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Key Points:

- We clarify the application of mixing ratio approach to multicomponent systems with fixed mineral assemblages
- We formalize how to select secondary aqueous species to be used, and we fix an error in the approach
- We demonstrate the approach to formulate the solution with multiple minerals present

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Revisiting the Analytical Solution Approach to Mixing-Limited Equilibrium Multicomponent Reactive Transport Using Mixing Ratios: Identification of Basis, Fixing an Error, and Dealing With Multiple Minerals

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Abstract Multicomponent reactive transport involves the solution of a system of nonlinear coupled partial differential equations. A number of methods have been developed to simplify the problem. In the case where all reactions are in instantaneous equilibrium and the mineral assemblage is constant in both space and time, de Simoni et al. (2007) provide an analytical solution that separates transport of aqueous components and minerals using scalar dissipation of “mixing ratios” between a number of boundary/initial solutions. In this approach, aqueous speciation is solved in conventional terms of primary and secondary species, and the mineral dissolution/precipitation rate is given in terms of the scalar dissipation and a chemical transformation term, both involving the secondary species associated with the mineral reaction. However, the identification of the secondary species is nonunique, and so it is not clear how to use the approach in general, a problem that is keenly manifest in the case of multiple minerals which may share aqueous ions. We address this problem by developing an approach to identify the secondary species required in the presence of one or multiple minerals. We also remedy a significant error in the de Simoni et al. (2007) approach. The result is a fixed and extended de Simoni et al. (2007) approach that allows construction of analytical solutions to multicomponent equilibrium reactive transport problems in which the mineral assemblage does not change in space or time and where the transport is described by closed-form solutions of the mixing ratios.

1. Introduction

The mixing-components approach to multicomponent equilibrium reactive transport (de Simoni et al., 2007) is an important contribution to the upscaling of subsurface reactive transport because it quantitatively distinguishes chemical controls from transport limitations on the net rate of transformations in the general class of mixing-limited reactive problems between solutions that are otherwise in equilibrium. As an analytical solution relying on closed-form solution of transport, it is free of operator-splitting errors and allows writing the mineral dissolution/precipitation rate in closed-form, providing a useful expression for its quantification without having to rely on balancing the species at every time step. In brief it works like this. Consider the case of very fast bimolecular reaction, $M \rightleftharpoons C_1 + C_2$ where the quantity M is a pure mineral phase with assumed unit chemical activity, and corresponding law of mass action $K = C_2 C_1$ where K is the equilibrium constant of the mineral equilibrium. Suppose this equilibrium is satisfied respectively by both chemical compositions of two solutions that obey advective-dispersive transport. De Simoni et al. (2005) showed that the time rate of change of the volumetric mass or molar density of M is the product of the scalar dissipation rate $(\nabla C)^T n D \nabla C$ and the chemical transformation term $d^2 C_1 / dC^2$ where $C \equiv C_2 - C_1$ is a conventional chemical “component” (e.g., Bethke, 2006) that behaves as a passive tracer (resulting from the cancellation of the reaction term by subtraction of the mole balance equations for C_2 and C_1). The authors demonstrate how to do this also in the general multicomponent case, where the time rate of change of the mineral is factored into a mixing factor that is the scalar dissipation rate of aqueous components, and a chemical transformation term for the minerals’ secondary species that depends only on the components’ concentrations, each one again acting as a passive tracer.

This has resulted in an expansion of research on how to characterize the mixing limitation factor, whether it be a dilution index where the concentrations are weighted by their natural log, or a scalar dissipation rate where the gradient of concentration is squared, and how this applies to the idealized “bimolecular” reaction of de Simoni and beyond (e.g., Dentz et al., 2011; de Simoni et al., 2007; Le Borgne et al., 2014; Luo et al., 2008; Pelizardi et al., 2017; Sanchez-Vila et al., 2010; Willmann et al., 2010). The concept of de Simoni et al. (2005) was extended in de Simoni et al. (2007) to analysis of the same multicomponent reactive transport but this time using “mixing ratios” instead of explicit components, as will be explained below; furthermore in this same work, the authors extended the problem to include the mass action law written in terms of activities, rather than the simplified version where all activity coefficients are assumed equal to one.

Here our focus is on clarifying some aspects of the de Simoni et al. (2007) approach including fixing an important error in the mathematics, and extending it to the case of multiple minerals in equilibrium with the solutions involved. For simplicity, we assume all activity coefficients are unity, also that the activities of minerals (and under the dilute solution assumption) of water are all assumed unity; these assumptions can be relaxed as shown in de Simoni et al. (2005, 2007), referred to hereafter as dS05 and dS07, respectively. In this redress of the theory, we (section 2) briefly review the multicomponent reactive transport mole balance formulation when all the reaction rates are sufficiently fast on the time scales of observation; (section 3) clarify the number of mixing ratios that may be used for a given problem and recast the expression for components solution; (section 4) fix an error in the key result equation (13) of dS07; (sections 4.1 and 4.2) discuss the identification of the end-members and the impact of changes to the mineral assemblage; and (section 5) address the nonuniqueness of the (required) identification of secondaries in applying the method to the common case where more than one mineral equilibrium reaction is involved.

2. Summary of the Formulation of the Multicomponent Equilibrium Reactive Transport System

When N_R equilibrium reactions occur among a number N_S of chemical species, techniques of linear algebra can be applied to reduce the N_S mole balance expressions (one per species) to $N_S - N_R$ mole balance expressions, one per “component.” Construction of components is an elementary exercise in modeling equilibrium reaction networks and the stuff of textbooks and monographs (e.g., Bethke 2006; Lichtner, 1992; Lichtner, 1996; Morel & Hering, 1993; Steefel, 1992; Steefel & MacQuarrie, 1996; Wolery, 1992). In short, one associates a single chemical species (“secondary”) with each equilibrium reaction, and writes the reactions in terms of the remaining (“primary”) species, so that the secondaries appear only once, in their associated reaction, and not in any other reaction. This is always possible when reactions are independent. Then in the mole balance expressions, one eliminates the reaction rates by substituting the material derivatives of the secondaries for the occurrences of the (sufficiently fast on the time scales of observation) reaction rates in the mole balance expressions of the primaries. (In batch models, the material derivatives are ordinary time derivatives; in reactive transport scenarios they are partial time derivatives and transport operators.) Because each reaction corresponds to the material derivative of one and only one secondary species, by construction, this can be done easily. The resulting mole balance expressions give an $N_S - N_R$ ODE (PDE) system for linear combinations of primary and secondary species interacting in reactive batch (reactive transport) with all equilibrium reactions eliminated, and so in the absence of other, e.g., kinetically controlled reactions, the right-hand side of this ODE (PDE) system is zero and the dependent variables termed components act as conservative (i.e., not affected by reactions) species. The presence of immobile minerals disrupts the definition of components because they do not move while their associated primary or secondary aqueous species do.

Consider transport and interaction of N_S chemical species, the first N_C of which are immobile mineral species, and all of which may interact via N_R chemical reactions that have a vector of reaction rates \mathbf{r} . The N_R chemical reactions may be expressed as



where \mathbf{a}_c is the vector of N_C mineral species, \mathbf{a}'_a is the vector of $N_S - N_C - N_R$ “primary” aqueous species, \mathbf{a}''_a is the vector of N_R “secondary” aqueous species; \mathbf{S}_{ec} ($N_R \times N_C$) and \mathbf{S}'_{ea} ($N_R \times (N_S - N_C - N_R)$) are the

stoichiometric submatrices providing the moles of mineral species \mathbf{a}_c and primary aqueous species \mathbf{a}'_a , respectively, contributing to the row-wise reactions per unit of secondary species \mathbf{a}''_a , and where subscript "a" means "aqueous." \mathbf{I} is the $N_R \times N_R$ identity matrix, and so every independent reaction has one and only one secondary associated with it which appears nowhere else in the reaction system. There are multiple ways to assign primaries and secondaries. Denoting by \mathbf{c}'_a and \mathbf{c}''_a , the moles per aqueous volume of primary and secondary species, respectively, and assuming activity coefficients of both solutes and minerals are unity, the law of mass action can be written as a set of equations:

$$\log \mathbf{c}''_a = \mathbf{S}'_{ea} \log \mathbf{c}'_a - \log \mathbf{K} \quad (2)$$

