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A parallel global-implicit 2-D solver for reactive transport problems in porous media based on a reduction scheme and its application to the MoMaS benchmark problem

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Abstract In this article, an approach for the efficient numerical solution of multi-species reactive transport problems in porous media is described. The objective of this approach is to reformulate the given system of partial and ordinary differential equations (PDEs, ODEs) and algebraic equations (AEs), describing local equilibrium, in such a way that the couplings and nonlinearities are concentrated in a rather small number of equations, leading to the decoupling of some linear partial differential equations from the nonlinear system. Thus, the system is handled in the spirit of a global implicit approach (one step method) avoiding operator splitting techniques, solved by Newton's method as the basic algorithmic ingredient. The reduction of the problem size helps to limit the large computational costs of numerical simulations of such problems. If the model contains equilibrium precipitation-dissolution reactions of minerals, then these are considered as complementarity conditions and rewritten as semismooth equations, and the whole nonlinear system is solved by the semismooth Newton method.

Keywords Reactive transport · Porous media · Numerical simulation · Size reduction · Complementarity problems

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1 Introduction

We are considering multi-species reactive transport problems in porous media, which, in general, consist of partial and ordinary differential equations (PDEs and ODEs) for the mobile and immobile species concentrations coupled through nonlinear kinetic reaction rate terms and, if equilibrium reactions are considered, nonlinear algebraic equations (AEs) describing local equilibria. In order to reduce the size of the nonlinear system and, thus, the required computational resources, the system is transformed by (a) taking linear combinations between the differential equations, (b) the introduction of a new set of variables, i.e., a linear variable transform, and (c) the elimination of some of the new variables by substituting local equations, such as AEs and ODEs, into the PDEs. This leads to a reduction of the size of the nonlinear system, as some scalar linear transport equations decouple from the system. An alternative reformulation of the original PDE–ODE–AE system is, e.g. the Morel tableau, in which the MoMaS benchmark problem (see [3]) is formulated. A main difference in the derivation of the Morel formulation and ours is that our treatment carefully distinguishes between mobile and immobile entities in order to enable, after the variable transformation, the decoupling of some of the PDEs and ODEs.

In the literature of modelling reactive transport in porous media, there are already attempts to reduce the computational effort. In [15], the elimination of constant activity species is described. Otherwise, no reduction of the problem size can be achieved with the methods of [15]. Enhancements of this work can be found in [13]. The method there causes a decoupling of linear PDEs under the condition that all immobile species are either kinetic species or fixed activity species. Especially for adsorbed species, this condition is not fulfilled and, hence, no decoupling can be achieved. In the reduction scheme presented in this work, that condition is not needed, i.e., also for reaction networks with sorption reactions, a decoupling of linear PDEs is possible. In the case that the condition for the immobile species is fulfilled, the number of linear PDEs decoupling from the nonlinear system of the method in [13] and of our reduction scheme is equal. Furthermore, in [13], it is necessary to treat the reaction rates of kinetic reactions explicitly. By use of our reduction scheme, you do not have this restriction. For a more detailed comparison, see [10, Sec. 5].

For models containing equilibrium reactions with minerals (e.g., the MoMaS benchmark, "hard test case"), the difficulty occurs that, in general, the two possibilities of a saturated state and of a state where the mineral is fully dissolved without saturation with respect to each mineral exist. A description of local equilibrium covering both cases consists of equations and inequalities. For an efficient numerical handling of systems containing such equilibrium conditions, we propose to consider the mineral equilibrium conditions as complementarity conditions (CCs). It is well known that CCs can be equivalently transformed into equations, and then the whole nonlinear system can be solved by the semismooth Newton method.

The described techniques were implemented in a software, running on parallel computers, which has been applied to the three MoMaS test cases in 1D and 2D.

2 A summary of the reformulation technique and comparison to the Morel formulation

Let I be the number of mobile species and $\bar{I}$ the number of immobile species. The starting point is the formulation

$$\partial_t c + \mathscr{L} c = S_{1,\mathrm{eq}} R_{\mathrm{eq}} + S_{1,\mathrm{kin}} R_{\mathrm{kin}}(c, \bar{c}) \tag{1}$$

$$\partial_t \bar{c} = S_{2,\mathrm{eq}} R_{\mathrm{eq}} + S_{2,\mathrm{kin}} R_{\mathrm{kin}}(c, \bar{c}) \tag{2}$$

$$Q(c, \bar{c}) = 0 \tag{3}$$

(compare, e.g., [15, eq. (19), (1)]) Here, $c = (c_1, \ldots, c_I)^T$ is the vector of mobile species concentrations, $\bar{c} = (\bar{c}_1, \ldots, \bar{c}_{\bar{I}})^T$ is the vector of immobile species concentrations, $\mathscr{L}$ is a linear transport operator, $R_{\mathrm{kin}}(c, \bar{c})$ is a vector with J_{kin} entries containing the kinetic rate laws (J_{kin} being the number of kinetic reactions), R_{eq} is a vector with J_{eq} entries containing the reaction rates for equilibrium reactions (J_{eq} being the number of equilibrium reactions), $Q(c, \bar{c})$ is a vector with J_{eq} entries consisting of (nonlinear) AEs describing the equilibrium conditions, and

$$S = \left(S_{\mathrm{eq}} \mid S_{\mathrm{kin}}\right) = \left(\frac{S_1}{S_2}\right) = \left(\begin{array}{c|c} S_{1,\mathrm{eq}} & S_{1,\mathrm{kin}} \\ \hline S_{2,\mathrm{eq}} & S_{2,\mathrm{kin}} \end{array}\right) \tag{4}$$

is a matrix of stoichiometric coefficients; the left J_{eq} columns correspond to equilibrium reactions, the right J_{kin} columns to kinetic reactions, the upper I rows correspond to mobile species, and the lower $\bar{I}$ rows to immobile species. A typical transport operator for time-independent θ[1] is

$$\mathscr{L}_i c_i = -\frac{1}{\theta} \nabla \cdot (D \nabla c_i - q c_i), \qquad i = 1, \ldots, I$$

with θ the volumetric water content, q the Darcy flux, and D the dispersion tensor. Note that the unknowns in this formulation are c, $\bar{c}$, *and* R_{eq}. For more details, see [10, 11]. In case of mass action reactions and ideal activities, Q reads

$$Q(c, \bar{c}) = \ln k + S_{\mathrm{eq}}^T \begin{pmatrix} \ln c \\ \ln \bar{c} \end{pmatrix}, \tag{5}$$

k being the vector of equilibrium constants.

