A mixing ratios-based formulation for multicomponent reactive transport

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[1] Chemical reactions are driven by disequilibrium, which is often caused by mixing. Therefore quantification of the mixing rate is essential for evaluating the fate of solutes in natural systems, such as rivers, lakes, and aquifers. We propose a novel mixing ratios-based formulation to evaluate solute concentrations and reaction rates when equilibrium aqueous reactions and precipitation/dissolution of minerals are driven by mixing of different end-members. Each end-member corresponds to a water from a given source with a specific chemical signature. The approach decouples the solute transport and chemical speciation problems, so that mixing ratios can be first obtained from the solution of conservative transport and then be used in general speciation codes to obtain the concentration of reacting species. One key finding is a general expression for reaction rates which demonstrates that the amount of reactants evolving into products depends on the rate at which solutions mix. Our formulation constitutes a general framework according to which one can design and interpret experimental analyses devoted to study mixing-driven reactive processes and obtain transverse dispersion coefficients.

The formulation is also proposed as a useful tool to derive analytical solutions of reactive transport problems and may result computationally advantageous when compared to previous approaches to reactive transport modeling. We apply the developed formulation to provide an analytical solution of the reactive transport process resulting from mixing different CaCO 3 -saturated waters in a two-dimensional setup.


1. Introduction

[2] The relevance of mixing in reactive transport phenomena is well documented; mixing controls chemical speciation in aquatic systems [Witters, 1998; Aucour et al., 2003] and has a significant impact in pollutant concentrations where surface and subsurface waters interact [Choi et al., 1998; Tonkin et al., 2002; Balistrieri et al., 2003]. Moreover, mixing of waters originally in equilibrium with a mineral drives precipitation and dissolution of mineral species [Rezaei et al., 2005; Emmanuel and Berkowitz, 2005]. Because of their complexity and extension, special attention has been given to mixing-driven processes governing the geochemistry of carbonate systems [e.g., Sanford and Konikow, 1989; Corbella et al., 2003; Singurindy et al., 2004; Rezaei et al., 2005; Romanov and Dreybrodt, 2006], including karst development [Gabrovšek and Dreybrodt, 2000; Kaufmann, 2003]. Mixing may also be the governing process for microbial reactions [Nambi et al., 2003; Chu et al., 2005; Knutson et al., 2005], which are relevant in natural attenuation problems [Cirpka et al., 1999]. Hence it is not surprising that emphasis has been placed in characterizing mixing [Gramling et al., 2002; Jose and Cirpka, 2004].

[3] Mixing can be characterized in terms of mixing ratios, which are defined as the proportion of each of the mixing waters in the mixed sample. The original mixing waters, from which all mixtures are derived, are often called end-members. Presumably, end-members differ in the concentrations of some species (that is, they display different “chemical signatures”). The concentration of a conservative solute in a mixture is obtained by linear combination of the concentrations of the end-members. Mixing ratios are useful because they can be quantified from the analysis of conservative chemical species even when end-members are uncertain [Carrera et al., 2004; Rueedi et al., 2005]. Deviations from perfect mixing may be used to identify the chemical processes controlling the system [Tonkin et al., 2002; Aucour et al., 2003] or to determine parameters characterizing plume transport [Cirpka et al., 2006].

[4] Formulations of mixing-driven chemical processes are complex. Some of these can be eliminated using equilibrium relations, according to the phase rule. For example, carbonate systems are typically governed by six aqueous species (H + , OH − , Ca 2+ , HCO 3 − , CO 3 2− , CO 2(aq) ) and four reactions (water, HCO 3 − and CO 3 2− dissociation, and calcite dissolution), plus two constant activity species (H 2 O and CaCO 3 ). So the system has two degrees of freedom [e.g., Rezaei et al., 2005]. Yet, Sanford and Konikow [1989]
correctly solved the problem using one independent variable. We attribute this paradox to the fact that their problem was driven by mixing, so that the proportion of one of the end-members (i.e., the mixing ratio) was the only independent variable. The question is, thus, whether reactive transport problems can be formulated in terms of mixing ratios.

The objective of this paper is to present a novel mixing ratios-based formulation to solve reactive transport problems in the case of equilibrium aqueous reactions and precipitation/dissolution of minerals induced by mixing of different solutions. The work extends that of De Simoni et al. [2005], who solved multispecies reactive transport using components and assuming chemical equilibrium. As such, it does not apply to cases where reactions need to be treated kinetically (that is, their characteristic reaction time is long compared to diffusive mixing characteristic times) nor to reactions where immobile species display variable activity (for example, coprecipitation, solid mixtures, or ion exchange reactions).

2. Theoretical Developments

Modeling reactive transport involves two coupled ingredients, mass balances of species and a set of equations describing reactions among species.

