends on temperature, pressure and chemical composition of the solution [e.g., Philips, 1991; Berkowitz et al., 2003].

In the following we first solve a simple binary system and then generalize the methodology to deal with classical heterogeneous and homogeneous chemical reactions at equilibrium.

3. Binary System

3.1. Problem Statement

We consider a reaction of pure dissolution/precipitation [Philips, 1991] at equilibrium, where an immobile solid mineral $S_{3s}$ dissolves reversibly to yield ions $B_1$ and $B_2$:

$$B_1 + B_2 \rightleftharpoons S_{3s}. \tag{12}$$

We further assume that the mineral, $S_{3s}$, is a pure phase, so that its activity equals 1. With the notation of section 2, vector $\mathbf{m}_c$ contains the mass per unit volume of medium, $m_1 = nc_1$ and $m_2 = nc_2$, of the aqueous species $B_1$ and $B_2$ respectively, while vector $\mathbf{m}_a$ contains the mass per unit volume of medium, $m_3$, of the solid mineral, $S_{3s}$. The stoichiometric matrix of the system described by (12) is

$$\mathbf{S}_e = \begin{pmatrix} -1 & -1 & 1 \end{pmatrix}. \tag{13}$$

The stoichiometric equation [20] is

$$\mathbf{m}_c = \mathbf{S}_{eq} \mathbf{m}_a = \mathbf{S}_{eq} \mathbf{u} \mathbf{c}_1 - \mathbf{S}_{eq} \mathbf{u} \mathbf{c}_2. \tag{14}$$

This implies that one needs to solve the transport problem for only one conservative component $u = \mathbf{u} \mathbf{c}_1 \mathbf{c}_1 - \mathbf{c}_2$. Notice that simply subtracting (16b) from (16a) leads to the...
equation which governs the transport of the conservative component $u = (c_1 - c_2)$. In other words, dissolution or precipitation of the mineral $S_{12}$ equally affects $c_1$ and $c_2$ so that the difference $(c_1 - c_2)$ is not altered.

[23] 2. Transport of the conservative components: Since only one component is evidenced in this case, one needs to solve (11) for $u$.

[24] 3. Speciation: Here one needs to compute the concentrations of $(N_e - N_s)$ mobile species from the concentrations of the components. In our binary system, this implies solving

$$c_1 - c_2 = u \quad (18a)$$

$$\log c_1 + \log c_2 = \log K. \quad (18b)$$

[25] Assuming that $K$ is independent of $c_1$ and $c_2$, the solution of (18a) and (18b) is

$$c_1 = \frac{u + \sqrt{u^2 + 4K}}{2} \quad (19a)$$

$$c_2 = \frac{-u + \sqrt{u^2 + 4K}}{2}. \quad (19b)$$

[26] 4. Evaluation of the reaction rate: Substitution of the concentration of the secondary species, $B_2$, into its transport equation (16b) leads to (see Appendix B for details)

$$r = \frac{\partial c_2}{\partial K} \left[ -\frac{\partial K}{\partial n} + L_{\Pi}(K) \right] + \frac{\partial^2 c_2}{\partial u^2} \nabla^T u \nabla u + \frac{2}{\partial u \partial K} \nabla^T u \nabla K$$

$$+ \frac{\partial^2 c_2}{\partial K^2} \nabla^T K \nabla K. \quad (20)$$

When $K$ is a function of conservative quantities such as salinity, $s$, equation (20) can be rewritten (see Appendix C for details) as

$$r = \frac{\partial^2 c_2}{\partial s^2} \nabla^T s \nabla s + \frac{\partial^2 c_2}{\partial u^2} \nabla^T u \nabla u + \frac{2}{\partial u \partial K} \nabla^T u \nabla K. \quad (21)$$

Moreover, in the case of constant $K$, equation (20) reduces to

$$r = \frac{\partial^2 c_2}{\partial u^2} \left( \nabla^T u \mathbf{D} \nabla u \right) \quad (22a)$$

$$\frac{\partial^2 c_2}{\partial u^2} = \frac{2K}{(u^2 + 4K)^{3/2}}. \quad (22b)$$

In general, the reaction rates should be used to compute the mass change of solid mineral. In turn, this would cause a modification in the medium properties. Here, however, we will neglect such changes assuming 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.

[27] The results encapsulated in (20), (21) and (22) deserve some discussion. First of all, under chemical equilibrium conditions, they provide a way to compute directly the rate of dissolution/precipitation as a function of quantities such as the concentrations of components, the equilibrium constants, and the dispersion coefficients, without the need to actually evaluate the concentrations of the dissolved species. We note that (21) includes the model of Philips [1991] as a particular case.

[28] Furthermore, equation (22) shows that the reaction rate is always positive (i.e., precipitation occurs) in systems where $K$ is constant. This is consistent with the comments of Rubin [1983], who points out that, in the case of the reaction described by (12), reactive transport processes cannot result in dissolution of the solid mineral. This is also evident from Figure 1a. Figure 1a displays another interesting feature. The equilibrium point can be obtained by drawing a line from the conservative mixing point toward the equilibrium line. The slope of this line is equal to the ratio of the stoichiometric coefficients and is equal to 1 in our example.

[29] Equations (20) and (22) clearly demonstrate that the reaction rate depends on chemistry, which controls $\partial^2 c_2/\partial u^2$ (equation (22b)), but also on transport processes, controlling the gradient of $u$. Figure 1b qualitatively shows a synthetic example which allows evaluating the relative importance of the two factors (chemistry and transport) in the reaction rate. We note that it would be hard to make general statements about which one is more important, which is consistent with the sensitivity analysis of Tebes-Stevens et al. [2001]. One of the most paradoxical features of Figure 1b is that reaction does not necessarily take place where concentrations attain their maximum values. In fact, the reaction rate equals zero when $u$ is maximum or minimum (i.e., when $c_1$ or $c_2$ reach their maximum value, respectively). In general (see equation (20)), the reaction rate depends on both the gradients of $u$ and $K$. A nonzero gradient of $K$, for example, can occur when the mixing of different waters induces spatial variability in temperature or salinity [Berkowitz et al., 2003; Rezaei et al., 2005].