It is general practice to eliminate the unknowns R_{eq} from the system. Before we describe the decoupling technique, let us look at one of the state-of-the-art methods to obtain a system in which R_{eq} does not occur, called the *Morel tableau*. For this, assuming that the equilibrium reactions, i.e., the columns of the stoichiometric matrix S_{eq} are linear independent on restructures S_{eq} in a Gauss-Jordan-like manner such that S_{eq} obtains the structure

$$S_{\mathrm{eq}} = \left(\begin{array}{c|c} C & A \\ \hline -Id & 0 \\ \hline\hline 0 & B \\ \hline 0 & -Id \end{array}\right). \tag{6}$$

The rows are split in four blocks having the sizes $I - J_{\mathrm{mob}}$, J_{mob}, $\bar{I} - J_{\mathrm{sorp}}$, and J_{sorp}, and the columns are split in two blocks having the sizes J_{mob} and J_{sorp} (J_{mob} being the number of equilibrium reactions with only mobile species and J_{sorp} being the number of equilibrium "sorption" reactions, i.e., heterogeneous without mineral species; it holds $J_{\mathrm{eq}} = J_{\mathrm{mob}} + J_{\mathrm{sorp}}$). So

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[1] Extension to time-dependent θ is easily possible.

C is a $(I - J_{\mathrm{mob}}) \times J_{\mathrm{mob}}$ matrix, A is $(I - J_{\mathrm{mob}}) \times J_{\mathrm{sorp}}$ matrix, and B is a $(\bar{I} - J_{\mathrm{sorp}}) \times J_{\mathrm{sorp}}$ matrix.

Then one searches a matrix $S_{\mathrm{eq}}^{\perp}$ with linear independent columns, which are orthogonal to the columns of S_{eq}, such that the columns of S_{eq} and $S_{\mathrm{eq}}^{\perp}$ form a basis; so we have the orthogonality relation

$$\left(S_{\mathrm{eq}}^{\perp}\right)^T S_{\mathrm{eq}} = 0. \tag{7}$$

We may choose

$$S_{\mathrm{eq}}^{\perp} = \left(\begin{array}{c|c} Id & 0 \\ \hline C^T & 0 \\ \hline\hline 0 & Id \\ \hline A^T & B^T \end{array}\right).$$

By multiplying Eqs. 1 and 2 by $(S_{\mathrm{eq}}^{\perp})^T$, the R_{eq} vanishes due to the orthogonality relation (Eq. 7) and one obtains, after a splitting of the mobile concentrations into $I - J_{\mathrm{mob}}$ primary and J_{mob} secondary variables and of the immobile concentrations into $\bar{I} - J_{\mathrm{sorp}}$ primary and J_{sorp} secondary variables,

$$c = \begin{pmatrix} c_{\mathrm{prim}} \\ c_{\mathrm{sec}} \end{pmatrix}, \quad \bar{c} = \begin{pmatrix} \bar{c}_{\mathrm{prim}} \\ \bar{c}_{\mathrm{sec}} \end{pmatrix}$$

the formulation

$$\begin{aligned} &\begin{pmatrix} (\partial_t + \mathscr{L})\,(c_{\mathrm{prim}} + C c_{\mathrm{sec}}) + \partial_t A \bar{c}_{\mathrm{sec}} \\ \partial_t\,(\bar{c}_{\mathrm{prim}} + B \bar{c}_{\mathrm{sec}}) \end{pmatrix} \\ &\quad = \left(S_{\mathrm{eq}}^{\perp}\right)^T S_{\mathrm{kin}} R_{\mathrm{kin}}(c_{\mathrm{prim}}, c_{\mathrm{sec}}, \bar{c}_{\mathrm{prim}}, \bar{c}_{\mathrm{sec}}) \\ &\quad =: f(c_{\mathrm{prim}}, c_{\mathrm{sec}}, \bar{c}_{\mathrm{prim}}, \bar{c}_{\mathrm{sec}}) \end{aligned} \tag{8}$$

with the equilibrium conditions in Eq. 3 together with Eq. 5, which read

$$\begin{aligned} \ln c_{\mathrm{sec}} &= C^T \ln c_{\mathrm{prim}} + \ln k_1 \\ \ln \bar{c}_{\mathrm{sec}} &= A^T \ln c_{\mathrm{prim}} + B^T \ln \bar{c}_{\mathrm{prim}} + \ln k_2. \end{aligned} \tag{9}$$