2.1. Species Transport Equations

Species mass balance can be written [e.g., Saaltink et al., 1998; Molins et al., 2004] as

\[ \frac{\partial N}{\partial t} = M\mathbf{c} + f. \]  

Here vector \( M \) contains the mass of species per unit volume of medium, and vector \( c \) contains species concentrations (for \( M \) and \( c \), we assume solutions of chemical species are plug flow, so that \( M = \) a constant, and \( c \) is a source/sink term, which is used to represent chemical reactions. The linear operator \( L(c) \) in equation (1) is defined as \( L(c) = -\nabla \cdot (nvc) + \nabla \cdot (a\nabla c) \), where \( D \) is the dispersion tensor and \( v \) is the fluid velocity (we assume that \( D \) and \( v \) are the same for all species).

2.2. Equilibrium Reactions

Chemical reactions can be assumed at equilibrium when their rate is fast compared to transport processes. When their rate is slow compared to transport processes, some species (here called constant activity species), such as water and minerals, can be assumed to be constant. Species mass balance can be written [e.g., Saaltink et al., 1998; Steefel and Mac Quarrie, 1996; Saaltink et al., 1998]. We choose as primary species the \( N_c \) constant activity species plus \( N_r - N_c \) aqueous species. Since we consider mineral species to have constant activities, all secondary species are aqueous. We split vector \( a \) as \( a = (a_0, a_r, a'_r) \), where \( a_0 \) contains the activities of the \( N_c \) constant activity species. \( a'_r \) contains the \( N_r \) (\( = N_r - N_c \) aqueous activity species. Likewise, we subdivide \( S_a \) into three parts. It is always possible to redefine the chemical system so that the contribution of the secondary species to \( S_a \) is minus the identity matrix \( I \). That is, the \( S_a \) matrix is decomposed as \( S_a = (S_{ae}|S_{ec}' - I) \), where \( S_{ae} \) and \( S_{ec}' \) correspond to the stoichiometric coefficients of constant activity and primary species, respectively. This allows an explicit calculation of the secondary species activities from mass action laws as

\[ \log a'_r = S_{ec}' \log a'_r - \log K. \]  

Alternatively, equation (2) can be written in terms of concentrations \( c = (c_0, c_r) = (c_e, c'_e, c'_r) \), that is, \( c_e \) and \( c'_e \) represent concentrations of primary and secondary species, respectively as

\[ \log c'_r = S_{ec}' \log c'_e - \log K_e. \]  

where \( K_e \) is a vector of equivalent equilibrium constants defined as

\[ \log K_e = \log K - (S_{ec} - I) \log c_e. \]  

\( \gamma_e \) being the vector of activity coefficients.

2.3. Components

Solution of reactive transport problems can be simplified upon defining components [Lichtner, 1985; Steefel and Mac Quarrie, 1996; Saaltink et al., 1998; Molins et al., 2004; De Simoni et al., 2005] by introducing an auxiliary component matrix, \( U \). Among the different possible definitions for matrix \( U \), we chose to define it so that \( US_{ec}' = (S_{ec} 0)^T \). Since \( S_{ec} = (S_{ae}|S_{ec}' - I) \), an expression for \( U \) is

\[ U = \begin{pmatrix} \mathbf{U}_a \\ \mathbf{U}_r \end{pmatrix} = \begin{pmatrix} N_c \\ 1 \ 0 \ 0 \\ 0 \ 1 \ S_{ec}' \end{pmatrix} \]  

Multiplication of equation (1) by \( U \) leads to

\[ \frac{\partial (Mu)}{\partial t} = M_L(u) + S_{ec}' \mathbf{r}, \]  

\[ \frac{\partial (Mu)}{\partial t} = L(u) \]
where vector $\mathbf{m}$ contains the mass of constant activity species and $\mathbf{u}$ is a vector of $N_a$ (aqueous) components defined as

$$\mathbf{u} = \mathbf{U}_0 \mathbf{c} = \mathbf{c}_0 + (\mathbf{S}_{a0})^T \mathbf{c}_0.$$  

(8)

[13] Equation (7) represents $N_a$ transport equations without reaction sink/source terms. That is, components are indeed conservative quantities in systems at equilibrium. Vector $\mathbf{u}$ contains only aqueous species so that we can leave out matrix $\mathbf{M}$ in equation (7), while $\mathbf{M}_i$ [equation (6)] is the part of $\mathbf{M}$ referring to constant activity species.

[14] Once equation (7) is solved (with appropriate boundary and initial conditions), (aqueous) solutes concentrations are obtained from the expression of $\mathbf{u}$ in terms of concentrations species [equation (8)] and the mass action law [equation (3)]. Equilibrium reaction rates are then defined from transport equations [equation (1)] of secondary species [De Simoni et al., 2005] as:

$$\mathbf{r} = \mathbf{L}(\mathbf{c}_e) - \frac{\partial (\mathbf{n}_a)}{\partial t}.$$  

(9)

The mass evolution of the constant activity species is finally obtained upon substituting $\mathbf{r}$ into equation (6).