[30] It is interesting to notice that, in the absence of the first contribution on the right hand side of (20), all terms are proportional to the dispersion tensor, $\mathbf{D}$, thus strengthening the relevance of mixing processes to the development of such reactions. In particular, the term $\nabla^T u \mathbf{D} \nabla u$ can be used as a measure of the mixing rate, which is consistent with the concept of dilution index, as defined by Kitidis [1994] on the basis of entropy arguments. This result also suggests that evaluating mixing rates may help to properly identify not only the sources of water [Carrera et al., 2004], but also the geochemical processes occurring in the system.

[31] In general, the amount of $S_3$ that can precipitate is controlled by the less abundant species. Thus we expect precipitation to be highest when mixing induces similar values of $c_1$ and $c_2$. Mathematically, this is evidenced by the dependence of the reaction rate on $\partial^2 c_2/\partial u^2$, that reaches a maximum when $u = 0$ (see equation (22b)). We also notice that the rate (22a) increases with decreasing $K$, since solubility also decreases (in a system described by (12), solubility is the square root of $K$).

[32] The methodology we have presented can easily be extended to deal with solute transport in the presence of multiple reactions. This is shown in section 4. It is then relevant to stress the point that analytical solutions for these types of systems are possible whenever an analytical solu-
3.3. Analytical Solution: Pulse Injection in a Binary System

[33] In this section we apply the general methodology to derive a closed-form solution for a mixing-driven precipitation reaction. Closed-form solutions provide basic means to investigate the physical underlying processes and to analyze the relative importance of the parameters involved. Moreover, analytical solutions are potentially useful as benchmark for numerical codes and can be of assistance in developing methodologies for the setup of laboratory experiments and procedures for data analysis and/or interpretation.

[34] We consider a three-dimensional homogeneous porous formation, of constant porosity, \( n \), under uniform flow conditions. The system is affected by an instantaneous point-like injection of water containing the same constituents as the initial resident water. This problem can be used as a kernel for other injection functions. We consider the case of constant \( K \). We assume that the velocity is aligned with the \( x \) coordinate, \( V = q/n = V_{e} \) (\( i \) being the unit vector parallel to the \( x \) axes), and that the dispersion tensor is diagonal, \( D_{L} \) and \( D_{T} \) respectively being its longitudinal and transverse components. We further assume that the time of the reaction is small as compared to the typical time of transport (i.e., equilibrium condition).

[35] The reactive transport system is governed by (12), (15), and (16). The boundary conditions are

\[
e_{i\infty} = c_{i}(x \to \infty, t) = c_{i0}, \quad i = 1; 2.
\]

Initially, we displace resident water by injecting a volume \( V_{e} \) of solution with concentration \( e_{i\text{inj}} = c_{i0} + c_{i\text{e}} \). In order to find an analytical solution for small \( V_{e} \), it is mathematically convenient to write the initial concentration condition, after equilibrium is reached at the injection point, as

\[
c_{i}(x, t = 0) = c_{i0}V_{e}\delta(x)/n + c_{i0}, \quad i = 1; 2.
\]

where equilibrium must be satisfied at all points in the aquifer. This implies that (1) \( c_{10} + c_{20} = K \), and (2) \( c_{10} + c_{1e} \) (\( c_{20} + c_{2e} \)) = \( K \). From these two equilibrium conditions, it should be clear that \( c_{1e} \) and \( c_{2e} \) would have different signs.

[36] With this in mind, we then follow the steps detailed in section 3.2. The (conservative) component \( u = c_{1} - c_{2} \) satisfies (11) with boundary and initial conditions

\[
u_{\infty} = u(x \to \infty, t) = c_{1}(x \to \infty, t) - c_{2}(x \to \infty, t) = u_{0} \quad \text{(25a)}
\]

\[
u(x, t = 0) = u_{e}V_{e}\delta(x)/n + u_{0} \quad \text{(25b)}
\]

With this definition, \( u_{e} \) is then the excess of the injected component \( u \) that remains in the aquifer immediately after injection. The solution of (11), subject to boundary and initial conditions (25a) and (25b) is [Domenico and Schwartz, 1997, p. 380]

\[
u(x, t) = u_{0} + \frac{18}{(2\pi)^{1/2}} \frac{u_{e}}{V_{d}} \exp \left[ -\frac{1}{2} \rho^{2} \right], \quad \text{(26)}
\]

where \( \rho \) is the normalized radial distance from the center of the plume, defined as

\[
\rho = \sqrt{\frac{(x - V_{d}t)^{2}}{2D_{L}} + \frac{y^{2} + z^{2}}{2D_{T}}}.
\]

The dimensionless quantity \( V_{d} \) is the ratio between the volume containing about the 99, 7% of the excess of injected mass [Domenico and Schwartz, 1997] and the injection volume

\[
V_{d} = \frac{72\pi n^{2}h^{3/2}}{V_{e}}
\]

and is a measure of the temporal evolution of the dispersive effect.

[37] Substituting (26) into (19a) and (19b), we obtain the concentrations, \( c_{1} \) and \( c_{2} \), of the dissolved species. Finally the expression of the local mineral mass precipitation rate, \( r \), per unit volume of medium is derived from (22) as

\[
r(x, t) = nK \left( \frac{18}{(2\pi)^{1/2}} \frac{u_{e}}{V_{d}} \right) \rho^{2} \exp[-\rho^{2}]
\]

We notice that the rate, \( r \), vanishes in the trivial case of \( u_{e} = 0 \), since the concentrations of the two injected species are the same as the resident ones and there is no excess of injected mass in the solution right after the injection. The rate vanishes also when \( V_{d} \to \infty \). The latter situation describes a scenario where gradients of the component \( u \) are negligible because of large dispersion effects or because a large amount of time has elapsed since injection.