After the definitions $T_M := c_{\mathrm{prim}} + C c_{\mathrm{sec}}$, $T_F := A \bar{c}_{\mathrm{sec}}$, $T := T_M + T_F$, and $T_S := \bar{c}_{\mathrm{prim}} + B \bar{c}_{\mathrm{sec}}$, one gets the formulation

$$\begin{aligned} \partial_t (T_M + T_F) + \mathscr{L} T_M &= f_1(c_{\mathrm{prim}}, c_{\mathrm{sec}}, \bar{c}_{\mathrm{prim}}, \bar{c}_{\mathrm{sec}}) \\ \partial_t\, T_S &= f_2(c_{\mathrm{prim}}, c_{\mathrm{sec}}, \bar{c}_{\mathrm{prim}}, \bar{c}_{\mathrm{sec}}) \end{aligned} \tag{10}$$

together with the chemical problem

$$\begin{aligned} T &= c_{\mathrm{prim}} + C c_{\mathrm{sec}} + A \\ \bar{c}_{\mathrm{sec}} \ln c_{\mathrm{sec}} &= C^T \ln c_{\mathrm{prim}} + \ln k_1 \\ T_S &= \bar{c}_{\mathrm{prim}} + B \bar{c}_{\mathrm{sec}} \\ \ln \bar{c}_{\mathrm{sec}} &= A^T \ln c_{\mathrm{prim}} + B^T \ln \bar{c}_{\mathrm{prim}} + \ln k_2 \end{aligned} \tag{11}$$

and the conservation laws

$$\begin{aligned} rlT &= T_M + T_F \\ T_F &= A \bar{c}_{\mathrm{sec}}\,. \end{aligned} \tag{12}$$

This formulation corresponds to the one used in the benchmark. Possible solution strategies may be, for example, (a) to substitute the secondary variables c_{sec}, $\bar{c}_{\mathrm{sec}}$ (Eq. 9) into Eq. 8, (b) to solve the formulation Eqs. 10–12 directly, or (c) in the case $f_1 = f_2 = 0$ to solve Eq. 11 formally for $\bar{c}_{\mathrm{sec}}$ and substitute this in Eq. 12, which is then solved together with Eq. 10 (see [1]).

A drawback of strategy a is that the substitution leads to couplings and nonlinearities in the transport operator, which causes many non-zero entries in the Jacobian. The drawback of strategy b is that it consists of quite a large number of equations and unknowns, urging for splitting techniques, which might (of course strongly depending on the specific problem) require small time steps to obtain accuracy (in the non-iterative case) or convergence (in the iterative case).

The reformulation we use tries to decouple some linear PDEs from the nonlinear system and, thus, reduces the size without splitting techniques (see [6, 10, 11] for details). The strategy is to try to avoid a "mixing" of mobile and immobile entities (such as "$T_M + T_F$" in Eq. 10) in at least some of the PDEs. Therefore, our approach multiplies the PDE block (Eq. 1) and the ODE block (Eq. 2) *separately* by certain matrices. We start by restructuring S_{eq} such that it has the shape of Eq. 4 with

$$S_{\mathrm{eq}} = \left(\begin{array}{c|c|c} S_{1,\mathrm{mob}} & S_{1,\mathrm{sorp}} & 0 \\ \hline 0 & S_{2,\mathrm{sorp}} & S_{2,\mathrm{immo}} \end{array}\right), \tag{13}$$

with the columns of $(S_{1,\mathrm{mob}}|S_{1,\mathrm{sorp}})$ and $(S_{2,\mathrm{sorp}}|S_{2,\mathrm{immo}})$ being void of any linear dependence; this can be achieved by a Gaussian-type elimination (see [10]). Then, matrices S_1^* and S_2^* are defined by

$$S_1^* = (S_{1,\mathrm{mob}}|S_{1,\mathrm{sorp}}|S_{1,\mathrm{kin}}^*), \quad S_2^* = (S_{2,\mathrm{sorp}}|S_{2,\mathrm{immo}}|S_{2,\mathrm{kin}}^*).$$

They contain the linear independent columns of S_1 and S_2, respectively (see [10] for details).

Matrices $S_1^{\perp}$, $S_2^{\perp}$, consisting of columns being orthogonal to each column of S_1^*, S_2^*, respectively, are constructed. We choose matrices B_1 and B_2 being of the same size as S_1^*, S_2^*, respectively, which fulfil the condition that the columns of B_i, $S_i^{\perp}$ form a basis of the whole space. The simplest choice is $B_1 = S_1^*$, $B_2 = S_2^*$.[2] Analogous to $S_1^{\perp}$, $S_2^{\perp}$ matrices $B_1^{\perp}$, $B_2^{\perp}$ are

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[2] In [6, 10, 11], this choice is taken.

constructed from B_1, B_2. Multiplication of the PDE block by $\left((S_1^\perp)^T B_1^\perp\right)^{-1}(S_1^\perp)^T$ and by $(B_1^T S_1^*)^{-1} B_1^T$, and multiplication of the ODE block by $\left((S_2^\perp)^T B_2^\perp\right)^{-1}(S_2^\perp)^T$ and by $(B_2^T S_2^*)^{-1} B_2^T$ and a few more simple steps [10] lead to the system

$$\begin{aligned}
\partial_t \eta + \mathscr{L}\eta &= 0\\
\partial_t \bar\eta &= 0\\
\partial_t(\xi_{\text{sorp}} - \bar\xi_{\text{sorp}}) + \mathscr{L}\xi_{\text{sorp}} &= g_1(\eta, \bar\eta, \xi, \bar\xi)\\
\partial_t \xi_{\text{kin}} + \mathscr{L}\xi_{\text{kin}} &= g_2(\eta, \bar\eta, \xi, \bar\xi)\\
\partial_t \bar\xi_{\text{kin}} &= g_3(\eta, \bar\eta, \xi, \bar\xi)\\
Q(\eta, \bar\eta, \xi, \bar\xi) &= 0,
\end{aligned} \tag{14}$$

where we applied the linear variable transformation for the mobile and the immobile species (separately):

$$\eta := \left((S_1^\perp)^T B_1^\perp\right)^{-1}(S_1^\perp)^T c, \quad \bar\eta := \left((S_2^\perp)^T B_2^\perp\right)^{-1}(S_2^\perp)^T \bar c \tag{15}$$

$$\xi := \left(B_1^T S_1^*\right)^{-1} B_1^T c, \qquad \bar\xi := \left(B_2^T S_2^*\right)^{-1} B_2^T \bar c$$

and inverse

$$\begin{aligned}
c &= S_1^* \xi + B_1^\perp \eta\\
\bar c &= S_2^* \bar\xi + B_2^\perp \bar\eta,
\end{aligned} \tag{16}$$

and where the vectors ξ and $\bar\xi$ were split into subvectors $\xi =: (\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{kin}})$, $\bar\xi =: (\bar\xi_{\text{sorp}}, \bar\xi_{\text{immo}}, \bar\xi_{\text{kin}})$. The g_i in Eq. 14 contain the kinetic terms, which are zero in the "easy test case" of the benchmark problem. The equilibrium conditions in Eq. 14 are as well expressed in terms of the new variables $\xi, \eta, \bar\xi, \bar\eta$, which are indeed the variables in which the system is discretized and solved.