[15] Here we focus on reactive transport problems induced by mixing. We define mixing ratio, $\alpha_i$, as the proportion of end-member $i$ in a water sample. Thus, the concentration of a conservative species can be written in terms of the mixing ratios and the concentrations of the end-members as:

$$c = \sum_{i=1}^{N} \alpha_i c_i.$$  

(10)

where $c$ is the concentration of the water sample and $c_i$ the concentration of the ith end-member. In equation (10), $N$ is the number of end-members, which is equal to the number of mixing ratios defining the problem. Actually the number of independent variables that could be used to fully define the system is equal to $N_i - 1$, since the $\alpha_i$ values should satisfy $\sum_{i=1}^{N} \alpha_i = 1$.

[16] From equation (10), it turns out that the mixing ratios are conservative quantities, and thus it is possible to define the transport problem as a suite of transport equations for the different mixing ratios. This constitutes the starting point of our mixing ratios-based formulation.

3. Solution Methodology

[17] The methodology to evaluate solute concentrations and reaction rates in mixing-driven reactive transport processes is developed over four steps.

3.1. Step (1) Evaluation of the Mixing Ratios

[18] As explained in the previous section, the independent mixing ratios $\alpha_i$ ($i = 1, N_i - 1$) satisfy conservative transport equations

$$\frac{\partial \alpha_i}{\partial t} = L(\alpha_i).$$  

(11)

with homogeneous boundary and initial conditions, except where end-member $i$ is initially present or enters the system. Equation (11) can be solved using analytical techniques or numerical tools to provide mixing ratios at any location and time. Mixing ratios can also be mapped from chemical analyses at locations where water is sampled [Carrera et al., 2004] without the need for solving equation (11).

3.2. Step (2) Evaluation of Components

[19] Components are defined by means of equation (8); being conservative quantities, they are linearly related to $\alpha_i$

$$\mathbf{u} = \sum_i \alpha_i \mathbf{u}_i,$$  

(12)

where $\mathbf{u}_i$ is the vector of components concentrations in the ith end-member. Equation (12) can also be obtained directly from equations (8) and (10).

3.3. Step (3) Speciation Calculations

[20] Once system components have been evaluated, $\mathbf{c}_e = (\mathbf{c}_e \mathbf{c}_e)^T$ is obtained from the nonlinear algebraic system of equations (3) and (8). Vector $\mathbf{c}_e$ may depend on several factors, including pH, salinity, and temperature. This generally leads to nonlinear functional dependences on mixing ratios. Thus, speciation may be computationally demanding; yet it is a standard option on speciation codes, such as PHREEQC [Parkhurst, 1995]. Speciation calculations can be done for a prespecified set of mixing ratios (for example, considering two end-members, one could compute the solution for $\alpha_i$ ranging between 0 and 1 with an appropriate step). These in conjunction with solutions of step (1), these calculations would provide the spatial and temporal distribution of $\mathbf{c}_e$. Thus, there is no need to solve the system of equations (3) and (8) at all domain nodes for every time step and the computational efficiency in speciation calculations may increase.

3.4. Step (4) Calculation of Reaction Rates

[21] Speciation provides the concentrations of primary and secondary species as a (nonlinear) function of mixing ratios. Substituting $\mathbf{c}_e = \mathbf{c}_e(\alpha_i)$ into equation (9), and after some algebra, leads to [De Simoni et al., 2005]:

$$\mathbf{r} = n \sum_i \frac{\partial \mathbf{c}_e}{\partial \alpha_i} (\nabla^T \alpha_i \mathbf{D} \nabla \alpha_i).$$  

(13)

[22] This is a key result in our analysis and highlights that reaction rates are given by the sum of the individual contributions which themselves are the product of two terms. The first one reflects the nonlinearity in the speciation (notice that a linear variation of $\mathbf{c}_e$ with $\alpha_i$ would lead to a null second derivative). The second term is the contribution due to transport and is always positive; hence the sign of the reaction rate is governed by the first term. Once $\mathbf{r}$ is computed, $\mathbf{m}_i$ can be obtained from equation (6).

[23] Evaluation of reaction rates may be further simplified. The term $(\nabla^T \alpha_i \mathbf{D} \nabla \alpha_i)$ in equation (13) is known once the mixing ratio is evaluated (step 1). Several alternatives are available to provide the first term on the right-hand side of equation (13). In relatively simple cases, $\partial^T c_{mn} / \partial \alpha_i$ ($c_{mn}$ represents the mth secondary species) may be evaluated analytically or numerically (for instance by means of a MATLAB procedure, as we do for the example provided in
4. Illustrative Example

[24] We consider a two-dimensional homogeneous domain under uniform flow conditions. The velocity, \( V \), is aligned along the x axis (Figure 1a). Mixing is controlled by a uniform dispersion tensor \( D_L \) and \( D_T \) being the longitudinal and transverse components, respectively. Two end-members enter the domain at \( x = 0 \), creating a mixing zone of transverse extent \( \delta \) (Figure 1a).