[38] To illustrate the features of this solution we consider the following problem: we start with a resident water characterized by \( c_{10}/\sqrt{K} = 0.25 \) and \( c_{20}/\sqrt{K} = 4.00 \) (\( u_{0}/\sqrt{K} = -3.75 \)); we then inject water from an external source, characterized by \( c_{1e}/\sqrt{K} = 0.184 \), \( c_{2e}/\sqrt{K} = 5.434 \) (\( u_{e}/\sqrt{K} = -5.25 \)). Equilibrium condition is satisfied when \( c_{1e}/\sqrt{K} = -0.066 \), \( c_{2e}/\sqrt{K} = 1.434 \) (\( u_{e}/\sqrt{K} = -1.5 \)). Figure 2a depicts the dependence of the dimensionless concentrations \( \tilde{c}_{1} = c_{1}/\sqrt{K} \) and \( \tilde{c}_{2} = c_{2}/\sqrt{K} \) on the normalized distance from the center of the (moving) plume, \( \sqrt{2D_{L}} \) (while \( z = y = 0 \)), and \( V_{d} = 3.5 \). Dimensionless concentrations \( \tilde{c}_{1NR} \) and \( \tilde{c}_{2NR} \) for the corresponding nonreactive system are also shown for comparison. Notice that while both concentrations are higher than the initial ones in the nonreactive case, in the reactive case \( \tilde{c}_{1} \) decreases while \( \tilde{c}_{2} \) increases (in agreement with the fact that \( c_{1e} < 0 \) and \( c_{2e} > 0 \)).

[39] The spatial distribution of the (local) dimensionless reaction rate, \( \tilde{r} = rt/(n\sqrt{K}) \), for the same conditions of Figure 2a, is depicted in Figure 2b. A comparison of Figures 2a and 2b clearly elucidates that the system is chemically active (i.e., the reaction rate is significant) at locations where concentration gradients of both species are relevant. This implies, in turn, that strong gradients of the component \( u \) give rise to significant reaction rates, in agreement with (22a). In general, no reactions occur within the system when concentration gradients vanish. As a consequence, no reaction occurs...
at the (moving) center of the plume, that is, at the points of highest (or lowest) concentration values.

Figures 3a and 3b display the same quantities of Figures 2a and 2b but for $\nu_d = 16$. A comparison between Figures 2a and 3a reveals that the concentration profiles display a lower amplitude when $\nu_d$ increases. A larger value for $\nu_d$ (equation (28)) can be seen as an increase either in elapsed time or in the effects of dispersion for a given time. Thus it is expected that more dispersed plumes are associated to weaker gradients of $u$ and thus to reduced precipitation rates. This behavior is not observed in the range of small dispersion effects ($\nu_d \ll 1$), where an increase of dispersion phenomena enhances the mixing process and the related reaction. This feature can be observed mathematically by taking the limit of (29) when $\nu_d$ tends to zero.

From (29) we also observe that a change in $D_T$ has stronger effects rather than a modification in $D_L$. This is so since $D_T$ is not squared in the definition of $\nu_d$ and is also clear when considering that dispersion is enhanced along two directions by increasing $D_T$, while an increase in $D_L$ affects only one spatial direction. We will comment further on this topic in the following.

[41] The sensitivity of the reaction rate to $u_e$ for a given $u_0$ is presented in Figure 4, with reference to a resident water with $u_0/\sqrt{K} = -20$ ($c_{10}/\sqrt{K} = 0.05; c_{20}/\sqrt{K} = 0.05$). We start by considering the case with a negative $u_e$ ($u_e/\sqrt{K} = -30$). The dimensionless mixing volume is set as $\nu_d = 3.5$. The shape of the reaction rate function is displayed in Figure 4a at the plane $z = 0$. From the plot it is clear that, at any given time, precipitation would concentrate in a (three-

Figure 2. Dependence of (a) dimensionless concentrations $\tilde{c}_1$, $\tilde{c}_2$ and (b) dimensionless reaction rate, $\tilde{\nu}$, on the normalized distance from the center of the (moving) plume, $(x - \nu_t)/\sqrt{2tD_L}$, for $z = y = 0$, $\nu_d = 3.5$, $u_e/\sqrt{K} = -1.5$, and $u_0/\sqrt{K} = -3.75$. In Figure 2a, the dimensionless concentrations $\tilde{c}_{1NR}$, $\tilde{c}_{2NR}$ are those of a nonreactive system; the dashed line indicates the initial concentrations of the two species within the system.

Figure 3. Dependence of (a) dimensionless concentrations $\tilde{c}_1$, $\tilde{c}_2$ and (b) dimensionless reaction rate, $\tilde{\nu}$, on the normalized distance from the center of the (moving) plume, $(x - \nu_t)/\sqrt{2tD_L}$, for $z = y = 0$, $\nu_d = 16$, $u_e/\sqrt{K} = -1.5$, and $u_0/\sqrt{K} = -3.75$. In Figure 3a, the dimensionless concentrations $\tilde{c}_{1NR}$, $\tilde{c}_{2NR}$ are those of a nonreactive system; the dashed line indicates the initial concentrations of the two species within the system.
dimensional) aureole around the moving center of the plume. The actual location and shape of this aureole is governed by (29), and would depend on $D_L$, $D_T$ and $u_c$. One should note that Figure 4a displays an artificial symmetry, as coordinate $x$ is normalized by $\sqrt{2tD_L}$, while the $y$ direction is normalized by $\sqrt{2tD_T}$. Figure 4b depicts radial profiles of the dimensionless reaction rate, $\tilde{r}$, for different $u_c$. Because of the symmetry of the solution with respect to the normalized coordinates, we display only radial profiles starting from the plume center. Figure 4b is organized in such a way that while the curves resulting from positive values of $u_c$ are displayed on the larger scale, those arising by negative values of $u_c$ are displayed within the insert. Figure 4b reveals that the reaction rate is larger when $u_c/\sqrt{K}$ and $u_0/\sqrt{K}$ have opposite signs. An explanation of this is provided with the aid of Figure 5 where, for the sake of discussion, we consider the effect of $|u_c/\sqrt{K}| = 30$. From the points reached on the equilibrium curve right after injection, characterized by $(c_{ie} + c_{0} )/\sqrt{K}$, concentrations would evolve until they reach the asymptotic condition characterized by the same concentrations as the resident water. In the case of conservative solutes, the paths would be the straight lines depicted in Figure 5 as dashed lines. For reactive solutes the path would be along the hyperbola (equilibrium line: $c_1c_2 = 1$). From Figure 5 we see that there is no symmetry: in the case of $u_c < 0$ reactive and conservative solutes paths are quite

**Figure 4.** Dependence of the dimensionless reaction rate, $\tilde{r}$, on the dimensionless distance from the center of mass of the plume for $u_0/\sqrt{K} = -20$ and $\tilde{\nu}_d = 3.5$: (a) three-dimensional view for $u_c/\sqrt{K} = -30$ and (b) radial sections for $u_c/\sqrt{K} = -20, -30, -40, 20, 30,$ and $40$.