Note that mineral equilibria are included in this system despite the absence of mineral activities that are assumed unity. Writing a reaction network in this way with a subset \mathbf{a}''_a of the reactants isolated to singleton appearances as secondaries can always be done as a result of the phase rule and when the reactions are independent (e.g., Steefel & MacQuarrie, 1996, p. 99, with exceptions due to dependent reactions discussed on p. 89), and allows formal reduction of the number of unknowns as will be shown in batch (equations (4)) and reactive transport (equations (7)) formulations that are spanned by the primary chemical species \mathbf{a}'_a , which thus serve as a *basis* for the problem in the sense of vector spaces. This allows us to reduce the original N_S mole balance equations to $N_S - N_R$ mole balances of "components" that are linear combinations of singleton primary and multiple secondary species concentrations. Introducing the molar concentrations where \mathbf{m}_c are moles of mineral species per unit bulk volume and n is porosity, mole balance of the N_S chemical species can be written in terms of the reaction rates \mathbf{r} , as (e.g., Lichtner, 1996; Steefel & MacQuarrie, 1996):

$$\frac{\partial \mathbf{m}_c}{\partial t} = \mathbf{S}^T_{ec} \mathbf{r} \quad (3a)$$

$$\frac{\partial n \mathbf{c}'_a}{\partial t} - L(n \mathbf{c}'_a) = \mathbf{S}^T_{ea} \mathbf{r} \quad (3b)$$

$$\frac{\partial n \mathbf{c}''_a}{\partial t} - L(n \mathbf{c}''_a) = -\mathbf{I} \mathbf{r} \quad (3c)$$

Note that in equations (3a) we adopt only aqueous secondaries, so henceforth all minerals (stable since the mineral assemblage is assumed a constant) are treated here as primaries.

If the reactions are treated at equilibrium always, then the reaction rates \mathbf{r} are sufficiently fast on the time scale of observation and only limited by the capability of the reactants to meet, and are eliminated by substitution of the left-hand side of the secondaries' mole balances (3c) for \mathbf{r} in the mole balances for minerals (3a) and for primaries (3b). We do this first for the case of no transport (i.e., $L = \text{null}$ and the partial derivatives become total derivatives in equations (3a)) in which case (3a) and (3b) with substitution of (3c) become

$$\frac{d\mathbf{m}}{dt} = 0 \quad (4a)$$

$$\frac{d n \mathbf{u}}{dt} = 0 \quad (4b)$$

where N_C mineral and N_U aqueous components are defined, respectively, by

$$\mathbf{m} = \mathbf{m}_c + n \mathbf{S}^T_{ec} \mathbf{c}''_a \quad (5)$$

$$\mathbf{u} = \mathbf{c}'_a + \mathbf{S}^T_{ea} \mathbf{c}''_a \quad (6)$$

A simple example formulation following equations (1–6) is given in Appendix A. The solution procedure (for constant n) starts by noticing that the solution of (4) for homogeneous initial conditions is $\mathbf{m} = \mathbf{m}_0$ and $\mathbf{u} = \mathbf{u}_0$, the subindex indicating the initial values. Then (2) and (6) become a system of $N_R + N_U$ algebraic equations that can be solved with simple numerical models. Finally from (5) it is possible to obtain the \mathbf{m}_c components explicitly (N_C equations). The alternative is to solve together the full system of $N_C + N_U + N_R = N_S$ ODEs with N_R law of mass action equation (2) that can be solved with combined time stepping and Newton-Raphson algorithm. Details of these classical formulations are given in, e.g., Steefel

and MacQuarrie (1996) and Bethke (2006), with further attention to electroneutrality, the phase rule, and mineral formation, as well as basis swapping and mineral elimination and other extended topics.

In the case of transport and equilibrium reactions, elimination of \mathbf{r} in (3) yields

$$\frac{\partial \mathbf{m}_c}{\partial t} = \mathbf{S}_{ec}^T \left[-\frac{\partial n \mathbf{c}_a''}{\partial t} + L(n \mathbf{c}_a'') \right] \quad (7a)$$

$$\frac{\partial n \mathbf{u}}{\partial t} + L(n \mathbf{u}) = 0 \quad (7b)$$

Note the disruption in analogy caused by transport: aqueous components \mathbf{u} in (7b) are just as useful as they were in (4b), but mineral components \mathbf{m} are not as useful in (7a) as they were in (4a) because their corresponding primary species (minerals \mathbf{m}_c) do not move, unlike their respective secondaries $n \mathbf{S}_{ec}^T \mathbf{c}_a''$, and so while aqueous components \mathbf{u} are conservative per (7b), minerals per (7a) do not solve an independent conservation expression and cannot be solved in terms of \mathbf{m}_c alone. This inconvenience is ultimately what blocks analytical solutions to problems with varying mineral assemblages as described in section 4.2.

This system (7) of $N_c + N_u$ equations is closed when it is combined with the N_R nonlinear equilibrium law of mass action equation (2) and component definitions (6), giving $N_c + N_u + N_R + N_U = N_S + N_U$ equations with $N_S + N_U$ unknowns. The simplest classical workflow of a time stepping solution to calculate mineral moles over time is to: solve (7b) for \mathbf{u} , that is then used in (6) to obtain an expression for \mathbf{c}_a'' in terms of \mathbf{c}_a' , which in turn is substituted in (2) to get

$$\log \mathbf{c}_a'' = \mathbf{S}_{ea}' \log (\mathbf{u} - \mathbf{S}_{ea}^T \mathbf{c}_a') - \log \mathbf{K}$$

as done in codes such as PHREEQCII (Parkhurst & Appelo, 1999) to obtain \mathbf{c}_a'' , which allows solution of (7a) for \mathbf{m}_c per time step.

This and other more sophisticated law of mass action (LMA)-based schemes are described, e.g., in Steefel and MacQuarrie (1996) and Bethke (2006), and recently reviewed in Steefel et al. (2015), as well as in the book Zhang et al. (2012) that discusses the major codes developed on this basis. Additional surveys are found in Steefel et al. (2005) on applications in earth sciences and in MacQuarrie and Mayer (2005) on reactive transport in fractured media. As noted in Steefel et al. (2015), "Other approaches are possible in which kinetic and equilibrium reactions are decoupled. This approach allows for the use of free energy minimization routines." The origin of this "Gibbs energy minimization" (GEM) approach is summarized in Steefel and MacQuarrie (1996, p. 100) and in Bethke (2006, p. 3, where the controversy between proponents of LMA versus GEM proponents is colorfully reviewed). Recent contributions to the GEM approach include Kulik et al. (2013) and Leal et al. (2014, 2016a, 2016b). Leal et al. (2016b) hybridized GEM with LMA to construct an "extended LMA" method where equilibrium is calculated at each time step using Lagrange multipliers to solve the GEM problem, with a wide set of LMAs (thus the extended) that covers all possible unstable phases. Here since we assume the simple case of one stable aqueous phase, and a number of stable mineral phases making up the mineral assemblage, and because our focus is on developing analytical solutions to mixing-limited reactions, we build on the LMA approach for which speciation code modules are widely available (e.g., Charlton & Parkhurst, 2011).

The form of (7a) suggests a more direct approach to calculating mineral moles over time, that takes advantage of the assumed wholly equilibrium reaction network and that relies on the transport of the secondaries \mathbf{c}_a'' alone, an approach that was originally developed in dS05 and dS07 (summarized below). We next introduce the conversion of (7a) using the approach of dS05/dS07, clarifying a few important issues/errors on the way in sections 3 and 4, and then turn to the question of how to define the secondaries in the general case of multiple minerals in section 5.