Comparing Eq. 14 to Eqs. 10–12, we see that some *linear scalar* transport equations for the unknowns η (consisting of only mobile entities) decouple from the system, while some equations are pure ODEs, consisting only of immobile entities $\bar\xi_{\text{kin}}$. Furthermore, the $\bar\eta$ are constant in time, hence fully determined by the initial conditions. The block of PDEs for the ξ_{sorp}, ξ_{kin} is, in all situations, smaller than or equal to the block of PDEs in Eq. 10. Both the block of ODEs and the block of AEs in Eq. 14 can (after discretization in time) be solved for certain secondary variables $\xi_{\text{sec}} := (\xi_{\text{mob}}, \bar\xi_{\text{sorp}}, \bar\xi_{\text{immo}}, \bar\xi_{\text{kin}})$ and substituted into the remaining nonlinear PDEs for the primary variables $\xi_{\text{prim}} := (\xi_{\text{sorp}}, \xi_{\text{kin}})$, which results in a small nonlinear problem

$$\begin{aligned}
&\partial_t(\xi_{\text{sorp}} - \bar\xi_{\text{sorp}}(\xi_{\text{sorp}}, \xi_{\text{kin}})) + \mathscr{L}\xi_{\text{sorp}}\\
&\qquad = g_1(\eta, \bar\eta, \xi_{\text{sorp}}, \xi_{\text{kin}}, \xi_{\text{sec}}(\xi_{\text{sorp}}, \xi_{\text{kin}}))\\
&\partial_t \xi_{\text{kin}} + \mathscr{L}\xi_{\text{kin}}\\
&\qquad = g_2(\eta, \bar\eta, \xi_{\text{sorp}}, \xi_{\text{kin}}, \xi_{\text{sec}}(\xi_{\text{sorp}}, \xi_{\text{kin}})),
\end{aligned} \tag{17}$$

which is solved in each time step, after the time step for the linear η equations is done.

From the algorithmic point of view, this problem is solved by a Newton iteration. While each Newton step gives an update for the primary variables, the secondary variables are updated by a nested Newton iteration for ξ_{sec} (since the local equations cannot be solved analytically), which can be performed "locally" at each mesh point. No slow fixed-point-type iteration is required. The solution of the ODEs and the block of AEs in Eq. 14 for ξ_{loc} for given ξ_{glob} is called the *local problem*.

Note that the substitution of the local equations into the PDEs only takes place under the time derivative and in the kinetic terms, but not in the transport operator, leaving the transport term *linear*. To summarize the motivation for the variable transformation: The introduction of $\eta, \bar\eta$ allows the decoupling of linear equations. The introduction of $\xi, \bar\xi$ in the nonlinear equations allows the solution of the local equations with respect to the ξ_{sec}. One can prove that the number of remaining PDEs (Eq. 17) is less than or equal to the number of PDEs of Eq. 8 [9] and that resolution functions of the local equations exist under mild assumptions [9, 10].

In the Appendix, the equations and the variables of the reduction scheme (including the modifications of the following section) are explicitly written down for a simple example. For comparison, you can also find there the Morel formulation of the example.

3 Modifications

The computations of the MoMaS benchmark are based on the formulation summarized in Section 2; however, some modifications were carried out in order to enhance the robustness of the algorithm in cases where the concentrations vary over many magnitudes, and where some concentrations may be zero or very close to zero, which happens in the benchmark problem. First, an additional variable

$$\tilde\xi_{\text{sorp}} := \xi_{\text{sorp}} - \bar\xi_{\text{sorp}} \tag{18}$$

was introduced. It appears in the time derivative of Eq. 14. The equation defining $\tilde{\xi}_{\mathrm{sorp}}$ becomes part of the global problem (Eq. 17) and the variable $\tilde{\xi}_{\mathrm{sorp}}$ becomes a primary variable $\xi_{\mathrm{prim}} := (\tilde{\xi}_{\mathrm{sorp}}, \xi_{\mathrm{sorp}}, \xi_{\mathrm{kin}})$. Because of the new variable, there is some freedom of choice in the retransformation (Eq. 16) and in the resolution function for the secondary variables ξ_{sec}. It is possible to formulate the retransformation (considering the structure of Eq. 13) using either ξ_{sorp} or $\tilde{\xi}_{\mathrm{sorp}}$. We chose the formulation with $\tilde{\xi}_{\mathrm{sorp}}$

$$c = S_{1,\mathrm{mob}}\xi_{\mathrm{mob}} + S_{1,\mathrm{sorp}}\big(\tilde{\xi}_{\mathrm{sorp}} + \bar{\xi}_{\mathrm{sorp}}\big) + S^{*}_{1,\mathrm{kin}}\xi_{\mathrm{kin}} + B_1^{\perp}\eta \tag{19}$$
$$\bar{c} = S_{2,\mathrm{sorp}}\bar{\xi}_{\mathrm{sorp}} + S^{*}_{2,\mathrm{kin}}\bar{\xi}_{\mathrm{kin}} + B_2^{\perp}\bar{\eta}\,.$$