**Figure 5.** Scheme of a pure dissolution/precipitation reaction induced by a point-like injection. The equilibrium condition at the injection point is characterized by $|u_c/\sqrt{K}| = 30$, while the initial water is identified by $u_0/\sqrt{K} = -20$ (the initial point is also the final equilibrium point). Dashed lines outline the path of the reaction in the case of conservative solutes. For reactive solutes, the path would develop along the hyperbola (equilibrium line).
similar, which is not the case when \( u_e > 0 \). As a consequence, in the latter case a larger amount of precipitation is needed in order to reach equilibrium at all locations and times. Going back to Figure 4b, we observe that the largest absolute value of \( u_e \sqrt{K} \) produces the largest reaction rate, as a consequence of the mixing of increasingly different waters, thus inducing significant gradients of \( u_e \).

[42] Knowledge of the local rate is essential to evaluate the global reaction rate

\[
 r_{\Omega}(t) = \int_{\Omega} r(x, t) \, d\Omega, \tag{30a}
\]

which is an integral measure of the rate of precipitation of the mineral mass of the system at any given time. Here, \( \Omega \) is the entire volume of the medium. This information is of practical interest for experimental applications devoted to analyze precipitation/dissolution processes, such as those reported by Berkowitz et al. [2003] and Singurindy et al. [2004].

[43] In general, a closed form solution for the integral (30a) does not exist. Upon using spherical coordinates, the three-dimensional integral (30a) can be written as the following one-dimensional integral,

\[
 r_{\Omega} = \frac{n K V_e V_d}{t} \int_0^{\infty} \left( \frac{18}{\left(2\pi^2/5\right) V_d} \right)^2 \rho^2 \exp[-\rho^2] \left[ u_0 + \frac{18}{\left(2\pi^2/5\right) V_d} \exp \left( -\frac{1}{2} \rho^2 \right) \right]^{-3/2} 4\pi \rho^2 \, d\rho. \tag{30b}
\]

As evidenced by (30b) all information related to dispersion is concentrated in \( V_d \). Thus, the sensitivity of \( r_{\Omega} \) on dispersion can be analyzed from the following expression,

\[
 \frac{\partial r_{\Omega}}{\partial V_d} = \frac{\partial r_{\Omega}}{\partial V_d} \frac{\partial V_d}{\partial D_L} = \frac{\partial r_{\Omega}}{\partial V_d} \frac{V_d}{2D_L} = \frac{D_T}{2D_L} \frac{\partial r_{\Omega}}{\partial D_L}. \tag{31}
\]

Equation (31) shows that the overall reaction rate, \( r_{\Omega} \), is much more sensitive to \( D_T \) than to \( D_L \). Considering that longitudinal dispersion is often taken to be about five to ten times of transverse dispersion, equation (31) implies that the overall reaction rate would be ten to twenty times more sensitive to \( D_T \) than to \( D_L \). Furthermore, the input of solutes is frequently continuous in time and reactants do not enter directly into the flow domain, as they are laterally driven into it. Both factors would tend to enhance the role of transverse dispersion in reactive transport problems. This is particularly relevant in view of the uncertainties surrounding the actual values of transverse dispersion. While some argue that transverse dispersion tends to zero in three-dimensional domains for large travel times [Dagan, 1989], others [Neuman and Zhang, 1990; Zhang and Neuman, 1990; Attinger et al., 2004] show that this is not the case, thus corroborating the idea that the actual transverse dispersion is linked to the interplay between spatial heterogeneity and time fluctuations of velocity [Cirpka and Attinger, 2003; Dentz and Carrera, 2003].

[44] An asymptotic expression for (30b) (see Appendix D for details) can be derived analytically in the presence of large dispersion effects (i.e., large \( V_d \)) as

\[
 r_{\Omega}(t) = \frac{V_e K u_e^2}{t} \frac{27}{V_d 4\pi^{3/2}(c_{10} + c_{20})^{1/2}}. \tag{32}
\]

Recalling the definition of \( \bar{V}_d \) (equation (28)), expression (32) reveals that, for large \( \bar{V}_d \), the global reaction rate, \( r_{\Omega} \), decreases with time proportionally to \( t^{-5/2} \). Figure 6 depicts the dependence of the dimensionless global reaction rate, \( r_{\Omega} = r_{\Omega}(\sqrt{V_e} \sqrt{K}) \), on \( \bar{V}_d \) for different \( u_e \sqrt{K} \) and \( u_0 \sqrt{K} = -20 \); bold lines are the asymptotic solution (32), while thin lines with symbols correspond to \( r_{\Omega} \) as obtained by numerical solution of (30b). We observe that \( r_{\Omega} \) increases with \( \bar{V}_d \) in the range of small dispersion effects (\( \bar{V}_d < 9 \)), as the prevailing effect of the enhanced dispersion effects is a reduction of concentration gradients and thus of precipitation. Consistently with our previous comments, for small dispersion effects \( \bar{r}_{\Omega} \) is larger when \( u_0 \sqrt{K} \) and \( u_0 \sqrt{K} \) have opposite signs, while it is independent of the sign of \( u_e \sqrt{K} \) and \( u_0 \sqrt{K} \) when dispersion effects are large.

[45] We note that the asymptotic solution (32) coincides with the exact results of the numerical integration of (30b) when \( \bar{V}_d \approx 100 \). Considering, as an example, a medium characterized by \( D_T = 0.21 \) m$^2$/day and \( D_L = 2.1 \) m$^2$/day and setting \( V_e/n = 1 \) m, this means that the precipitation phenomenon starts decreasing according to a factor \( t^{-5/2} \) after 1 day from the injection. This suggests that the bulk of the reactive process develops at early time and is confined within a region of the domain which is relatively close to the injection point.

[46] As a final result, Figures 7a and 7b depict the spatial distribution of the dimensionless total rate of precipitation obtained by numerical integration of (29) on the horizontal plane \( z = 0 \) for the entire duration of the process. Figures 7a and 7b have been obtained on the basis of the initial condition \( u_0 \sqrt{K} = -20 \), while the boundary conditions are \( u_e \sqrt{K} = \pm 20 \).