3. Clarification of the Number of Mixing Ratios That May Be Used

DS05 showed that, in the case of constant porosity and equilibrium coefficients (7a), and assuming that the transport operator includes advection and dispersion with tensor hydrodynamic dispersion coefficient \mathbf{D} , the bracketed term of (7a) is

$$\left[-\frac{\partial n\mathbf{c}_a''}{\partial t} + L(n\mathbf{c}_a'') \right] = n \sum_{i=1}^{N_u} \sum_{j=1}^{N_u} \frac{\partial^2 \mathbf{c}_a''}{\partial u_i \partial u_j} \nabla^T u_i \cdot \mathbf{D} \cdot \nabla u_j \quad (8)$$

This resulted from making use of the fact that $\mathbf{c}_a'' = \mathbf{c}_a''(\mathbf{u}(\mathbf{x}, t))$ through equations (6) and (2). The second derivatives of the secondary species concentrations are taken with respect to the concentrations of the component species. This result, which gives an analytical solution for the bracketed term of (7a) that successfully decouples reactions and transport through the first and second factors of the sum, respectively, was generalized in dS07 to the case where transport is entirely characterized through index species α_i , termed “mixing ratios,” with i indicating boundary of origin, as follows. The mixing ratio $\alpha_i(\mathbf{x}, t)$ is the solution to the nonreactive transport of a tracer emanating from time or space boundary i with unity boundary or initial condition there and zero elsewhere, so that $\forall i, 0 < \alpha_i(\mathbf{x}, t) < 1$, and

$$\sum_{i=1}^{N_i} \alpha_i(\mathbf{x}, t) = 1 \quad (9)$$

where N_i is the number of mixing ratios we want to consider (generally the number of chemically distinct aqueous boundary/initial conditions, and most frequently named end-members, as in Pelizardi et al., 2017). This allows the aqueous components, vector \mathbf{u} , to be expressed as

$$\mathbf{u}(\mathbf{x}, t) = \sum_{i=1}^{N_i} \mathbf{u}_i \alpha_i(\mathbf{x}, t) \quad (10)$$

where \mathbf{u}_i is the end-member component vector corresponding to the composition of the solution at the i th boundary. Thus, one can find the component vector solution $\mathbf{u}(\mathbf{x}, t)$ given the $i = 1, \dots, N_i$ boundary component lists \mathbf{u}_i and the (mathematical) solution for transport of each passive tracer $\alpha_i(\mathbf{x}, t)$ emanating (with unit b.c.) from each of the N_i respective boundaries. Only $N_i - 1$ such functions are needed, however, because of the restriction imposed by equation (9), providing for instance, $\alpha_{N_i} = 1 - \sum_{i=1}^{N_i-1} \alpha_i(\mathbf{x}, t)$, allowing us to rewrite 10 as

$$\mathbf{u}(\mathbf{x}, t) = \sum_{i=1}^{N_i-1} \Delta \mathbf{u}_i \alpha_i(\mathbf{x}, t) + \mathbf{u}_{N_i} \quad (11)$$

where $\Delta \mathbf{u}_i \equiv \mathbf{u}_i - \mathbf{u}_{N_i}$. While in dS07 equations (9) (paragraph 15) and (10) (equation (12)) are pointed out, (11) is not. This is relevant because (11) tells us that if we use $N_i - 1$ end-members, we must preprocess the end-member components into $\Delta \mathbf{u}_i$ instead of using \mathbf{u}_i , and, later we are going to be relying on partial differentiation with respect to the α_i . In practice, either $N_i - 1$ or N_i end-members may be used as noted in the next section.

4. Fixing an Error in the Key Result Equation (13) of De Simoni et al. (2007)

Continuing with dS07, the generalization of equation (8) for the case of mixing ratios appears as equation (13) in dS07. However, that form is ambiguous due to unspecified upper limit of summation as just noted, and erroneous due to the use of second derivatives in α_i without cross-derivatives. The incorrect form given as (13) in dS07 (with our left-hand side replacing the reaction rates \mathbf{r} of dS07 which is mere convention and not a problem) is

$$\left[-\frac{\partial n\mathbf{c}_a''}{\partial t} + L(n\mathbf{c}_a'') \right] = n \sum_i \frac{\partial^2 \mathbf{c}_a''}{\partial \alpha_i^2} \nabla^T \alpha_i \cdot \mathbf{D} \cdot \nabla \alpha_i \quad (12)$$

and the correct form is

$$\left[-\frac{\partial n\mathbf{c}_a''}{\partial t} + L(n\mathbf{c}_a'') \right] = n \sum_{i=1}^{N_i-1} \sum_{j=1}^{N_i-1} \frac{\partial^2 \mathbf{c}_a''}{\partial \alpha_i \partial \alpha_j} \nabla^T \alpha_i \cdot \mathbf{D} \cdot \nabla \alpha_j \quad (13)$$

This equation is derived by writing $\mathbf{c}_a'' = \mathbf{c}_a''(\alpha(\mathbf{x}, t))$ ($\alpha = \alpha_i(\mathbf{x}, t)$, $i = 1, \dots, N_i - 1$) and expanding the terms on the left-hand side by the chain rule as shown in Appendix B. (The incorrect form 12 sufficed for all the

examples presented and cited in dS07 because all of those examples involved either 2-D steady state or 1-D transient problems so that $N_i - 1 = 1$.)

With this result (7a) becomes:

$$\frac{\partial \mathbf{m}_c}{\partial t} = n \mathbf{S}_{ec}^T \left[\sum_{i=1}^{N_i-1} \sum_{j=1}^{N_i-1} \frac{\partial^2 \mathbf{c}_a''}{\partial \alpha_i \partial \alpha_j} \nabla^T \alpha_i \cdot \mathbf{D} \cdot \nabla \alpha_j \right] \quad (14)$$

This relation gives us a new way to solve for the mineral accumulation (by precipitation or dissolution) rates, in terms of the passive transport of the mixing ratios and the Hessians of each term of the vector $\mathbf{c}_a''(\boldsymbol{\alpha})$ that tells how the secondary aqueous species concentrations depend on the mixing ratios through speciation. The latter is a tabulation calculation that can be done completely independently of transport. Thus, this relation effectively factors reactions and transport. As a final point, one may suspect that one *must* use only the $N_i - 1$ independent ratios because partial differentiation with respect to one of the α_i requires the other α_j be held constant; however, this is erroneous, as pointed out by an anonymous reviewer, and in fact the same result is obtained when all N_i end-members are used as long as the system of equations knows that they sum to unity.

This scheme gives an analytical solution to multicomponent reactive transport problems given: invariant mineral assemblage, closed-form solutions for the mixing ratios $\alpha_i(\mathbf{x}, t)$, $i = 1, \dots, N_i - 1$, and the calculated Hessians of each term of the vector $\mathbf{c}_a''(\boldsymbol{\alpha})$, as follows. Step 1: solve (11) for $\mathbf{u}(\mathbf{x}, t)$; step 2: solve (6) with the law of mass action equation (2) for \mathbf{c}'_a and \mathbf{c}''_a and solve (14) for rates of change of mineral moles \mathbf{m}_c . Note that the Step 2 calculation of mineral rates (that requires only $\alpha_i(\mathbf{x}, t)$ and their gradients) is completely independent of the calculation of the aqueous species \mathbf{c}'_a and \mathbf{c}''_a , and vice versa. There are no numerical grid, operator-splitting, or time-discretization errors, and mineral moles can be computed a posteriori by numerical integration of equation (14). As noted by an anonymous reviewer the Hessians in (14) may be estimated by finite differences or by combining (2), (6), and (11) to obtain an expression for \mathbf{c}''_a in terms of $\boldsymbol{\alpha}$, and differentiating twice. The latter may give fully analytical, albeit quite complex, forms.

Note that the chemistry aspects of the solution for mineral mole concentrations are exclusively captured in the second derivative (Hessian) terms, each of which provide a mapping from (\mathbf{x}, t) through the mixing ratios α_i to the value of the second derivatives of each secondary with respect to pairs of mixing ratios. Given a particular mineral assemblage and $N_i - 1$ mixing ratios, one may tabulate the Hessian of each component of \mathbf{c}''_a with respect to each possible pair of the $N_i - 1$ mixing ratios. This may be done as noted in dS07 numerically or by curve fitting, but there the suggestion was erroneously for only the diagonal terms of the Hessian. In fact one needs the full Hessian, including the cross-terms as shown in equation (14). For instance, assume 3-D (could be 2-D) transient reactive transport problem with $N_i - 1 = 3$, for each component of vector \mathbf{c}''_a , one would need to fit all second derivatives (i.e., with respect to: α_i, α_j ; $i, j = 1, \dots, 3$, with a total of six as Schwartz's Theorem applies). Each of these $6N_R$ second derivatives would be mapped a priori over the three-dimensional domain (defined in all the internal points of a tetrahedron limited by points $[0,0,0]$, $[1,0,0]$, $[0,1,0]$, $[0,0,1]$ in space $[\alpha_1, \alpha_2, \alpha_3]$). This task needs only be done once per mineral assemblage and can then serve as a look-up table for any problem with the same number of mixing ratios and the same minerals, resulting in formidable savings in the solution over that of the classical approach that requires solving (2) with (7) every time step on a spatial grid.

4.1. Identification of the End-Members

Defining the end-members becomes critical. One option consists of making a partition of the boundary and running the conservative transport equation for a homogeneous problem where the initial or the boundary value is set to the unity. This is most probably not the smartest solution.