The resolution function for the secondary variables ξ_{sec} was chosen as a function of the variables $(\tilde{\xi}_{\mathrm{sorp}}, \xi_{\mathrm{kin}})$. So altogether, the new nonlinear problem reads

$$\begin{aligned} \tilde{\xi}_{\mathrm{sorp}} &= \xi_{\mathrm{sorp}} - \bar{\xi}_{\mathrm{sorp}}\big(\tilde{\xi}_{\mathrm{sorp}}, \xi_{\mathrm{kin}}\big) \\ \partial_t\tilde{\xi}_{\mathrm{sorp}} + \mathscr{L}\xi_{\mathrm{sorp}} &= g_1\big(\eta, \bar{\eta}, \tilde{\xi}_{\mathrm{sorp}}, \xi_{\mathrm{kin}}, \xi_{\mathrm{sec}}\big(\tilde{\xi}_{\mathrm{sorp}}, \xi_{\mathrm{kin}}\big)\big) \\ \partial_t\xi_{\mathrm{kin}} + \mathscr{L}\xi_{\mathrm{kin}} &= g_2\big(\eta, \bar{\eta}, \tilde{\xi}_{\mathrm{sorp}}, \xi_{\mathrm{kin}}, \xi_{\mathrm{sec}}\big(\tilde{\xi}_{\mathrm{sorp}}, \xi_{\mathrm{kin}}\big)\big)\,. \end{aligned} \tag{20}$$

The motivation for this formulation is the following: By solving the original formulation (Eq. 17) with Newton's method, the derivatives $\frac{\partial\xi_{\mathrm{sec}}}{\partial(\xi_{\mathrm{sorp}},\xi_{\mathrm{kin}})}$ appear in the Jacobian matrix. These derivatives can assume high values and cause convergence problems in cases where equilibrium constants of sorption reactions assume extreme values. With the modifications of this section, the derivatives $\frac{\partial\xi_{\mathrm{sec}}}{\partial(\tilde{\xi}_{\mathrm{sorp}},\xi_{\mathrm{kin}})}$ appear in the Jacobian matrix. But these derivatives are bounded. So the introduction of the new variable $\tilde{\xi}_{\mathrm{sorp}}$ improves the convergence of the method.

Another modification which turned out to be useful for these kinds of problems concerns the formulation of the local problem. Solving the local problem

$$\begin{aligned} &\partial_t\bar{\xi}_{\mathrm{kin}} &&= g_3(\eta, \bar{\eta}, \xi, \bar{\xi}) \\ &Q(\eta, \bar{\eta}, \xi, \bar{\xi}) = 0 \end{aligned}$$

with Newton's method leads to very ill-conditioned linear systems for the benchmark problem (condition number $\approx 10^{100}$). To avoid this, the defining equations for the transformed variables $\eta, \tilde{\xi}_{\mathrm{sorp}}, \xi_{\mathrm{kin}}, \bar{\eta}, \bar{\xi}_{\mathrm{kin}}$ are added as additional equations to the local problem. Furthermore, $\bar{\xi}_{\mathrm{kin}}$ and the logarithms of the concentrations

$$l := \ln(c), \qquad \bar{l} := \ln(\bar{c})$$

are used as unknowns. The other secondary unknowns $(\xi_{\mathrm{mob}}, \bar{\xi}_{\mathrm{sorp}}, \bar{\xi}_{\mathrm{immo}})$ are calculated a posteriori with help of their definition equations. Altogether, in the local problem, we have to solve the nonlinear system (the indices $1, 2, 3$ denote the splitting of ξ and $\bar{\xi}$ into subvectors, see paragraph after Eq. 16)

$$\begin{aligned} \partial_t\bar{\xi}_{\mathrm{kin}} &= g_3\big(\exp(l), \exp(\bar{l})\big) \\ Q(l, \bar{l}) &= 0 \\ \eta &= \Big(\big(S_1^{\perp}\big)^T B_1^{\perp}\Big)^{-1}\big(S_1^{\perp}\big)^T \exp(l) \\ \tilde{\xi}_{\mathrm{sorp}} &= \Big(\big(B_1^T S_1^{*}\big)^{-1} B_1^T \exp(l)\Big)_2 \\ &\quad -\Big(\big(B_2^T S_2^{*}\big)^{-1} B_2^T \exp(\bar{l})\Big)_1 \\ \xi_{\mathrm{kin}} &= \Big(\big(B_1^T S_1^{*}\big)^{-1} B_1^T \exp(l)\Big)_3 \\ \bar{\eta} &= \Big(\big(S_2^{\perp}\big)^T B_2^{\perp}\Big)^{-1}\big(S_2^{\perp}\big)^T \exp(\bar{l}) \\ \bar{\xi}_{\mathrm{kin}} &= \Big(\big(B_2^T S_2^{*}\big)^{-1} B_2^T \exp(\bar{l})\Big)_3 \end{aligned} \tag{21}$$

with the unknowns $(l, \bar{l}, \bar{\xi}_{\mathrm{kin}})$. Solving this system with Newton's method leads to much better conditioned linear systems. However, the local problem is now larger than the version of Section 2, which therefore is preferable if problems with *moderate* values for equilibrium constants and concentrations are simulated.

4 Implementation

The algorithm was implemented using a software kernel for parallel computations in the field of PDEs called M++ [16]. M++ itself is an object-oriented code based on C++. The code is implemented for 2-D problems and uses conformal finite elements on unstructured grids. For solving the nonlinear systems of equations, Newton's method is used. Different iterative linear solvers (e.g., GMRES, BiCGStab, QMRCGStab) and different standard preconditioners (e.g., SSOR) are implemented.

As a standard, linear finite elements on triangular meshes and the implicit Euler time stepping scheme are used and all terms that are not coming from spatial derivatives are discretized using mass lumping; however, changes are easily possible just by modifications of the script file, by which the user specifies the problem including the chemistry, ansatz spaces, the discretization parameters, etc. For convection-dominated problems, a FV stabilization is available.