[47] Figures 7a and 7b corroborate the findings that the system is active within a region close to the injection point. We note that the reaction can be considered exhausted when \( V_e/D_L > 0.5 \) and \( V_e/D_T > 2 \). Considering, as an example, a medium characterized by \( D_T = 0.21 \) m$^2$/day and \( D_L = 2.1 \) m$^2$/day, setting \( V_e/n = 1 \) m$^2$/m and \( V = 0.5 \) m/day, this means that the precipitation process is negligible for \( x > 2.1 \) m and \( y > 0.85 \) m.

4. Generalization of the Methodology of Solution

[48] We now extend the methodology illustrated in section 3 to describe multispecies transport processes in the presence of generic homogeneous and classical hetero-
geneous reactions. We assume that all the variable activity species are mobile, so that mass balances (equation (6)) for dissolved and constant activity species are expressed as

$$\frac{\partial (n_c)}{\partial t} = L_c(c_a) + S_c^r r \tag{34a}$$

$$\frac{\partial (m_c)}{\partial t} = M_c L_c(m_c) + S_c^m r \tag{34b}$$

where matrix $M_c$ is diagonal and its diagonal terms equal 1 when a given constant activity species is mobile or zero otherwise. Our aim is to evaluate the concentrations of dissolved species, $c_a$ ($N_a - N_c$ unknowns) and the rates of the reactions, $r$ ($N_r$ unknowns). Once $r$ is known, (34b) provides the rates of mass change of the constant activity species. In order to calculate $c_a$ and $r$, we need to solve the algebraic-differential system given by the $N_a - N_c$ partial differential equations of transport for $c_a$ (equation (34a)) and the $N_r$ nonlinear algebraic equilibrium conditions (equation (4)). The general methodology of solution of this system of equations is detailed in the following.

4.1. Step 1: Definition of Mobile Conservative Components

[49] The first step of the methodology consists of defining the chemical system (species and reactions, that is, the stoichiometric matrix of (1)) and reducing the number of equations describing transport of dissolved species by eliminating the source term in (34a). To this end, we use the components matrix, $U$, defined by (9).

4.2. Step 2: Transport of Components

[50] Since components are conservative, equation (11) can be used to describe their transport. The initial and/or
boundary conditions for (11) are given by \( \mathbf{u}_0 = \mathbf{Uc}_0 \), \( \mathbf{c}_0 \) being the vector of initial and/or boundary species concentrations. Since the reaction sink/source terms have been eliminated, all components are independent. Moreover, the resulting transport equation is identical for all components, the only difference being in the boundary conditions. Only in some particular cases (such as in the example of section 3.3) a closed-form analytical solution is possible. Otherwise, any conventional transport simulator can be used. The underlying hypotheses are that (1) the mobile species are subject to the same advective flow field and (2) the same dispersion processes apply to all species, with equal dispersion coefficients. Other than that, the formulation does not impose any additional restrictions on the nature of flow. That is, flow can be steady or transient, saturated or unsaturated, single phase or multiphase, and temperature may be constant or variable.

4.3. Step 3: Speciation

[51] This step is devoted to evaluating the concentrations of the \( N_r - N_c \) aqueous species, \( \mathbf{c}_a \). The components, computed in step 2, provide \( N_u = N_r - N_c - N_s \) equations. The mass action law for each reaction provides the remaining \( N_r \) equations. Thus one needs to solve the nonlinear algebraic system

\[
\mathbf{u} = \mathbf{Uc}_a \quad (35a)
\]

\[
\log \mathbf{c}_a^u = \mathbf{S}_a \log \mathbf{c}_a^u - \log \mathbf{K}. \quad (35b)
\]

It is clear that the system is nonlinear, both explicitly (simultaneous linear dependence on \( \mathbf{c}_a \), and \( \log \mathbf{c}_a \)) and implicitly (in general, \( \mathbf{K} \) may depend on activity coefficients and thus be a nonlinear function of \( \mathbf{c}_a \), as discussed in section 2.1). The solution of this system can be very complex. However, in some geochemical problems (such as the binary system of section 3) it is possible to derive an analytical solution. Formally, one can substitute (35b) into (35a), obtaining \( N_u \) nonlinear algebraic equations for \( \mathbf{c}_a \). Their solution renders \( \mathbf{c}_a \), as a function of \( \mathbf{u} \) and \( \mathbf{K} \), which is then substituted in (35b) to obtain \( \mathbf{c}_a^u \). In summary, we can write

\[
\mathbf{c}_a = \mathbf{c}_a(\mathbf{u}, \mathbf{K}) \quad (36a)
\]

\[
\log \mathbf{c}_a = \log \mathbf{c}_a(\mathbf{u}, \mathbf{K}). \quad (36b)
\]

4.4. Step 4: Evaluation of Reaction Rates and Mass Change of Constant Activity Species

[52] Here, we substitute the concentrations computed in step 3 into the mass balance equations to obtain the \( N_r \) reaction rates. We recall (section 2) that each equilibrium reaction yields a secondary species and that the corresponding transport equation solely depends on its reaction rate, as the redefined matrix of the stoichiometric coefficients of the secondary aqueous species coincides with the opposite of the identity matrix, \( \mathbf{I} \). Therefore, considering the \( N_r \) transport equations of the secondary species leads to

\[
\mathbf{r} = L_r(\mathbf{c}_a^u) - \frac{\partial (n \mathbf{c}_a^u)}{\partial t}. \quad (37)
\]

Substituting the functional dependences of (36b) into (37), it is possible to evaluate the rates of the reactions (see Appendix E for details). The rate of the \( m \)th reaction (we switch temporarily to index notation to avoid ambiguities) is given by

\[
\begin{align*}
\mathbf{r}_m &= \sum_{n=1}^{N_r} \frac{\partial c_{m,n}^u}{\partial c_n} \left( - \frac{\partial K_{p,n}}{\partial t} \mathbf{V} \cdot \nabla K_{p,n} + \mathbf{V} \cdot (D \nabla K_{p,n}) \right) + \sum_{n=1}^{N_r} \sum_{j=1}^{N_r} \frac{\partial^2 c_{m,n}^u}{\partial c_n \partial c_j} \nabla^T \mathbf{u} \mathbf{D} \nabla \mathbf{u} + 2 \sum_{n=1}^{N_r} \sum_{j=1}^{N_r} \frac{\partial^2 c_{m,n}^u}{\partial c_n \partial K_{q,n}} \nabla^T \mathbf{u} \mathbf{D} \nabla K_q + 2 \sum_{n=1}^{N_r} \sum_{j=1}^{N_r} \frac{\partial^2 c_{m,n}^u}{\partial c_n \partial K_{q,j}} \nabla^T \mathbf{K}_p \mathbf{D} \nabla K_q. \quad (38)
\end{align*}
\]