[25] A large number of environmental problems can be modeled by means of this scheme, mixing of freshwater and seawater in coastal aquifers [Rezaei et al., 2005; Romanov and Dreybrodt, 2006], hydrochemistry at river confluences [Aucour et al., 2003], or processes of river water infiltrating in aquifers [Balistreri et al., 2003]. It can also depict the mixing of two parallel streams, respectively, containing an electron acceptor and donor when modeling growth of dechlorinating microorganisms [Nambi et al., 2003; Chu et al., 2005].

[26] This scheme may be helpful in designing/interpreting field or laboratory experiments to analyze chemical reactions in mixing zones [Singurindy et al., 2004]. A relevant quantity in defining the setup for these experiments is the extent, \( \delta \), of the mixing zone. Inside this zone, dispersive and advective time-scales are of the same order of magnitude, that is \( \delta^2 / D_T \approx x / V \), thus revealing that \( \delta \) increases with \( \sqrt{x} \) [Nambi et al., 2003; Chu et al., 2005] and also with \( \sqrt{D_T} \) [Rezaei et al., 2005].

[27] We apply our proposed formulation to analytically solve the process arising from the mixing of two CaCO3-saturated end-members under chemical equilibrium conditions. The two end-members have different chemistry composition but are both saturated with respect to calcite. We exclude the possibility of complete mineral dissolution, so that equilibrium with respect to calcite is assumed in the whole domain at all times. In addition to steady state flow, we assume pseudo-steady state transport; that is, aqueous concentrations do not change with time even though minerals do. This geochemical setup is frequently employed to analyze the evolution of calcite dissolution/precipitation in coastal aquifers [e.g., Sanford and Tonkonow, 1985; Singurindy et al., 2004].

[28] The chemical system is described by four chemical reactions. These reactions are written putting on evidence aqueous primary species. Among the different possibilities available to select these species, we chose CO3\(_{aq}\) and H\(^+\) as aqueous primary species. Thus,

\[
\begin{align*}
R1 & \quad \text{HCO}_3^- = \text{CO}_3^{aq} + \text{H}_2\text{O} + \text{H}^+ \\
R2 & \quad \text{CO}_3^{2-} = \text{CO}_2^{aq} + \text{H}_2\text{O} - 2\text{H}^+ \\
R3 & \quad \text{Ca}^{2+} = \text{CaCO}_3 - \text{CO}_2^{aq} - \text{H}_2\text{O} + 2\text{H}^+ \\
R4 & \quad \text{OH}^- = \text{H}_2\text{O} - \text{H}^+ 
\end{align*}
\]

We identify CaCO3 and H2O as constant activity species, while Ca\(^{2+}\), HCO3\(^-\), CO3\(^{2-}\), and OH\(^-\) are secondary species, thus

\[
\mathbf{c} = (c \ \ c_a' \ \ c_{ac}')^T = (\text{CaCO}_3 \ \ \text{H}_2\text{O}|\text{CO}_3^{aq}) \ \ \text{H}^+|\text{HCO}_3^-|\text{CO}_3^{2-}|\text{Ca}^{2+}|\text{OH}^-)^T
\]

(15)

The ensuing stoichiometric matrix of the reactions R1–R4 [equations (14a)–(14d)] is

\[
\mathbf{S}_e = \begin{pmatrix}
\text{CaCO}_3 & \text{H}_2\text{O} & \text{CO}_2 & \text{H}^+ & \text{HCO}_3^- & \text{CO}_3^{2-} & \text{Ca}^{2+} & \text{OH}^- \\
0 & 1 & 1 & -1 & -1 & 0 & 0 & 0 \\
0 & 1 & 1 & -2 & 0 & -1 & 0 & 0 \\
1 & -1 & -1 & 2 & 0 & 0 & -1 & 0 \\
0 & 1 & 0 & -1 & 0 & 0 & 0 & -1
\end{pmatrix}
\]

(16)
Hence the source term in the species mass balance [equation (1)] is

\[ f = (S_c)^T \mathbf{r} \]

\[ = \left( r_1; r_1 + r_2 - r_3 + r_4; r_1 + r_2 - r_3; r_1 - 2r_2 + 2r_3 - r_4; -r_2; -r_3; -r_4 \right)^T \]  

(17)

and vector \( \mathbf{K}^* = (K_1^* K_2^* K_3^* K_4^*)^T \) [equation (4)] reads

\[ \mathbf{K}^* = \left( \frac{K_1^* \gamma_{CO_2} \gamma_{H^+}}{\gamma_{CO_2}}; \frac{K_2^* \gamma_{CO_2} \gamma_{H^+}}{\gamma_{CO_2}}; \frac{K_3^* \gamma_{Ca^2+} \gamma_{CO_2}}{\gamma_{H^+}}; \frac{K_4^* \gamma_{OH^-} \gamma_{H^+}}{\gamma_{H^+}} \right)^T \]  

(18)

Here \( K_1, K_2, K_3, \) and \( K_4 \) are the equilibrium constants of reactions R1–R4 [equations (14a)–(14d)], \( (K_1 = 10^{9.3447}, K_2 = 10^{16.6735}, K_3 = 10^{-8.1934}, K_4 = 10^{13.9938}) \), while \( \gamma_m \) is the activity coefficient of species \( m \).