Table 1 CPU time with and without extrapolation, advective easy test case in 2D

	CPU time	Time steps	Newton steps
With extrapolation	5,838.7	13,044	2.18
Without extrapolation	8,918.8	17,100	2.88

The discrete transport operator is only assembled once in the beginning of the computation and stored in a matrix. In every time step, this matrix is used to assemble the Jacobian matrix. That way, CPU time is saved.

An adaptive time stepping is implemented. The time step size is chosen between given minimum and maximum values: $\Delta t_{\min} \le \Delta t \le \Delta t_{\max}$. The criterion of the time step choice depends on the number of Newton steps in the last time step. When it is necessary, a time step is repeated with a smaller time step size.

The starting values for both the η problem and the nonlinear problem are calculated by extrapolation from two time levels. For some applications, much CPU time can be saved in comparison to using just the value of the old time step as a starting value. In Table 1, the normalized CPU time for a computation of the "advective easy test case" in 2D is shown. The used grid consists of 26,660 triangles. In this computation, 35% of the CPU time can be saved by using extrapolation. As proposed in [3], the CPU time is measured in normalized units. The CPU time unit is defined as the time needed to compute the product of two (1,000 × 1,000) real matrices.

The Darcy velocity, on which the transport operator $\mathscr{L}$ is based, is either computed by solving the Richards equation (using hybrid mixed finite elements) or it can be provided by the user as an input. Two types of hybrid mixed finite elements are available: lowest-order Raviart–Thomas (RT_0) and lowest-order Brezzi–Douglas–Marini (BDM_1).

The speed-up of the parallelization is quite good. In Table 2, the CPU time for a computation using one processor and a computation using eight processors is shown. The considered problem is the "advective easy test case" in 2D on a grid consisting of 26,660 triangles without extrapolation. In this performance test, the speed-up factor is 6.05.

Table 2 CPU time with different numbers of processors, advective easy test case in 2D without extrapolation

	CPU time	Time steps	Newton steps
1 proc.	8,918.8	17,100	2.88
8 proc.s	1,473.4	16,987	2.89

5 The benchmark problem "advective easy test case" in 1-D

For the problem formulation of the benchmark, see [5]. The 2-D code is used to emulate the 1-D problem by replacing the 1-D computational domain by a narrow 2-D computational domain.

We use a preadapted mesh with different step sizes on the two media: step size h_1 on medium A and step size h_2 on medium B with $h_2 < h_1$. This turns out to reduce the oscillations that would occur in the timeplot of concentration C_5 when a coarse uniform mesh was used. Computation tests (see Fig. 1) show that a sufficiently fine mesh on the subdomain B, but not on A, is essential to avoid oscillations. The green and the blue line in Fig. 1 are almost the same, although h_1 differs by a factor of 4. These oscillations were also observed by other groups when using coarse uniform meshes.

The species of the benchmark (see [5]) are ordered in the following way:

$$c = (C_1, \ldots, C_5, X_1, \ldots, X_4)^T, \qquad \bar{c} = (S, CS_1, CS_2)^T.$$

The stoichiometric submatrices and one possible choice for the orthogonal complement corresponding to mobile species are

$$S_{1,\mathrm{mob}} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 1 & 4 & -4 \\ 0 & -1 & 0 & -1 & -3 \\ 0 & 0 & -1 & -3 & -1 \end{pmatrix}, \quad S_{1,\mathrm{sorp}} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ -3 & 3 \\ -1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$S_1^{\perp} = \begin{pmatrix} \frac{1}{36} & 0 \\ \frac{2}{36} & 0 \\ -\frac{2}{36} & 0 \\ -\frac{2}{36} & 0 \\ \frac{2}{36} & 0 \\ 0 & 1 \\ -\frac{1}{36} & 0 \\ \frac{3}{36} & 0 \\ -\frac{3}{36} & 0 \end{pmatrix}$$

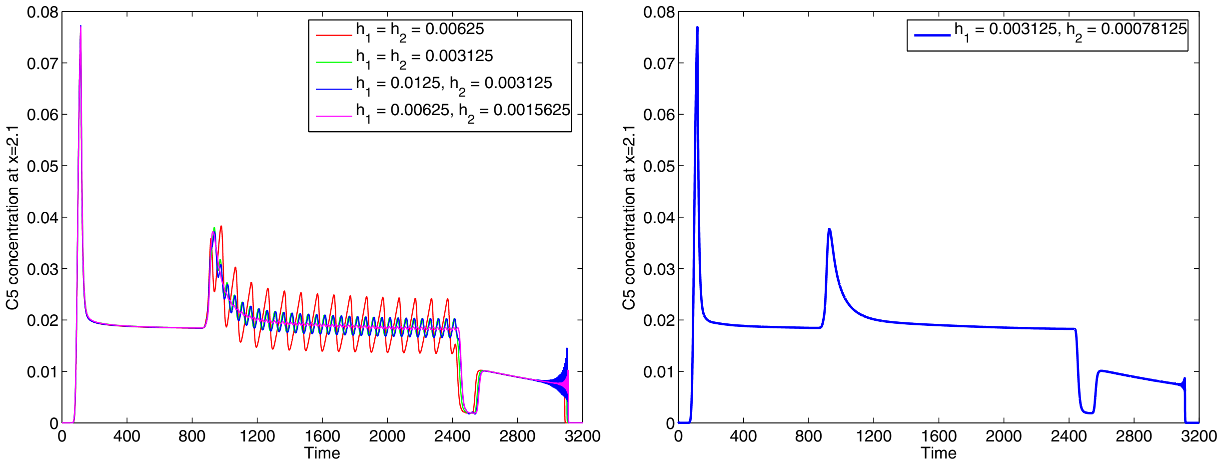


Fig. 1 Timeplots of C5 with different grids

and for the immobile ones

$$S_{2,\mathrm{sorp}} = \begin{pmatrix} -1 & -2 \\ 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad S_2^{\perp} = \frac{1}{6}\begin{pmatrix} 1 \\ 1 \\ 2 \end{pmatrix}.$$