This equation can be simplified when \( \mathbf{K} \) is a function of state variables satisfying nonreactive transport equation (recall equation (21)) and, especially, when \( \mathbf{K} \) is constant. The latter condition leads to

\[
\mathbf{r}_m = \sum_{n=1}^{N_r} \sum_{j=1}^{N_r} \frac{\partial^2 c_{m,n}^u}{\partial c_n \partial c_j} \nabla^T \mathbf{u} \mathbf{D} \nabla \mathbf{u}. \quad (39)
\]

Reverting to vector notation, (39) can then be expressed as

\[
\mathbf{r} = n \mathbf{H} \nabla \mathbf{u} \mathbf{D} \nabla \mathbf{u}. \quad (40)
\]

where \( \mathbf{H} \) is the vector of Hessian matrices (a third-order tensor) of the reactions (as represented by the corresponding secondary species) with respect to the components.

[53] The rate of mass change of constant activity species is then obtained by substituting the reaction rates into the corresponding mass balance equations (34b). In the case of immobile species (minerals subject to precipitation or dissolution), the rate of mass change is given directly by the reaction rate. Knowledge of these rates of solid mass change is of particular interest, since it is a prerequisite to estimate the characteristic time of changes in medium properties [Wood and Hewett, 1982; Philips, 1991].

[54] When the constant activity species are mobile (e.g., dissolved gases or some colloids), the formulation is still valid but more complex, as one would need to use the complete equation (34b) to obtain the reaction rate. If the species is water, then one is rarely interested in finding its concentration, other than in special cases, such as in the presence of osmotic effects. In such cases our formulation is still valid, but water would not be a constant activity species anymore.

4.5. Additional Considerations

[55] As previously pointed out, a key feature of our methodology is that it allows obtaining concentrations of solutes and reaction rates independently of constant activity species.

[56] As compared to existing formulations proposed in the literature to solve multispecies transport processes in the presence of a generic number of homogeneous and classical heterogeneous reactions [Rubin, 1990, 1992; Friedly and Rubin, 1992; Steefel and MacQuarrie, 1996; Saulitink et al., 1998, 2001; Molins et al., 2004], our method is simpler and more concise. It allows eliminating constant concentration species from the beginning, thus simplifying the formulation from the outset.
5. Conclusions

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

[60] 1. The methodology we propose allows obtaining the local concentrations of dissolved species and the rates, $r$, of the reactions occurring in the system. It also allows evaluating the rate of change of the mass of the solid minerals involved in the phenomena as a function of $r$; this is a prerequisite to estimate the characteristic timescale of changes in medium properties [Wood and Hewett, 1982; Phillips, 1991].

[61] 2. An appealing feature of our method is that it allows separating the solution of chemical equations to the mass balance equations of dissolved species. This leads to a reduced number of transport equations to be solved, and, more importantly, deconstructs the problem to the solution of a set of independent nonreactive advection-dispersion equations.

[62] 3. From a practical standpoint, our methodology is a very powerful tool in deriving analytical solutions for multispecies systems where homogeneous or classical heterogeneous reactions occur [Rubin, 1983] on the basis of known classical solutions describing nonreactive processes. It can also be used to develop and/or simplify numerical codes for solving reactive transport problems.

[63] 4. As compared to formulations previously proposed in the literature to solve multispecies transport phenomena in the presence of a generic number of homogeneous and classical heterogeneous reactions [Rubin, 1990, 1992; Friedly and Rubin, 1992; Steefel and MacQuarrie, 1996; Saaltink et al., 1998, 2001; Molins et al., 2004], our method is simpler and more concise. Moreover, it permits not only to evaluate concentrations of dissolved species, but also provides general expressions for the rates of the system reactions and for the rate of change in solid mass involved in the phenomena.

5. The general expression provided for the reaction rates highlights that mixing processes control equilibrium reaction rates and evidences the possibility of inducing reaction by simply mixing waters at different equilibrium conditions. This type of mixing-driven chemical reactions can help in explaining the enhancement of reaction processes observed when different solutions mix in carbonate systems [Gabrovšek and Dreybrodt, 2000; Corbella et al., 2003; Rezaei et al., 2005].

6. We applied the general methodology to a binary system and derived an original closed-form analytical solution of a mixing-driven precipitation reaction induced by a pulse injection in a three-dimensional homogeneous porous medium in the presence of uniform flow. Our results prove that in binary systems the mixing process of two waters, both of which are at equilibrium, induces precipitation processes throughout the system. The solution also demonstrates that (1) the presence of precipitation significantly modifies the concentrations of aqueous species, when compared to a nonreactive situation; (2) the features of the reactive process are strongly dependent on flow characteristics and on the difference in the concentrations of both the initial and the injected water; (3) the bulk of the reactive process develops at early time, thus remaining confined within a region of the domain which is relatively close to the injection point; and (4) the overall reaction rates are more sensitive to transverse than to longitudinal dispersion.

Appendix A: Illustrative Example of the Chemical Equilibrium Formulation

[66] As an example to help understanding the meaning of vectors and matrices employed within the mass action law (1), we analyze the system of reactions leading to dedolomitization [Ayora et al., 1998]. The system is governed by four equilibrium reactions ($N_r = 4$)

\[
\begin{align*}
CO_2^- &= HCO_3^- - H^+ & (A1a) \\
CO_2 &= HCO_3^- + H^+ - H_2O & (A1b) \\
CaMg(CO_3)_{2s} &= Ca^{2+} + Mg^{2+} + 2CO_3^{2-} & (A1c) \\
CaCO_3 &= Ca^{2+} + CO_3^{2-}. & (A1d)
\end{align*}
\]

We identify $H_2O$, $CaCO_3(s)$ and $CaMg(CO_3)_{2s}$, as constant activities species ($N_c = 3$; one aqueous and two solid species). As the total number of species involved is $N_s = 9$, we need to define $N_r = N_s - N_a = 2$ primary species. We then define $H^+$ and $HCO_3^-$ as the primary species and $CO_3^{2-}$, $CO_2$, $Mg^{2+}$ and $Ca^{2+}$ as the secondary species.