[29] The two end-members (Figure 1a) contain the six aqueous constituents [equation (15)] at different concentrations; they can also contain solutes which do not contribute directly to the carbonate system, such as \( Na^+ \) and \( Cl^- \) that may control water salinity. Since solutions may be not diluted, we model \( \gamma_m \) using the extended Debye-Hückel equation:

\[ \log \gamma_m = \frac{1}{1 + B \omega_m \sqrt{\xi}} \]  

(19)

where \( \bar{I} \), is the ionic strength, defined as \( \bar{I} = 0.5 \sum_{\alpha} e_{\alpha}^2 \omega_{\alpha} \gamma_{\alpha} \).

[20] In Table 1, \( C_{\alpha} \) are the valence and \( \omega_{\alpha} \) is the ionic radius of species \( \alpha \), respectively. \( \omega_{\alpha} \) is a characteristic constant; \( A \) and \( B \) are temperature dependent parameters. We set \( A = 0.5092, B = 0.3282 \) (values at 25°C), \( b = 0.041 \). Values of \( \omega_{\alpha} \) are provided in Table 1.

[21] The concentration of the primary species CO\(_2\)(aq) (such as calcium and bicarbonate), the ionic strength of a mixture of two waters is \( \bar{I} = \alpha \bar{I}_1 + (1 - \alpha) \bar{I}_2 \), where subscripts 1 and 2 refer to the two end-members and \( \alpha \) is the mixing ratio, which corresponds in this case to the contribution of end-member 2 (thus the fraction of end-member 1 is \( 1 - \alpha \)). This assumption, which basically implies assuming that precipitation or dissolution of calcite does not change the ionic strength, simplifies the mathematical problem. Indeed, the dependence of \( \bar{I} \) on species, such as calcium and bicarbonate, would bring \( \mathbf{K}^* \) to depend on these species concentrations and thus would lead an additional nonlinearity to the problem.

[30] We apply the methodology outlined in section 3 to obtain the spatial and temporal distribution of species concentration and reaction rates.

4.1. Step (1) Evaluation of the Mixing Ratios

[32] We consider an advective-dominated transport problem, characterized by a large Peclet number, \( Pe = Vx / D_f \). In steady state and neglecting longitudinal dispersion [Rezaei et al., 2005], equation (11) becomes \(-V \frac{\partial}{\partial x} + D_f \frac{\partial^2}{\partial y^2} = 0 \). The domain of the problem is \( (x \in [0, +\infty]; y \in [-\infty, +\infty]) \), and the mixing ratio is prescribed along the boundary as \( \alpha(x = 0, y \in [0, +\infty]) = 0, \alpha(x = 0, y \in [0, -\infty]) = 1 \). The mathematical solution of this problem is [e.g., Haberman, 1998, p. 449]

\[ \alpha = \frac{1}{2} \left(1 - \text{erf} \left( \frac{y}{\sqrt{2} \bar{I}} \right) \right), \]  

(20)

where \( \eta = \sqrt{Pe}y/x \) is a similarity variable, representing a normalized transverse coordinate and \( \text{erf}[\cdot] \) is the error function.

[33] The dependence of mixing ratios on \( \eta \) is illustrated in Figure 1b. Since \( \alpha \) depends solely on \( \eta \) [equation (20)], Figure 1b is representative of a generic section transverse to flow (\( x = \text{constant} \)).

4.2. Step (2) Evaluation of Components

[34] Using equation (5) for \( U \) and equation (16) for \( S_c \), we obtain two components

\[ u = \left( \frac{c_{Ca^2+} - c_{Ca^2+}^*}{c_{Ca^2+}^* - c_{Ca^2+}}; \frac{c_{CO_2} - c_{CO_2}^*}{c_{CO_2}^* - c_{CO_2}}; \frac{c_{H^+} - c_{H^+}^*}{c_{H^+}^* - c_{H^+}}; \frac{c_{OH^-} - c_{OH^-}^*}{c_{OH^-}^* - c_{OH^-}} \right) \]  

(21)

where \( u_0 \) is the initial total dissolved carbon minus calcium, and \( u_1 \) is the total charges which are indeed conservative quantities [Andre and Rajaram, 2005]. Since \( u_1 \) is already known [equation (20)], \( u(x, y) \) (actually \( u(\eta) \)) may be evaluated using equation (12).