We suggest to obtain N_i from a combination of the inverse problem and equation (11). The choice is based upon the actual hydrogeological setup that would indicate potential sources of water that eventually reach and mix within the study area. Each one of the end-members is then characterized by a given chemical signature that can be stated in terms of components. There is a compromise in the total number. Setting a large number for N_i allows for a large degree of flexibility in reproducing observations; on the other hand, it would reduce the robustness in the estimation of the α_i values at each individual point in space and time. Again, there is nonuniqueness in this process.

Once the number of end-members is set, there is a need to characterize their chemical signatures. This is based both on a priori knowledge of the recharge or contributing sources of groundwater, plus on the actual measurements of water sampled at the site. The a posteriori chemical signatures can be obtained with the methodology outlined in Carrera et al. (2004) and in Pelizardi et al. (2017). An iterative process can be used so that if two chemical signatures are quite similar it would be possible to consider them as the same end-member, recomputing again all chemical compositions.

4.2. What About Changes to the Mineral Assemblage?

Equation (14) can be used in place of (7a) in any conventional time stepping solution workflow, or in the analytical approach outlined above when the mineral assemblage remains the same everywhere in the domain, as demonstrated in dS07. But in fact the minerals initially present may be heterogeneous in their occurrence, may dissolve completely in some parts of the domain, and equally challenging, some minerals not originally present may come into existence. The treatment of this aspect is currently not within the capability of the dS07 approach (despite the suggestion in paragraph 55, dS07 that it is), because when the mineral assemblage changes with space, the structure of \mathbf{u} (and of $\mathbf{c}'_{a'}$, $\mathbf{c}''_{a'}$ and \mathbf{S}'_{ea}) becomes a property of space through (6), i.e., an Eulerian quantity, that must be updated as minerals (dis)appear at different times and points in space. For instance, when a solution previously in equilibrium with calcite moves into a place without calcite, the length of \mathbf{u} must increase by one because there is one less reaction in the reaction network. That is, while conventional basis-swapping can always be used to make a basis given the minerals that are present (e.g., Bethke, 2006), the part of the basis corresponding to the aqueous components \mathbf{u} changes in dimension, preventing mathematical mixing of the components corresponding to different bases. This challenge so far requires a numerical discretization of space which defeats the relative computational simplicity of the mixing ratios approach, and is a key area for future study of the mixing ratios approach. One promising possibility is to combine the extended LMA approach of Leal et al. (2016b) with the scalar dissipation rate concept to reconstruct (14) in a way that admits varying mineral assemblages.

5. Which Species Do We Use as the Secondaries and How Do We Identify the Corresponding Matrices \mathbf{S}_{ec} and \mathbf{S}'_{ea} When multiple Minerals Are Present?

The purpose of this section is to introduce and demonstrate a direct way to compute the relevant stoichiometric matrices needed for the dS07 approach when multiple minerals (that may share ions) are involved. Mineral reactions are assumed independent (e.g., aragonite and calcite are treated as the same mineral) so that minerals can be expressed as independent combinations of primary species. The fact that the choice of secondaries is nonunique means that the vector of secondary species concentrations $\mathbf{c}''_{a'}$ and so the bracketed quantity in (14), are not uniquely defined. This is a pragmatical and not fundamental problem because for every distinct set of secondaries there is a corresponding \mathbf{S}_{ec} so that the right-hand side of (14) (and (7a)) itself is unique and invariant of the secondaries selection. Nevertheless, the identification of the secondaries is still a requirement for writing equation (14) and since this is not uniquely determined when using practical computational codes for the solution of (2) such as PHREEQC, this requirement leaves the solution of more realistic problems with multiple minerals ambiguous. Thus, applications of the dS05/dS07 approach are heretofore mainly upon simple systems, e.g., dS07 and Dreybrodt et al. (2009) use Ca^{++} as the secondary for calcite mineral equilibrium (termed "Ce_q" in Romanov & Dreybrodt, 2006) and no other minerals used, and Guadagnini et al. (2009) used total calcium and manually calculated \mathbf{S}_{ec} (gathered all species containing Ca and in aqueous form), without explaining why.

Thus it is not straightforward how to apply the dS07 approach for three reasons: (1) multiple choices for the set of secondaries exist, (2) the manual construction of \mathbf{S}_{ec} (as well as \mathbf{S}'_{ea}) for each choice is manual, and (3) in the natural case of multiple minerals sharing an ion, the secondaries appearing in one mineral may appear in another. For more realistic simulations involving a full suite of compounds that exist in environmental aqueous solutions, or when available multicomponent codes such as PHREEQC are used with comprehensive thermodynamic databases including very many aqueous and mineral species by default, we need a simple way to determine a set of feasible secondaries $\mathbf{c}''_{a'}$ and corresponding matrices \mathbf{S}_{ec} and \mathbf{S}'_{ea} for a given problem that works for the general case. This would allow the modeler wishing to apply the dS07 approach to more realistic multiminer problems to select from the set of feasible secondaries $\mathbf{c}''_{a'}$ and to

immediately calculate the \mathbf{S}_{ec} and \mathbf{S}'_{ea} matrices needed for computations of rates of mixing-limited reactions in systems with multiple minerals possibly sharing ions. Here we outline such a method.

Our approach is to formulate the reaction network twice, once with all the minerals out of the basis (this is called the “reference” basis), and once with all the minerals included in the basis (this is called the “new” basis). Note that while there may be multiple ways to write the reference basis, the ions or compounds comprising the minerals are necessarily primaries in all possible versions because the role of secondary is already taken by the mineral per mineral reaction, by construction. Thus, for any given reference basis, the question is which of the ions or compounds comprising the minerals will be swapped out of the basis when the minerals are swapped into the new basis? Enumeration of the possible permutations of this new basis gives the set of possible secondaries for the given mineral assemblage. We first show how to determine the matrices \mathbf{S}_{ec} and \mathbf{S}'_{ea} for any one of these new bases. The procedure is a novel application of the mathematics of basis swapping as described in Bethke (2006) and relies on the linear algebra of basis swapping, a basic tour through which is given in Appendix C.

Because the old basis necessarily contains all the ions needed to make the minerals, the new basis can be written as a linear transformation of the old basis:

$$\mathbf{b}_{New} = \mathbf{T} \mathbf{b}_{Ref} \quad (15)$$

For such a transformation of the basis of any vector space, the components of a vector in the old basis are converted to those of the same vector in the new basis by (Lipschutz, 1968, p. 153; note that our \mathbf{T} is Lipschutz' \mathbf{P}^T and is Bethke's β):

$$\mathbf{v}_{New} = [\mathbf{T}^{-1}]^T \mathbf{v}_{Ref} \quad (16)$$

Because the material derivatives of the components of the reaction network are vectors in the vector space defined by the basis, then they too can be converted this way leading to

$$\dot{\mathbf{u}}_{New} = [\mathbf{T}^{-1}]^T \dot{\mathbf{u}}_{Ref} \quad (17)$$

and because the new components vector \mathbf{u}_{New} contains the minerals, this gives us a way to calculate the rate of change of mineral species as linear combinations of the rates of change of that mineral's dissolution ions that necessarily appear in the old components vector \mathbf{u}_{Ref} . An example of this conversion is given in Appendix C. For present purposes, this does not provide complete information on \mathbf{S}_{ec} however, because the composition of the old components (e.g., all the species contributing to one component, such as carbonate(s)) is not explicit in the above equations. To fix this, we write the reaction network according to the two bases, and then find a relation between their respective stoichiometric matrices that gives the needed information.