[67] We write the vector of activities, $\mathbf{a}$, as

\[
\mathbf{a} = (H^+, HCO_3^-, CO_3^{2-}, CO_2, Mg^{2+}, Ca^{2+}, CaMg(CO_3)_{2s}, CaCO_3s, H_2O)^T,
\]

which is written respecting the order presented in section 2, first the primary species, then the secondary, and last the constant activity species. The stoichiometric matrix is
Note that negative and positive coefficients in \( S_s \) are related to reactants and products of the reactions, respectively. Multiplying \( S_{ea} \) and \( S'_{ea} \) by \(-S_{ea}^{-1}\) we rewrite the stoichiometric matrix so that the matrix of the stoichiometric coefficients of the secondary species coincides with the opposite of the identity matrix, \( I \), and redefine the matrices \( S_{ea} \) as

\[
(S'_{ea} | -I) = \begin{pmatrix}
H^+ & HCO_3^- & CO_3^{2-} & CO_2 & Mg^{2+} & Ca^{2+} \\
-1 & 1 & -1 & 0 & 0 & 0 \\
1 & 1 & 0 & -1 & 0 & 0 \\
0 & 0 & 2 & 0 & 1 & 1 \\
0 & 0 & 1 & 0 & 0 & 1
\end{pmatrix}
\]

This last operation has simply implied rewriting the last two reactions (A1c) and (A1d) in terms of primary species (i.e., eliminating \( CO_3^{2-} \)), so that the last two reactions now read

\[
\begin{align*}
Mg^{2+} &= CaMg(CO_3)_{2a} - CaCO_3_{3a} + H^+ - HCO_3^- \quad (A5a) \\
Ca^{2+} &= CaCO_3_{3a} + H^+ - HCO_3^- \quad (A5b)
\end{align*}
\]

**Appendix B: Reaction Rate for a Binary System**

Here we detail the steps leading to a general expression for the rate of the reaction of pure precipitation/dissolution processes in a binary system (given by equation (20)). We start from the transport equation of the species \( B_2 \) (equation (16b)) and assume \( n \) to be constant. Recalling (19b), the time derivative of \( c_2 \) can be expressed as

\[
\frac{\partial [n c_2(u, K)]}{\partial t} = n \left( \frac{\partial c_2}{\partial u} + \frac{\partial c_2}{\partial K} \right) \quad (B1)
\]

We introduce the advective and diffusive linear operators, \( L_{r, adv} \) and \( L_{r, dr} \), defined as

\[
L_r(c) = n[L_{r, adv}(c) + L_{r, dr}(c)] \quad (B2)
\]

where

\[
L_{r, adv}(c) = -V \cdot \nabla c \quad (B3a)
\]

\[
L_{r, dr}(c) = \nabla \cdot (D \nabla c) \quad (B3b)
\]

and \( V = q/n \).

Finally, substituting (B1) and (B6) into (16b) and recalling (11), yields

\[
\begin{align*}
\frac{r}{n} &= \frac{\partial c_2}{\partial K} \left[ \frac{-\partial K}{\partial t} + \frac{1}{n} L_r(K) \right] + \frac{\partial^2 c_2}{\partial u^2} \nabla^T u D \nabla u + \frac{2 \partial^2 c_2}{\partial u \partial K} \nabla^T u D \nabla K + \frac{\partial^2 c_2}{\partial K^2} \nabla^T K D \nabla K.
\end{align*}
\]

**Appendix C: Reaction Rate for a Binary System When the Equilibrium Constant Depends on Conservative Quantities**

This Appendix is devoted to finding the expression for the rate of the reaction of pure precipitation/dissolution, when the equilibrium constant, \( K \), is a function of a given quantity, \( s \), satisfying a nonreactive form of the advection-dispersion equation. This could be, for example, the case of salinity.

We start from the general expression of the reaction rate (20)

\[
\begin{align*}
\frac{r}{n} &= \frac{\partial c_2}{\partial K} \left[ \frac{-\partial K}{\partial t} + \frac{1}{n} L_r(K) \right] + \frac{\partial^2 c_2}{\partial u^2} \nabla^T u D \nabla u + \frac{2 \partial^2 c_2}{\partial u \partial K} \nabla^T u D \nabla K + \frac{\partial^2 c_2}{\partial K^2} \nabla^T K D \nabla K.
\end{align*}
\]
As $K$ is function of $s$, the time derivative of $K$ can be expressed as
\[
\frac{\partial K(s)}{\partial t} = \frac{\partial K}{\partial s} \cdot \frac{\partial s}{\partial t}.
\] (C2)

Recalling the definition of advective and diffusive linear operators, $L_{u, adv}$ and $L_{u, d}$ (equations (B3a) and (B3b)), we split the operator $L_t (K)$ as
\[
\frac{1}{n} L_t(K) = L_{u, adv}(K) + L_{u, d}(K).
\] (C3)

Applying the advective operator to $K$ leads to
\[
L_{u, adv}(K) = \frac{\partial K}{\partial s} \cdot (-\nabla \cdot n s).
\] (C4)

The diffusive operator acting on $K$ provides
\[
L_{u, d}(K) = \nabla \cdot \left( \frac{\partial K}{\partial s} (\nabla s) \right) = \frac{\partial K}{\partial s} \cdot (\nabla s) \nabla s + \frac{\partial^2 K}{\partial s^2} \nabla^2 s \nabla s.
\] (C5)

By virtue of (C4) and (C5), (C3) results
\[
\frac{1}{n} L_t(K) = \left\{ \frac{\partial K}{\partial s} \cdot (-\nabla \cdot n s + \nabla \cdot (\nabla s)) + \frac{\partial^2 K}{\partial s^2} \nabla^2 s \nabla s \right\}.
\] (C6)

Substituting (C2) and (C6) into (C1), and recalling that $s$ satisfies a nonreactive format of the advection-dispersion equation, leads to
\[
\frac{r}{n} = \frac{\partial c_2}{\partial K} \left( \frac{\partial^2 K}{\partial s^2} \nabla^2 s \nabla s \right) + \frac{\partial c_2}{\partial u} \nabla^2 u \nabla u + 2 \frac{\partial^2 c_2}{\partial u \partial s} \nabla^2 u \nabla s \nabla u + \frac{\partial^2 c_2}{\partial K^2} \nabla^2 K \nabla s.
\] (C7)