4.3. Step (3) Speciation Calculations

[35] Once \( u \) is given, aqueous species concentrations are the solution of the nonlinear algebraic system provided by equations (21) and (21). We first calculate \( c'_{\alpha} \) using the mass action laws [equations (3)] to eliminate secondary species from equation (21) leads to a sixth order polynomial for \( c'_{Hi}: \)

\[ c'_{Hi} \left( 4K^*_1 - 1 \right) + c_{Hi} \left[ 2(u_1 + u_2) - K^*_1 + 4K^*_1 K^*_3 \right] + c_{Hi}^2 \left[ -2u_1(u_1 + u_2) + K^*_3 (3u_1 + 2u_2) + 2K^*_4 - K^*_3 + K^*_3 K^*_3 \right] + c_{Hi}^3 \left[ -K^*_3 (u_1 + u_2)(2u_1 + u_2) - 3(2u_1 + u_2)K^*_4 + 2K^*_4 K^*_3 + 2K^*_4^2 (2u_1 + u_2) \right] + c_{Hi}^4 \left[ -K^*_3 K^*_4 (3u_1 + 2u_2) - K^*_4^2 - K^*_4 (2u_1 + u_2)^2 + 2K^*_4 K^*_4 \right] + c_{Hi}^5 \left[ -2K^*_4 K^*_4 (2u_1 + u_2) - K^*_3 K^*_4^2 - K^*_4 K^*_4^2 \right] = 0 \]  

(21a)

The concentration of the primary species CO\(_2\)(aq) is

\[ c_{CO_2} = \frac{-c^2_{Hi} + c_{Hi} (2u_1 + u_2) + K^*_4^2}{2c_{Hi} - K^*_4} \]  

(21b)

Given \( c'_{\alpha} \), concentrations of secondary species are provided by equation (3). From a practical point of view, \( c_{Hi} \) and \( c_{CO_2} \) are calculated solving (numerically) equation (21a) and
the absence of either algebraic or ionic strength effects. The last term contributes to reaction rates when the end-members have different ionic strength, for example, in the fresh-saltwater mixing zone of coastal aquifers. We recall that both concentrations have to be real and positive.

### 4.4. Step (4) Calculation of Reaction Rates

Using equation (13), the reaction rates result

$$ r = \frac{nV}{x} \frac{\partial^2 c_a^n}{\partial x^2} (\frac{d\alpha}{d\eta})^2, $$

where \( d\alpha / d\eta = -1/(2\sqrt{\pi})\exp[-\frac{\eta^2}{4}] \). Substituting in equation (3) \( c_a^n \) as function of \( \alpha \) and \( K(\alpha) \) allows defining the functional dependence \( c_a^n = c_a^n(\alpha) \), then an ad hoc code can be employed to evaluate \( \partial^2 c_a^n / \partial \alpha^2 \) and quantify \( r \) by means of equation (23). Equation (3) reveals that every \( c_a^n \) depends on \( \alpha \) through \( c_a^n \) and \( K_m \). Thus, we can set \( c_a^n = w(c_a)(K_m) \) \((w(\cdot) \text{ and } g(\cdot) \text{ being functions specified by mass action laws})\) and separate three contributions in \( \partial^2 c_a^n / \partial \alpha^2 \):

$$ \frac{\partial^2 c_a^n}{\partial \alpha^2} = \frac{\partial^2 w(c_a)}{\partial x^2} + \frac{\partial w(c_a)}{\partial \alpha} \frac{\partial g(K_m)}{\partial \alpha} + \frac{\partial g(K_m)}{\partial \alpha} \frac{\partial w(c_a)}{\partial x^2}, $$

The first term on the right-hand side of equation (24) is related to primary species variations and is typically referred to as algebraic effect [Corbella et al., 2003; Molins et al., 2004]. The last term contributes to reaction rates when the end-members have different ionic strength, for example, in the fresh-saltwater mixing zone of coastal aquifers. We recall that both concentrations have to be real and positive.

At this stage, the system is fully solved, and we use the solution to simulate dissolution and precipitation of calcite because of the mixing of two CaCO₃-saturated waters inside the fresh-saltwater mixing zone of coastal aquifers. We recall that the derived analytical solution is limited to high Porosity and groundwater velocity. While these effects may be included in RETRASO (via updating medium properties), it is complex to integrate them in the context of analytical solutions. Thus, in this example, we neglect such effects and assume that modifications in the amount of calcite only involve very thin layers of the matrix, so that no significant variations of the pore system and flow field occur.