The reaction system corresponding to the “New” basis (minerals are included in the basis) is already presented as



which can be written with secondaries (entirely aqueous by construction) on the left-hand side as



The modeler must split these New basis aqueous secondaries \mathbf{a}''_a into: \mathbf{a}''_{ao} that will remain secondaries in the “Reference” basis, and the remainder \mathbf{a}''_{ac} , that will become primaries in the “Reference” basis where they will replace the minerals. Then the reaction system in the “New” basis is expressed as



The same reaction network expressed in the “Reference” basis has \mathbf{a}''_{ac} as primaries replacing minerals \mathbf{a}_c that appear as secondaries in the Reference basis:

$$\begin{bmatrix} \mathbf{a}_c \\ \mathbf{a}_{ao}'' \end{bmatrix} \iff [\mathbf{P}_{eac}'', \mathbf{P}'_{ea}] \cdot \begin{bmatrix} \mathbf{a}_{ac}'' \\ \mathbf{a}'_a \end{bmatrix} \quad (21)$$

Equation (21) can be written with partitioned matrices \mathbf{P}'_{eac} ($N_C \times N_C$), \mathbf{Q}''_{eac} ($(N_R - N_C) \times N_C$), \mathbf{P}'_{ea} ($N_C \times (N_S - N_R - N_C)$), and \mathbf{Q}'_{ea} ($(N_R - N_C) \times (N_S - N_R - N_C)$), as

$$\begin{bmatrix} \mathbf{a}_c \\ \mathbf{a}_{ao}'' \end{bmatrix} \iff \begin{bmatrix} \mathbf{P}'_{eac} & \mathbf{P}'_{ea} \\ \mathbf{Q}''_{eac} & \mathbf{Q}'_{ea} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{a}_{ac}'' \\ \mathbf{a}'_a \end{bmatrix} \quad (22)$$

and then with 0_{ao} ($N_C \times (N_R - N_C)$ zero matrix), \mathbf{I}_{ao} ($(N_R - N_C) \times (N_R - N_C)$ identity), \mathbf{I}_c ($N_C \times N_C$ identity), and 0_c ($(N_R - N_C) \times N_C$ zero matrix) as

$$\begin{bmatrix} -\mathbf{P}'_{eac} & 0_{ao} \\ -\mathbf{Q}''_{eac} & \mathbf{I}_{ao} \end{bmatrix} \begin{bmatrix} \mathbf{a}_{ac}'' \\ \mathbf{a}_{ao}'' \end{bmatrix} \iff \begin{bmatrix} -\mathbf{I}_c & \mathbf{P}'_{ea} \\ 0_c & \mathbf{Q}'_{ea} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{a}_c \\ \mathbf{a}'_a \end{bmatrix} \quad (23)$$

where the bracketed matrix on the left-hand side is square with dimensions $N_R \times N_R$ and that on the right-hand side has dimensions $N_R \times (N_S - N_R)$. While there may be multiple choices for the swapping species \mathbf{a}_{ac}'' , the selection is not totally arbitrary because \mathbf{a}_{ao}'' remain secondaries in both (20) and (21). Thus, \mathbf{a}_{ac}'' must be selected so that (per (20)) they can be constructed from \mathbf{a}_c and \mathbf{a}'_a . This is achieved by selecting \mathbf{a}_{ac}'' so that square \mathbf{P}'_{eac} is invertible. Because the mineral reactions are independent, the matrix $[\mathbf{P}'_{eac} \ \mathbf{P}'_{ea}]$ is of full row rank N_C , and there are (generally multiple) choices of the N_C columns of it corresponding to the \mathbf{a}_{ac}'' from which one can compose invertible \mathbf{P}'_{eac} . This is not difficult to see in practice because if the \mathbf{a}_{ac}'' were to be chosen so that \mathbf{P}'_{eac} were singular then the mineral reactions corresponding to the first N_C rows of (22) would not be independent.

With invertible \mathbf{P}'_{eac} we finally isolate the secondaries of the previous "New" basis by premultiplying by the inverse of the bracketed matrix on the left-hand side, as

$$\begin{bmatrix} \mathbf{a}_{ac}'' \\ \mathbf{a}_{ao}'' \end{bmatrix} \iff \begin{bmatrix} -\mathbf{P}'_{eac} & 0_{ao} \\ -\mathbf{Q}''_{eac} & \mathbf{I}_{ao} \end{bmatrix}^{-1} \begin{bmatrix} -\mathbf{I}_c & \mathbf{P}'_{ea} \\ 0_c & \mathbf{Q}'_{ea} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{a}_c \\ \mathbf{a}'_a \end{bmatrix} \quad (24)$$

the inversion can be performed using the relation for 2×2 block matrix inversion to write (24) as

$$\begin{bmatrix} \mathbf{a}_{ac}'' \\ \mathbf{a}_{ao}'' \end{bmatrix} \iff \begin{bmatrix} -\mathbf{P}'_{eac} - 1 & 0_{ao} \\ -\mathbf{Q}''_{eac} \mathbf{P}'_{eac} - 1 & \mathbf{I}_{ao} \end{bmatrix} \begin{bmatrix} -\mathbf{I}_c & \mathbf{P}'_{ea} \\ 0_c & \mathbf{Q}'_{ea} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{a}_c \\ \mathbf{a}'_a \end{bmatrix} \quad (25)$$

By equivalence of (20) and (25) we have an expression for the sought-after matrices given any valid specification of secondaries per mineral reaction \mathbf{a}_{ac}'' :

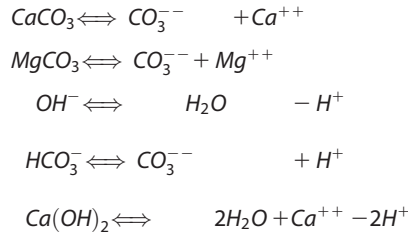
$$[\mathbf{S}_{ec}, \mathbf{S}'_{ea}] = \begin{bmatrix} -\mathbf{P}'_{eac} - 1 & 0_{ao} \\ -\mathbf{Q}''_{eac} \mathbf{P}'_{eac} - 1 & \mathbf{I}_{ao} \end{bmatrix} \begin{bmatrix} -\mathbf{I}_c & \mathbf{P}'_{ea} \\ 0_c & \mathbf{Q}'_{ea} \end{bmatrix} \quad (26)$$

which renders \mathbf{S}_{ec} and \mathbf{S}'_{ea} , respectively, as,

$$[\mathbf{S}_{ec}] = \begin{bmatrix} \mathbf{P}'_{eac} - 1 \\ \mathbf{Q}''_{eac} \mathbf{P}'_{eac} - 1 \end{bmatrix} \quad (27a)$$

$$[\mathbf{S}'_{ea}] = \begin{bmatrix} -\mathbf{P}'_{eac} - 1 \mathbf{P}'_{ea} \\ -\mathbf{Q}''_{eac} \mathbf{P}'_{eac} - 1 \mathbf{P}'_{ea} + \mathbf{Q}'_{ea} \end{bmatrix} \quad (27b)$$

Let us demonstrate the utility of (27) with an example that includes two minerals, calcite and magnesite. We write the reaction system in the Reference basis {carbonate, magnesium, water, calcium, protons}, with secondaries {calcite, magnesite, hydroxyl ion, bicarbonate, and calcium hydroxide}:



In the context of (21), we have

$$\mathbf{a}_c = \begin{bmatrix} \text{CaCO}_3 \\ \text{MgCO}_3 \end{bmatrix}, \mathbf{a}'_{ao} = \begin{bmatrix} \text{OH}^- \\ \text{HCO}_3^- \\ \text{Ca(OH)}_2 \end{bmatrix}, \mathbf{a}''_{ac} = \begin{bmatrix} \text{CO}_3^{--} \\ \text{Mg}^{++} \end{bmatrix}, \text{ and } \mathbf{a}'_a = \begin{bmatrix} \text{H}_2\text{O} \\ \text{Ca}^{++} \\ \text{H}^+ \end{bmatrix} \quad (28)$$

and we will swap secondary carbonate and magnesium into the basis for the two minerals calcite and magnesite. The matrices \mathbf{P}''_{eac} , \mathbf{Q}''_{eac} , and \mathbf{R}'_{ea} are

$$\mathbf{P}''_{eac} = \begin{bmatrix} 1 & 0 \\ 1 & 1 \end{bmatrix}, \mathbf{Q}''_{eac} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \\ 0 & 0 \end{bmatrix}, \mathbf{P}'_{ea} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \text{ and } \mathbf{Q}'_{ea} = \begin{bmatrix} 1 & 0 & -1 \\ 0 & 0 & 1 \\ 2 & 1 & -2 \end{bmatrix} \quad (29)$$

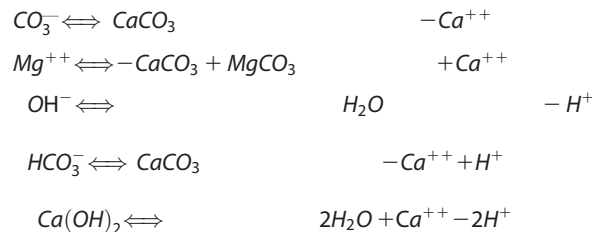
\mathbf{S}_{ec} is found from (27a) to be

$$[\mathbf{S}_{ec}] = \begin{bmatrix} 1 & 0 \\ -1 & 1 \\ 0 & 0 \\ 1 & 0 \\ 0 & 0 \end{bmatrix} \quad (30a)$$

and \mathbf{S}'_{ea} is found from (27b) to be

$$[\mathbf{S}'_{ea}] = \begin{bmatrix} 0 & -1 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & 1 \\ 2 & 1 & -2 \end{bmatrix} \quad (30b)$$