The transformation matrices were chosen in the following way:

$$B_1 = \begin{pmatrix} 1&0&0&0&0&0&0 \\ 0&1&0&0&0&0&0 \\ 0&0&1&0&0&0&0 \\ 0&0&0&1&0&0&0 \\ 0&0&0&0&1&0&0 \\ 0&0&0&0&0&0&0 \\ 0&0&0&0&0&0&0 \\ 0&0&0&0&0&-1&0 \\ 0&0&0&0&0&0&-1 \end{pmatrix}, \quad B_1^{\perp} = \begin{pmatrix} 0&0 \\ 0&0 \\ 0&0 \\ 0&0 \\ 0&0 \\ 0&1 \\ 1&0 \\ 0&0 \\ 0&0 \end{pmatrix},$$

$$B_2 = \begin{pmatrix} 0&0 \\ 1&0 \\ 0&1 \end{pmatrix}, \quad B_2^{\perp} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.$$

With this choice of the transformation matrices B_1, B_2, our variables $\xi_i, \eta_i, \ldots$ have a close correspondence to the variables C_i, T_i, TS, and CS_i in the formulation of the benchmark. With help of the definitions Eqs. 15 and 18 one gets

$$\begin{aligned}
\xi_{\mathrm{mob},i} &= C_i \qquad (i = 1, \ldots .5) \\
\eta_1 &= -C_1 - 2C_2 + 2C_3 + 2C_4 - 2C_5 + X_2 \\
&\quad -3X_3 + 3X_4 \\
&= T_2 - 3T_3 + 3T_4 \\
\eta_2 &= X_1 = T_1 \\
\tilde{\xi}_{\mathrm{sorp},1} &= -C_2 - C_4 - 3C_5 - X_3 - CS_1 = -T_3 \\
\tilde{\xi}_{\mathrm{sorp},2} &= -C_3 - 3C_4 - C_5 - X_4 - CS_2 = -T_4 \\
\bar{\eta} &= S + CS_1 + 2CS_2 = TS \\
\bar{\xi}_{\mathrm{sorp},i} &= CS_i \qquad (i = 1, 2).
\end{aligned}$$

The η equations reach a steady-state at $t \approx 200$ and $t \approx 5{,}200$, respectively. So one advantage of the decoupling of η equations by the reduction scheme is that, for $200 < t < 3{,}200$ and $5{,}200 < t < 6{,}000$, two fewer equations (those for η_1, η_2) have to be solved.

We have carried out computations for the 1-D and the 2-D "advective easy test case," the 1-D "diffusive easy test case," all "medium test cases," and the 1-D and the 2-D "advective hard test case" of the MoMaS benchmark. The normalized CPU time, the number of time steps, the number of (global) Newton steps (per

Table 3 CPU time 1D

	Nodes in x-direction	Cells 2D-grid	CPU time	Time steps	Newton steps	Local Newton steps
Advective easy	777	4,638	1,484.9	10,683	2.80	2.18
Diffusive easy	673	2,688	3,398.6	8,235	3.57	2.45
Advective medium	389	2,334	179.9	2,361	2.39	2.31
Diffusive medium	337	1,344	187.5	1,674	2.13	2.16
Advective hard	777	4,638	4,102.2	31,091	1.60[a]	2.39

[a] For $2{,}566.6 \leq t \leq 5{,}000$ (12,167 time steps) only one Newton step is required

Table 4 CPU time 2D

	Cells	CPU time	Time steps	Newton steps	Local Newton steps
Advective easy	107,520	45,092.6	18,990	3.14	1.78
Advective medium	26,880	6,991.9	12,810	2.07	1.94
Diffusive medium	26,880	7,436.0	7,880	2.98	2.13
Advective hard	26,880	19,212.7	27,199	2.17	1.86

time step), and the number of local Newton steps (per global Newton step and per grid point) are shown in Tables 3 and 4. Detailed results can be found in [7]. For the "easy test case," a comparison of the results and the CPU time of all benchmark participants can be found in [4].

6 Extension to equilibrium minerals

The handling of equilibrium minerals is required for the hard test case of the MoMaS benchmark. Equilibrium conditions with minerals have to cover both the unsaturated case, where the mineral concentration $\bar{c}_{\text{min},i}$ is zero, and the saturated case, where the mineral is present and the solubility product is constant. Mathematically, the fact that the solubility product is constant is an AE condition. We will denote this condition with $F_i(c) = 0$. For example, for the mineral reaction C(s) ↔ A(aq) + 2B(aq), we have $F(c_A, c_B) = K - c_A c_B^2$. Classical strategies to handle this composite equilibrium condition are iterative/combinatorical strategies (see [2]) or formulations as moving boundary problems (see [12]).

We describe the unified equilibrium condition for a mineral by

$$(F_i(c) = 0 \text{ and } \bar{c}_{\text{min},i} \geq 0) \text{ or } (F_i(c) \geq 0 \text{ and } \bar{c}_{\text{min},i} = 0),$$

which can be expressed by the equivalent *complementary condition*

$$F_i(c) \cdot \bar{c}_{\text{min},i} = 0 \text{ and } F_i(c) \geq 0 \text{ and } \bar{c}_{\text{min},i} \geq 0$$

(see [9] or [14, p. 85f]). It is well known in the field of optimization theory that such a complementary condition can be substituted by the equivalent equation

$$\varphi(F_i(c), \bar{c}_{\text{min},i}) = 0,$$

where $\varphi : \mathbb{R}^2 \to \mathbb{R}$ is a function with the property

$$\varphi(a, b) = 0 \Leftrightarrow (ab = 0 \wedge a \geq 0 \wedge b \geq 0)$$

(see, e.g., [8]). We implemented the choice

$$\varphi(a, b) := \min\{a, b\},$$

i.e., the equilibrium conditions with minerals read

$$\min\{F_i(c), \bar{c}_{\text{min},i}\} = 0\,.$$

Since the regularity of φ does not meet the usual assumptions of the classical Newton's method (φ only belongs to the class of strongly semismooth functions), the resulting system is solved using the semismooth Newton method (see [8]).