### Table 1. Ionic Radius, \( \bar{a}_{in} \), of the System Species

<table>
<thead>
<tr>
<th>Species</th>
<th>H⁺</th>
<th>OH⁻</th>
<th>Ca²⁺</th>
<th>HCO₃⁻</th>
<th>CO₃²⁻</th>
<th>CO₃₂⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{a}_{in} )</td>
<td>9.0</td>
<td>3.0</td>
<td>6.0</td>
<td>4.0</td>
<td>5.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

substituting the solution in equation (22b), under the constraint that both concentrations have to be real and positive.

### Table 2. Concentration of Primary Species and Ionic Strength of the End-Members Used in the Simulations

<table>
<thead>
<tr>
<th>End-Member</th>
<th>pH</th>
<th>( c_{CO_3} ) (mol/kg-water)</th>
<th>( I )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>7.3</td>
<td>3.40 E-4</td>
<td>0.005</td>
</tr>
<tr>
<td>(b)</td>
<td>7.16</td>
<td>3.51 E-4</td>
<td>0.625</td>
</tr>
<tr>
<td>(c)</td>
<td>7.3</td>
<td>3.40 E-4</td>
<td>0.35</td>
</tr>
<tr>
<td>(d)</td>
<td>7.3</td>
<td>3.40 E-5</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*All end-members are in equilibrium with respect to calcite.
in turn causes lower CO$_2$ concentrations. Increase in CO$_3^{2-}$/Ca$^{2+}$ concentrations is more important than for Ca$^{2+}$ in relative terms (the last is indeed hardly noticeable). The reason is that CO$_3^{2-}$/Ca$^{2+}$ concentrations are about 3 orders of magnitude lower than those of Ca$^{2+}$. Calcite dissolution releases equal amounts of Ca$^{2+}$ and CO$_3^{2-}$/Ca$^{2+}$ in absolute terms, having a greater effect on the low CO$_3^{2-}$/Ca$^{2+}$ concentrations in relative terms.

[45] Figures 4a and 5a contain the normalized rates, $\dot{r}_2 = r_2 \chi / (nVc_0)$ and $\dot{r}_3 = r_3 \chi / (nVc_0)$ (here $c_0$ is a reference concentration, set as unity), corresponding to one aqueous reaction (CO$_3^{2-}$/Ca$^{2+}$ depletion and calcite dissolution, respectively). In Figure 5a we also compare the analytical distribution of $\dot{r}_3$ with the numerical RETRASO solution at $x = 450$ m ($Pe = 150$). No numerical solution is presented in Figure 4a since the code does not provide aqueous reaction rates. Both $\dot{r}_2$ and $\dot{r}_3$ are negative. This implies that a source term is appearing in CO$_3^{2-}$/Ca$^{2+}$ and Ca$^{2+}$ mass balances and calcite dissolution occurs throughout the system. We notice (Figure 5a) that the maximum dissolution occurs at low $\alpha$ value, where freshwater is dominant. Figure 5a also displays the calcite saturation index profile ($SI = IAP / K$, IAP being the ion activity product and $K$ the equilibrium constant) for a nonreactive mixing. We notice that the predicted dissolution process is shifted toward much fresher zones than suggested by the $SI$ profile, which is based on nonreactive mixing. This highlights that rather than $SI$ being the most relevant factor controlling dissolution, it is in fact the interaction between transport and chemical reactions what really affects dissolution patterns. This finding is consistent with numerical results of Rezaei et al. [2005] and experimental evidences of Singurindy et al. [2004]. In Figure 4b we plot the dependence on $\alpha$ of the two factors, $(\partial a / \partial \psi)^2$ and $\partial^2 c_{\text{am}}^m / \partial a^2$, which contribute to $\dot{r}_2$. The first factor is controlled by transport features, while the second one is related to the nonlinearity in the speciation. A similar plot is provided for $\dot{r}_3$ in Figure 5b. Figures 4b and 5b confirm that both transport and chemical processes contribute to reaction rates and show that locations of reactive zones are mostly governed by $\partial^2 c_{\text{am}}^m / \partial a^2$ (notice that in Figures 4b and 5b, the $\alpha$ axes are plotted on a logarithmic scale). In Figures 4b and 5b, on a smaller scale, we also plot the three terms that contribute to $\partial^2 c_{\text{am}}^m / \partial a^2$ highlighted in equation (24). Notice that these terms need not be of the same sign. It would be hard to propose general rules stating which one of the addends is the dominant one, thus highlighting that both...
algebraic and ionic strength effects should be considered to properly evaluate reaction rates.

The agreement observed in Figures 2, 3, and 5a between analytical and numerical solutions for $Pe=150$ is quite satisfactory, thus revealing the small influence of the simplifications of negligible longitudinal dispersion and conservative ionic strength involved in the analytical solution. The minor discrepancies at values of $\alpha$ close to 1 are probably due to the presence of the numerical domain boundary, not incorporated in our analytical solution. Further, the slight underestimation of the (negative) peak of $\tilde{r}_3$ provided by RETRASO (Figure 5a) may be partly related to the fact that the analytical solution is valid for very large $Pe$ numbers. Indeed, the observed discrepancy between numerical and analytical solutions tends to decrease with increasing Peclet numbers.