We check this result by formulating the problem originally with the New basis {calcite, magnesite, water, calcium, protons}, with secondaries {carbonate, magnesium, hydroxyl ion, bicarbonate, and calcium hydroxide}:



where it is seen that \mathbf{S}_{ec} (and \mathbf{S}'_{ea}) corresponding to the minerals calcite and magnesite, is indeed as put in (30a) and (30b), respectively. This allows us to write the particular version of (14) corresponding to this selection of secondaries replacing minerals, as:

$$\begin{aligned} \frac{\partial m_{CaCO_3}}{\partial t} &= n \left[\sum_{i=1}^{N_i-1} \sum_{j=1}^{N_i-1} \frac{\partial^2 (c_{CO_3^-} - c_{Mg^{++}} + c_{HCO_3^-})}{\partial \alpha_i \partial \alpha_j} \nabla^T \alpha_i \cdot \mathbf{D} \cdot \nabla \alpha_j \right] \\ \frac{\partial m_{MgCO_3}}{\partial t} &= n \left[\sum_{i=1}^{N_i-1} \sum_{j=1}^{N_i-1} \frac{\partial^2 (c_{Mg^{++}})}{\partial \alpha_i \partial \alpha_j} \nabla^T \alpha_i \cdot \mathbf{D} \cdot \nabla \alpha_j \right] \end{aligned} \quad (31)$$

Where we have factored in the multiplication by the respective rows of \mathbf{S}_{ec}^T . This example demonstrates the impact of including two minerals that share an ion; in order to use carbonate as a secondary for the rate of change of calcite, one must correct for the simultaneous precipitation/dissolution of magnesite through inclusion of the magnesite-associated secondaries. If one were to have selected calcium instead of carbonate for the secondary swapping with calcite, it is easy to show by the same procedure that one would get

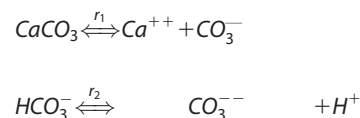
$$\begin{aligned} \frac{\partial m_{CaCO_3}}{\partial t} &= n \left[\sum_{i=1}^{N_i-1} \sum_{j=1}^{N_i-1} \frac{\partial^2 (c_{Ca^{++}} + c_{Ca(OH)_2})}{\partial \alpha_i \partial \alpha_j} \nabla^T \alpha_i \cdot \mathbf{D} \cdot \nabla \alpha_j \right] \\ \frac{\partial m_{MgCO_3}}{\partial t} &= n \left[\sum_{i=1}^{N_i-1} \sum_{j=1}^{N_i-1} \frac{\partial^2 (c_{Mg^{++}})}{\partial \alpha_i \partial \alpha_j} \nabla^T \alpha_i \cdot \mathbf{D} \cdot \nabla \alpha_j \right] \end{aligned} \quad (32)$$

6. Summary

Recent strides in mathematical approaches to decouple reactions and transport have opened new paths to upscaling quantitative biogeochemistry processes. Here we revisit the analytical approach of De Simoni et al. (2005, 2007) in order to clarify some opaque aspects of its use and to outline a way to extend the method to the more general cases of reactive transport involving multiple minerals. This entails construction of a certain, straightforward, and closed-form means to construct the necessary stoichiometric matrices for any given valid selection of “secondary” chemical species involved in the mineral formation, within the context of general multicomponent chemistry where these secondary species may participate in a number of other reactions including reactions forming other minerals. This opens the way for using the approach of De Simoni and coworkers with available codes such as PHREEQC that include very many such reactions within the various thermodynamic databases that come with the codes. Fortunately one need to only consider the subset of those reactions that involve the secondaries selected for swapping with the minerals, that we have termed here \mathbf{a}_{ac}'' . This allows relatively easy construction of the matrices \mathbf{P}_{eac}'' and \mathbf{Q}_{eac}'' needed for the construction of that \mathbf{S}_{ec} corresponding to the selected \mathbf{a}_{ac}'' .

Appendix A: Example for Equations (1–6)

Consider calcite precipitation/dissolution in batch with carbonate, bicarbonate, and protons, ignoring water dissolution. The species are $CaCO_3$, HCO_3^- , Ca^{++} , CO_3^{--} , and H^+ with reactions



the mole balances are

$$\frac{D}{Dt} \begin{bmatrix} CaCO_3 \\ HCO_3^- \\ Ca^{++} \\ CO_3^{--} \\ H^+ \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \\ +1 & 0 \\ +1 & +1 \\ 0 & +1 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \end{bmatrix}$$

and choosing HCO_3^- , Ca^{++} as secondaries leads to the equations (4) for this case:

$$\frac{D}{Dt} \begin{bmatrix} CaCO_3 + Ca^{++} \\ CO_3^- - Ca^{++} + HCO_3^- \\ H^+ + HCO_3^- \end{bmatrix} = 0$$

and equation (5) becomes (simplifying the notation to use chemical formulae for the compound mole concentrations):

$$m_{calcite} = CaCO_3 + n \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} Ca^{++} \\ HCO_3^- \end{bmatrix}$$

and equation (6) become

$$\mathbf{u} = \mathbf{c}'_a + \mathbf{S}_{ea}^T \mathbf{c}''_a \rightarrow \begin{bmatrix} u_{carbonate} \\ u_{proton} \end{bmatrix} = \begin{bmatrix} CO_3^- \\ H^+ \end{bmatrix} + \begin{bmatrix} -1 & 1 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} Ca^{++} \\ HCO_3^- \end{bmatrix}$$

Appendix B: Deriving the Corrected Form of (13) of dS07

$$\left[-\frac{\partial n \mathbf{c}''_a}{\partial t} + L(n \mathbf{c}''_a) \right] = n \sum_{i=1}^{N_i-1} \sum_{j=1}^{N_i-1} \frac{\partial^2 \mathbf{c}''_a}{\partial \alpha_i \partial \alpha_j} \nabla^T \alpha_i \cdot \mathbf{D} \cdot \nabla \alpha_j \quad (B1)$$

where

$$L(\cdot) \stackrel{\text{def}}{=} -\mathbf{q} \cdot \nabla(\cdot) + \nabla \cdot (n \mathbf{D} \cdot \nabla(\cdot)).$$

Following de Simoni et al. (2007), we presume the secondaries are determined solely as a function of the independent mixing ratios $\alpha = \alpha_i(\mathbf{x}, t)$, $i = 1, \dots, N_i - 1$, where N_i is the number of time-space boundaries to the problem. Thus,

$$c''_a = c''_a(\alpha(\mathbf{x}, t))$$

and for each of the terms on the right-hand side of (B1) we may expand as follows, respectively:

$$\frac{\partial n c''_a}{\partial t} = \frac{\partial n c''_a}{\partial \alpha} \cdot \frac{\partial \alpha}{\partial t} = \sum_{i=1}^{N_i-1} \frac{\partial n c''_a}{\partial \alpha_i} \frac{\partial \alpha_i}{\partial t}$$

$$\nabla c''_a(\alpha(\mathbf{x}, t)) = \left(\frac{\partial c''_a}{\partial \alpha} \cdot \frac{\partial \alpha}{\partial x}, \frac{\partial c''_a}{\partial \alpha} \cdot \frac{\partial \alpha}{\partial y}, \frac{\partial c''_a}{\partial \alpha} \cdot \frac{\partial \alpha}{\partial z} \right) = \sum_{i=1}^{N_i-1} \frac{\partial c''_a}{\partial \alpha_i} \nabla \alpha_i$$

$$\nabla \cdot (n \mathbf{D} \cdot \nabla c''_a(\alpha(\mathbf{x}, t))) = \sum_{j=1}^{I-1} \sum_{i=1}^{I-1} \frac{\partial^2 c''_a}{\partial \alpha_i \partial \alpha_j} \nabla \alpha_i^T \cdot n \mathbf{D} \cdot \nabla \alpha_j + \sum_{i=1}^{N_i-1} \frac{\partial c''_a}{\partial \alpha_i} \nabla \cdot (n \mathbf{D} \cdot \nabla \alpha_i)$$