Since $K$ is a function of $s$, the last two terms in (C7) can be written as
\[
\frac{\partial^2 c_2}{\partial u \partial s} \nabla^2 s \nabla s = \frac{\partial c_2}{\partial u} \nabla^2 u \nabla u \nabla s \nabla s
\] (C8)

\[
\frac{\partial^2 c_2}{\partial K^2} \nabla^2 K \nabla s = \frac{\partial c_2}{\partial K} \frac{\partial K}{\partial s} \nabla^2 s \nabla s
\] (C9)

Substituting (C8) and (C9) into (C7) and noticing that
\[
\frac{\partial^2 c_2}{\partial s^2} = \frac{\partial c_2}{\partial K} \frac{\partial K}{\partial s} + \frac{\partial^2 c_2}{\partial K^2} \left( \frac{\partial K}{\partial s} \right)^2,
\]
we finally obtain
\[
\frac{r}{n} = \frac{\partial c_2}{\partial s} \nabla^2 s \nabla s + \frac{\partial c_2}{\partial u} \nabla^2 u \nabla u + 2 \frac{\partial^2 c_2}{\partial u \partial s} \nabla^2 u \nabla s \nabla u + 2 \frac{\partial^2 c_2}{\partial K^2} \frac{\partial K}{\partial s} \nabla^2 s \nabla s. \] (C10)

**Appendix D: Analytical Solution for the Overall Reaction Rate in a Binary System**

[73] Here we provide the analytical expression of the overall rate, $r_\Omega$ (equation (30b)), in the case of large dispersion effects (large dimensionless volumes, $\tilde{V}_d$).

\[
\frac{\partial}{\partial t} \left( n c''_{a,m}(u, K) \right) = n \sum_{i=1}^{N_u} \frac{\partial c''_{a,m}}{\partial u_i} \frac{\partial u_i}{\partial t} + n \sum_{p=1}^{N_p} \frac{\partial c''_{a,m}}{\partial K_p} \frac{\partial K_p}{\partial t}
\] (E1)

where $N_u = N_s - N_e - N_r$ is the number of primary species.

[76] Application of the advective operator, $L_{u, adv}$ (equation (33a)), yields
\[
L_{u, adv}(c_{a,m}''(u, K)) = \sum_{i=1}^{N_u} \frac{\partial c_{a,m}''}{\partial u_i} \left( -\nabla \cdot n_s + \nabla \cdot (\nabla s) \right) + \sum_{p=1}^{N_p} \frac{\partial c_{a,m}''}{\partial K_p} \left( -\nabla \cdot n_s \nabla K_p \right)
\] (E2)

The diffusive operator, $L_{u, d}$ (equation (33b)), acting on $c_{a,m}''$ is expressed as
\[
L_{u, d}(c_{a,m}''(u, K)) = \sum_{i=1}^{N_u} \frac{\partial c_{a,m}''}{\partial u_i} \left( \nabla \cdot n_s \nabla u_i \right) + \sum_{p=1}^{N_p} \nabla \left( \frac{\partial c_{a,m}''}{\partial K_p} \right) \cdot \left( \nabla K_p \right)
\] (E3)

Upon noting that
\[
\nabla \left( \frac{\partial c_{a,m}''}{\partial u_i} \right) = \sum_{j=1}^{N_u} \frac{\partial^2 c_{a,m}''}{\partial u_i \partial u_j} \nabla u_j + \sum_{q=1}^{N_p} \frac{\partial^2 c_{a,m}''}{\partial u_i \partial K_q} \nabla K_q
\] (E4)
equation (E3) can be rewritten as
\[
L_{e,n} \left( \frac{\partial c_{i,a}^n}{\partial t} \right) = \sum_{i=1}^{N_c} \frac{\partial c_{i,a}^n}{\partial t} \nabla \cdot \left( D \nabla u_i \right) + \sum_{p=1}^{N_p} \frac{\partial c_{i,a}^n}{\partial t} \nabla \cdot \left( D \nabla K_p \right) + \frac{N_c}{n} \sum_{i=1}^{N_c} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T u_i D \nabla u_i + 2 \sum_{i=1}^{N_c} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T u_i D \nabla K_p + \sum_{p=1}^{N_p} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T K_p D \nabla K_p.
\]

(E5)

Using (E2) and (E5), the linear operator (7) acting on \( c_{i,a}^n \) can be written as
\[
L_i \left( c_{i,a}^n \right) = n \left\{ \sum_{i=1}^{N_c} \frac{\partial c_{i,a}^n}{\partial t} \left[ - \nabla \cdot \left( c_{i,a}^n \nabla K_p \right) \right] + \sum_{i=1}^{N_c} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T u_i D \nabla u_i + \sum_{p=1}^{N_p} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T K_p D \nabla K_p \right\}.
\]

(E6)

Substituting (E1) and (E6) into (37), when written for a single species, \( c_{i,a}^n \) and recalling (11), leads to
\[
r_m = \frac{n}{N_c} \sum_{i=1}^{N_c} \frac{\partial c_{i,a}^n}{\partial t} \left[ - \frac{\partial K_p}{\partial t} \nabla \cdot \left( \nabla K_p \right) \right] + \frac{n}{N_c} \sum_{i=1}^{N_c} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T u_i D \nabla u_i + 2 \sum_{i=1}^{N_c} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T u_i D \nabla K_p + \sum_{p=1}^{N_p} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T K_p D \nabla K_p.
\]

(E7)

Finally, the rate of reaction of the entire system is
\[
- \frac{r}{n} = \frac{n}{N_c} \sum_{i=1}^{N_c} \frac{\partial c_{i,a}^n}{\partial t} \left[ - \frac{\partial K_p}{\partial t} \nabla \cdot \left( \nabla K_p \right) \right] + \frac{n}{N_c} \sum_{i=1}^{N_c} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T u_i D \nabla u_i + 2 \sum_{i=1}^{N_c} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T u_i D \nabla K_p + \sum_{p=1}^{N_p} \frac{\partial^2 c_{i,a}^n}{\partial t^2} \nabla^T K_p D \nabla K_p.
\]

(E8)

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