We highlight that the analytical solution has evidenced that the functional dependences of the variables of interest can be synthesized using the single similarity variable $\eta$ (or $\alpha$) thus allowing depicting the behavior of each variable in a single one-dimensional plot (i.e., Figure 5a). To better exemplify the two-dimensional pattern of dissolution inside the system and demonstrate the capability of the proposed analytical solution to simulate calcite dissolution through the whole domain (and thus also in that part where $Pe$ is small), Figure 6 depicts the iso-lines of $r_3$ obtained analytically (continuum lines) and by using RETRASO (dashed lines). It clearly emerges that dissolution tends to develop inside the fresher part of the domain and is mostly concentrated near the end-members entrance side.

We notice that analytical results perfectly agree with the numerical $r_3$ distribution even at locations close to the end-members entrance side. Some discrepancies appear along the direction of maximum longitudinal development of the dissolution pattern, because of the approximation of neglecting longitudinal dispersive contributions in the analytical results.

In a mixing problem within the carbonate system, the presence of precipitation or dissolution of calcite depends on the composition of the end-members. The nonlinearity of the process makes it difficult to predict the system behavior (without fully solving the problem). As an example, we simulate the mixing of end-members (c) and (d) of Table 2.
The very similar concept was recently proposed by Knutson et al. [2005] to solve the reactive transport problem in terms of proportions of mixing (i.e., mixing ratios). The attractiveness of this approach is that the solution is then achieved by solving individual transport equations for as many mixing ratios as the number of end-members, \( N_i \), minus one. This feature may result in computational savings when \( N_i - 1 \) is smaller than the number of components needed to fully define the chemical system (in our example of section 4, these components were two).

Another advantage of the proposed approach is that it may allow deriving novel analytical solutions for reactive transport problems whenever analytical solutions are known for the transport equations of conservative quantities (i.e., for simple geometries, flow and transport configurations). These solutions can be used, for instance, as benchmark problems for testing numerical codes or in designing/interpreting experimental analyses devoted to study mixing-driven reactive transport processes.

In many practical problems, some species (such as minerals) may appear (in response to the changes caused by reactions) or disappear (by being totally dissolved) within regions of the domain. This feature can be handled within the context of our methodology by defining different chemical systems for each zone, to solve separately. This would lead to an increased computational burden because of the need to update the chemical system wherever and whenever new species appear or disappear. As an example, if no mineral is present at a point, it is impossible to guarantee chemical equilibrium at that particular point, and transport becomes, in practice, conservative for all aqueous species.

To illustrate potential applications and usefulness of the proposed formulation, we solve the pseudo-stationary mixing of two different CaCO\(_3\)-saturated solutions in a two-dimensional setup in the presence of uniform flow. Our methodology clearly demonstrates that the mixing-driven calcite dissolution/precipitation may be formulated in terms of a single conservative component, the mixing ratio. This methodology was independently developed by Sanford and Konikow [1989] to model calcite dissolution in the fresh-salt water mixing zone by transient tracer tests to estimate the dispersive properties of the system. In this sense, equation (13) could be used as an alternative to classical (reactive or conservative) tracer tests to estimate the dispersion tensor components. A very similar concept was recently proposed by Cirpka et al. [2006] for the particular case of acid-base reactions.

An innovation of the proposed methodology with respect to previous work [Lichtner, 1985; Steefel and Mac Quarrie, 1996; Saaltink et al., 1998; Molins et al., 2004; De Simoni et al., 2005] consists in reformulating the reactive transport problem in terms of proportions of mixing (i.e., mixing ratios). The attractiveness of this approach is the fact that the solution is then achieved by solving individual transport equations for as many mixing ratios as the number of end-members, \( N_i \), minus one. This feature may result in computational savings when \( N_i - 1 \) is smaller than the number of components needed to fully define the chemical system (in our example of section 4, these components were two). Another advantage of the proposed approach is that it may allow deriving novel analytical solutions for reactive transport problems whenever analytical solutions are known for the transport equations of conservative quantities (i.e., for simple geometries, flow and transport configurations). These solutions can be used, for instance, as benchmark problems for testing numerical codes or in designing/interpreting experimental analyses devoted to study mixing-driven reactive transport processes.
porting a single component, while, according to classical components-based formulations, two components are needed to fully define the system.

[57] The results we obtained in simulating calcite precipitation/dissolution in the saltwater mixing zone of coastal aquifers properly reproduce the nonlinear behavior of the process with modest computational efforts in comparison to multicomponent reactive transport numerical codes. Our solution is thus proposed as a promising tool to investigate the evolution of carbonate systems.

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References


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