which when used in (B1) converts the left-hand side of (B1) to

$$-\mathbf{q} \cdot \sum_{i=1}^{N_i-1} \frac{\partial c''_a}{\partial \alpha_i} \nabla \alpha_i + \sum_{j=1}^{N_i-1} \sum_{i=1}^{N_i-1} \frac{\partial^2 c''_a}{\partial \alpha_i \partial \alpha_j} \nabla \alpha_i^T \cdot n \mathbf{D} \cdot \nabla \alpha_j + \sum_{i=1}^{N_i-1} \frac{\partial c''_a}{\partial \alpha_i} \nabla \cdot (n \mathbf{D} \cdot \nabla \alpha_i) - \frac{\partial n c''_a}{\partial \alpha} \cdot \frac{\partial \alpha}{\partial t}$$

which, after some rearrangement and assuming n constant of time (actually it is enough if it is slowly varying as compared to concentrations or mixing ratios)

$$= \sum_{i=1}^{N_i-1} \frac{\partial c''_a}{\partial \alpha_i} \left(-\mathbf{q} \cdot \nabla \alpha_i + \nabla \cdot (n \mathbf{D} \cdot \nabla \alpha_i) - n \frac{\partial \alpha_i}{\partial t} \right) + \sum_{j=1}^{N_i-1} \sum_{i=1}^{N_i-1} \frac{\partial^2 c''_a}{\partial \alpha_i \partial \alpha_j} \nabla \alpha_i^T \cdot n \mathbf{D} \cdot \nabla \alpha_j$$

and, since the parenthetical quantity in the first term is zero by conservation of α_i ,

$$= \sum_{j=1}^{N_i-1} \sum_{i=1}^{N_i-1} \frac{\partial^2 c''_a}{\partial \alpha_i \partial \alpha_j} \nabla \alpha_i^T \cdot n \mathbf{D} \cdot \nabla \alpha_j$$

This equation corrects and replaces (13) of de Simoni et al. (2007).

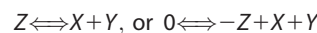
Appendix C: Basis Swapping

The list of primary species makes a linear algebraic basis for the vector space constructed of all the species identities and constrained by the equilibrium reaction relations. Basis swapping is the exchange of a subset of the primaries of the old or “reference” basis to become secondaries, and the same number of old secondaries to become primaries in the new basis. Basis swaps are called for as part of the numerical solution procedure especially when a species such as a mineral disappears (Bethke, 2006). However, quite little attention has been paid to this basis swapping, and this has been attributed to its limited role in assisting convergence of geochemical calculations, a role which vanishes when the solution is done in terms of logarithms of concentrations (Steefel & MacQuarrie, 1996). In the present context, however, basis swapping is fundamental to the identification of \mathbf{S}_{ec} given a valid set of secondaries, and to support this new use of basis swapping, this appendix provides a background in the topic.

The manipulations associated with basis swapping follow exactly the notions of linear transformations of bases in linear algebra (e.g., Lipschutz, 1968) and are briefly summarized in Steefel (1992) and Bethke (2006). Here we connect the operations to the mathematics of linear algebra in more detail, which is not available in the hydrology literature to our knowledge. We begin with an elementary case to set the concept and then move through the procedure details to an example.

C1. Elementary Case

Consider the three-dimensional vector space \mathbb{R}^3 described by the coordinates (X, Y, Z) which we conceptually associate with three chemical species, and a single reaction among them that proceeds from left to right at rate r :



If all variations in concentration are solely related to the reaction (e.g., no transport), we can write the ODE system

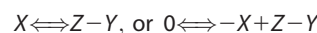
$$\begin{matrix} \dot{x} \\ \dot{y} \\ \dot{z} \end{matrix} = \begin{bmatrix} 1 \\ 1 \\ -1 \end{bmatrix} [r]$$

where x , y , and z are concentrations of the chemical species X , Y , and Z , respectively. The reaction rate provides a linear dependency among the three ODEs so we can eliminate one of them; we eliminate the ODE for z obtaining

$$\begin{bmatrix} \dot{(x+z)} \\ \dot{(y+z)} \end{bmatrix} \equiv \begin{bmatrix} \dot{u}_1 \\ \dot{u}_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{C1}$$

where we now have steady state quantities $(x+z)$ and $(y+z)$ termed “components” u_1 and u_2 . In this case, the “basis” is X and Y , and the two equations can be viewed as their respective conservation equations. The mass of X is contained in the component u_1 , either in x (its “primary” species) or in z (a “secondary” species), so the sum of these two quantities is a constant. Similarly, the mass of Y is contained in the component u_2 , either in its primary species y or in its secondary species z , the sum of which is also a constant.

Alternatively, we could eliminate the ODE for x . To do this with consistent nomenclature we term x the “secondary” species, and y and z primary species, and to do this with consistent writing of reactions with the secondary on the left-hand side we express the equation as:



now with rate $-r$. With these changes the new ODE system becomes

$$\begin{matrix} \dot{x} \\ \dot{y} \\ \dot{z} \end{matrix} = \begin{bmatrix} -1 \\ -1 \\ 1 \end{bmatrix} [-r]$$

and now eliminating the ODE for x we obtain

Table C1
Species, Components (of Basis), Primaries and Secondaries for Elementary Example

	Species	Basis	Primaries	Secondaries	Components
Reference basis	x, y, z	X, Y	x, y	z	$(x + z)$ $(y + z)$
New basis	x, y, z	Z, Y	z, y	x	$(z + x)$ $(y - x)$

$$\begin{bmatrix} (z+x) \\ (y-x) \end{bmatrix} \equiv \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad (C2)$$

where our new components are $u_1 = (y - x)$ and $u_2 = (z + x)$. Summarizing our two cases:

C2. Swapping From One Basis to Another Via the Transformation Matrix in a Linear Algebraic Formulation

The above demonstrates that the same chemical reaction system can be expressed in terms of two different bases following elementary linear algebra. More generally the same thing works in the context of vector spaces (e.g., Lipschutz, 1968, Chapter 7). Moreover, one can define a "transformation matrix" \mathbf{T} that defines the new basis in terms of the reference basis:

$$\mathbf{b}_{New} = \mathbf{T} \mathbf{b}_{Ref} \quad (C3)$$

and then the components of a vector in the old basis are converted to those of the same vector in the new basis by

$$\mathbf{v}_{New} = [\mathbf{T}^{-1}]^T \mathbf{v}_{Ref} \quad (C4)$$

So we can convert a (chemical components) vector that was defined in the reference basis to a components vector defined in the new basis by multiplying the components vector by the transpose of the inverse of the transformation matrix. Equation (C3) in the case of our elementary example is clearly

$$\begin{bmatrix} Z \\ Y \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix},$$

and then inverting and transposing the above transformation matrix

$$\left[\begin{bmatrix} 1 & 1 \\ 0 & 1 \end{bmatrix}^{-1} \right]^T = \begin{bmatrix} 1 & 0 \\ -1 & 1 \end{bmatrix}$$

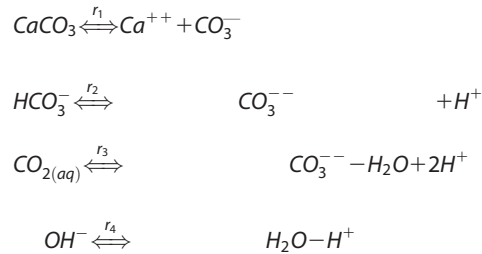
we execute (C4) by multiplying the reference components vector to obtain the new components vector:

$$\begin{bmatrix} 1 & 0 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix}_{Ref} = \begin{bmatrix} 1 & 0 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} x+z \\ y+z \end{bmatrix} = \begin{bmatrix} z+x \\ y-x \end{bmatrix} = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix}_{New}$$

and indeed we obtain the correct New components vector as already appears in Appendix Table C1 (Lipschutz, 1968, p. 153).

Next we demonstrate a basis switch for a larger system with eight species and four reactions. The basis is the species remaining after we assign exactly one species per reaction as the secondary species that appears in no other reactions. Then our system has four secondaries, and thus four remaining primary species corresponding to four components. Assuming each reaction is linearly independent from the others comprising the system, then one can always write the system so that each secondary appears only once in its respective reaction. In the case of linearly dependent reactions, the secondaries appear in more than one instance as described in Steefel and MacQuarrie (1996, p. 89), and this complicates the solution approach. It should be noted that for kinetically controlled reactions, linear dependency causes no difficulty. For present purposes, we assume all reactions independent

This system combines calcite precipitation (reaction 1) with simplified carbonate reactions (reactions 2 and 3) and water dissociation (reaction 4):



where the r_i are the rates of the reactions, with the convention that r_i is positive as the reaction proceeds from left-to-right. We have written the reactions with the secondaries already on the left-hand side, and so this establishes the Reference basis to include calcium, carbonate, water, and protons. The set of mass balance equations for the eight species is

$$\frac{D}{Dt} \begin{bmatrix} \text{CaCO}_3 \\ \text{HCO}_3^- \\ \text{CO}_{2(aq)} \\ \text{OH}^- \\ \text{Ca}^{++} \\ \text{CO}_3^- \\ \text{H}_2\text{O} \\ \text{H}^+ \end{bmatrix} = \begin{bmatrix} -1 & & & & & & & \\ & -1 & & & & & & \\ & & -1 & & & & & \\ & & & -1 & & & & \\ & & & & -1 & & & \\ & 1 & & & & & & \\ & & 1 & 1 & 1 & & & \\ & & & -1 & 1 & & & \\ & & & & & 1 & 2 & -1 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{bmatrix}$$

where the secondaries appear in the first four expressions. Components are formed by eliminating the reaction rates in a way that eliminates the equations for the secondaries, but direct substitution to get four equations for the components u_i corresponding to the reference basis:

$$\begin{bmatrix} \dot{u}_{Ca} \\ u_{CO_3} \\ u_{H_2O} \\ u_H \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 & 1 & 0 \\ 0 & 1 & 2 & -1 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \text{CaCO}_3 \\ \text{HCO}_3^- \\ \text{CO}_{2(aq)} \\ \text{OH}^- \\ \mathbf{Ca}^{++} \\ \mathbf{CO}_3^- \\ \mathbf{H}_2\text{O} \\ \mathbf{H}^+ \end{bmatrix} \tag{C5}$$

Notice that the matrix in (C5) can be written also as $[S_{ea}^T, \mathbf{I}]$ (we used bold to indicate the presence of the identity matrix). Now we establish the system for the new basis: if one were to choose Ca^{++} and

CO_3^{--} as secondaries instead of calcite and bicarbonate, the new components in this case would satisfy

$$\begin{bmatrix} u_{Ca}^{New} \\ u_{CO_3}^{New} \\ u_{H_2O}^{New} \\ u_H^{New} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & -1 & 1 & -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{CaCO}_3 \\ \mathbf{HCO}_3^- \\ \mathbf{CO}_{2(aq)} \\ \mathbf{OH}^- \\ \mathbf{Ca}^{++} \\ \mathbf{CO}_3^- \\ \mathbf{H}_2\mathbf{O} \\ \mathbf{H}^+ \end{bmatrix} \quad (C6)$$

with the new basis of calcite, bicarbonate, water and protons. Notice that similar to (C5), here we have highlighted in bold the primaries and the corresponding columns (becoming the identity matrix), so with a proper rearrangement in the species vector we could write it again as $[\mathbf{S}_{ea}^T, \mathbf{I}]$. Notice also that the two matrices \mathbf{S}_{ea}^T in (C5) and (C6) are different, to adapt to the choice of primary species done by the modeler.

One may obtain the new components from the original components using the same procedure as outlined above for the Elementary case. First we find the transformation matrix that gives the new basis in terms of the reference basis,

$$\begin{bmatrix} \mathbf{CaCO}_3 \\ \mathbf{HCO}_3^- \\ \mathbf{H}_2\mathbf{O} \\ \mathbf{H}^+ \end{bmatrix} = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{Ca}^{++} \\ \mathbf{CO}_3^- \\ \mathbf{H}_2\mathbf{O} \\ \mathbf{H}^+ \end{bmatrix}$$

Thus the transformation matrix \mathbf{T} is

$$\mathbf{T} = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

and the transpose of its inverse is

$$[\mathbf{T}^{-1}]^T = \begin{bmatrix} 1 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & -1 & 0 & 1 \end{bmatrix}$$

and if we use this matrix to multiply the original components,

$$[\mathbf{T}^{-1}]^T \begin{bmatrix} u_{Ca} \\ u_{CO_3} \\ u_{H_2O} \\ u_H \end{bmatrix}$$

we obtain the new components,

$$[\mathbf{T}^{-1}]^T \begin{bmatrix} u_{Ca} \\ u_{CO_3} \\ u_{H_2O} \\ u_H \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 & 1 & 0 \\ 0 & 1 & 2 & -1 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} CaCO_3 \\ HCO_3^- \\ CO_{2(aq)} \\ OH^- \\ Ca^{++} \\ CO_3^- \\ H_2O \\ H^+ \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & -1 & 1 & -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} CaCO_3 \\ HCO_3^- \\ CO_{2(aq)} \\ OH^- \\ Ca^{++} \\ CO_3^- \\ H_2O \\ H^+ \end{bmatrix} = \begin{bmatrix} u_{Ca}^{New} \\ u_{CO_3}^{New} \\ u_{H_2O}^{New} \\ u_H^{New} \end{bmatrix}$$

as can be seen by comparison to the already determined new components in equation (C6).

Notation

- N_i number of time-space boundaries for solution sources (end-members) in the transport.
- N_C number of mineral species in the reaction network.
- N_R number of reactions.
- N_S total number of chemical species in the reaction network.
- $N_{ij} (= N_S - N_R - N_C)$ number of aqueous components, equal to number of aqueous primary species

Following definitions are for the role played by the given symbols in the “New” basis unless otherwise noted

- $\alpha_i(\mathbf{x}, t)$ solution to the nonreactive transport of a tracer emanating from time or space boundary i with unity boundary or initial condition there and zero elsewhere [dimensionless].

a_c	N_C primary mineral species.
a'_a	$N_U (= N_S - N_R - N_C)$ primary aqueous species.
a''_a	N_R secondary aqueous species.
a''_{ac}	N_C secondary aqueous species corresponding to the mineral equilibria.
a''_{ao}	$N_R - N_C$ secondary aqueous species not corresponding to the mineral equilibria.
b_{New}	basis vector (of N_U dimensional vector space) defining New basis.
b_{Ref}	basis vector (of N_U dimensional vector space) defining Reference basis.
m_c	vector of N_C bulk-volumetric mineral moles [moles/vol].
N	porosity [volume/volume].
c'_a	vector of N_U aqueous-volumetric moles of primary species [moles/vol].
c''_a	vector of N_R aqueous-volumetric moles of secondary species [moles/vol].
u_i	end-member component vector corresponding to the composition of the solution at the i th boundary.
V_{New}	a vector of N_U components in the New basis.
V_{Ref}	a vector of N_U components in the Reference basis.
0_{ao}	$N_C \times (N_R - N_C)$ matrix of zeroes.
0_c	$(N_R - N_C) \times N_C$ matrix of zeroes.
I_{ao}	$(N_R - N_C) \times (N_R - N_C)$ Identity matrix.
I_c	$N_C \times N_C$ Identity matrix.
P''_{eac}	$N_C \times N_C$ upper partition of R''_{eac} corresponding to mineral equilibria reactions.
Q''_{eac}	$(N_R - N_C) \times N_C$ lower partition of R''_{eac} .
P'_{ea}	$N_C \times (N_S - N_R - N_C)$ upper partition of R'_{ea} corresponding to mineral equilibria.
Q'_{ea}	$(N_R - N_C) \times (N_S - N_R - N_C)$, lower partition of R'_{ea} .
$[R''_{eac}, R'_{ea}]$	$N_R \times (N_S - N_R)$ stoichiometric matrix for the reaction network expressed in the Reference basis.
R''_{eac}	$N_R \times N_C$ stoichiometric submatrix that is columns of $[R''_{eac}, R'_{ea}]$.
R'_{ea}	$N_R \times (N_S - N_R - N_C)$ stoichiometric submatrix that is columns of $[R''_{eac}, R'_{ea}]$.
$[S_{ec}, S'_{ea}]$	$N_R \times (N_S - N_R)$ stoichiometric matrix for the reaction network.
S_{ec}	$N_R \times N_C$ stoichiometric submatrix that is columns of $[S_{ec}, S'_{ea}]$ corresponding to mineral primaries.
S'_{ea}	$N_R \times (N_S - N_R - N_C)$ stoichiometric submatrix that is columns of $[S_{ec}, S'_{ea}]$ corresponding to aqueous primaries.
T	$N_U \times N_U$ Transformation matrix.

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