Now we want to apply the reduction scheme of Section 2 to the problem. We assume that the stoichiometric matrix S has the structure

$$S = \left(\begin{array}{c|c} S_{1,\text{eq}} & S_{1,\text{kin}} \\ \hline S_{2,\text{eq}} & S_{2,\text{kin}} \end{array}\right) = \left(\begin{array}{c|c|c||c} S_{1,\text{mob}} & S_{1,\text{sorp}} & S_{1,\text{min}} & S_{1,\text{kin}} \\ \hline\hline 0 & S_{2,\text{sorp}} & 0 & \tilde{S}_{2,\text{kin}} \\ \hline 0 & 0 & Id_{J_{\text{min}}} & 0 \end{array}\right).$$

The species (=rows) are ordered by mobile species c, immobile nonminerals $\bar{c}_{\text{nmin}}$ and immobile minerals $\bar{c}_{\text{min}}$. In the hard test case, some columns of $(S_{1,\text{sorp}}|S_{1,\text{min}})$ are linear dependent and so the matrix $S_1^T S_1$ is not invertible. Hence, some additional steps are necessary. We assume that we can write $S_{1,\text{sorp}}$ as

$$S_{1,\text{sorp}} = (S_{1,\text{sorp},li}|S_{1,\text{min}} A_{ld}) \tag{22}$$

with the columns of $(S_{1,\text{mob}}|S_{1,\text{sorp},li}|S_{1,\text{min}})$ linear independent, which is indeed the case for the hard test case of the benchmark. Then, we define the matrix S_1^* as

$$S_1^* := (S_{1,\text{mob}}|S_{1,\text{sorp},li}|S_{1,\text{min}}|S_{1,\text{kin}}^*).$$

Now we can apply the reduction scheme. Mainly, the same steps as in Section 2 have to be done. This leads to

$$\begin{aligned}
&\partial_t \eta + \mathscr{L}\eta &&= 0 \\
&\partial_t \bar{\eta} &&= 0 \\
&\partial_t(\xi_{\text{sorp}} - \bar{\xi}_{\text{sorp},li}) + \mathscr{L}\xi_{\text{sorp}} &&= g_1(\eta, \bar{\eta}, \xi, \bar{\xi}) \\
&\partial_t(\xi_{\text{min}} - \bar{\xi}_{\text{min}} - A_{ld}\bar{\xi}_{\text{sorp},ld}) + \mathscr{L}\xi_{\text{min}} &&= g_2(\eta, \bar{\eta}, \xi, \bar{\xi}) \\
&\partial_t \xi_{\text{kin}} + \mathscr{L}\xi_{\text{kin}} &&= g_3(\eta, \bar{\eta}, \xi, \bar{\xi}) \\
&\partial_t \bar{\xi}_{\text{kin}} &&= g_4(\eta, \bar{\eta}, \xi, \bar{\xi}) \\
&Q(\eta, \bar{\eta}, \xi, \bar{\xi}_{\text{nmin}}) &&= 0 \\
&\min\{\bar{\xi}_{\text{min},i}, F_i(\eta, \xi)\} &&= 0\,.
\end{aligned}$$

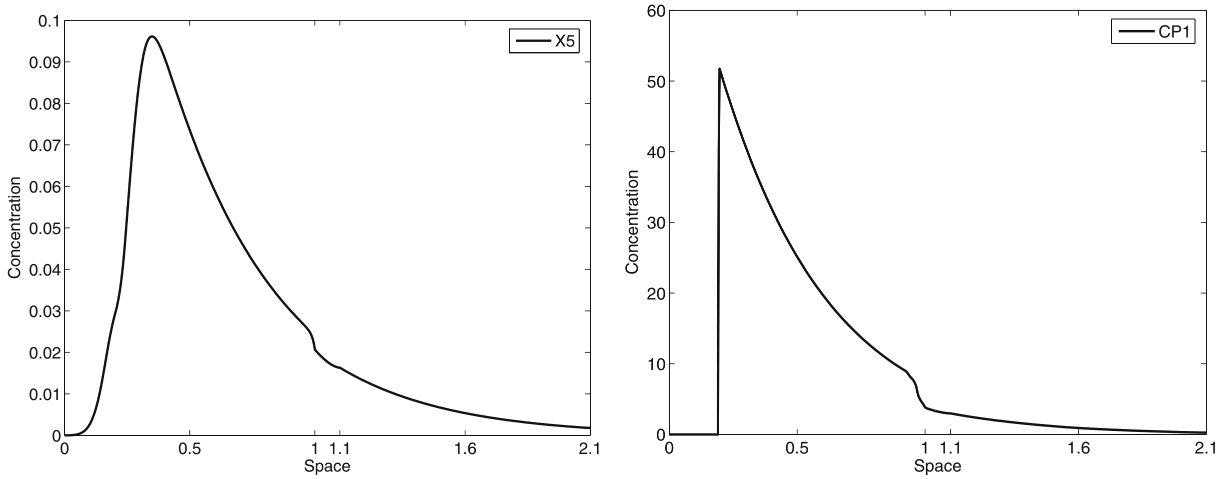


Fig. 2 Concentration profile at $t = 5010$ for $X5$ (*left*) and for the mineral CP1 (*right*) in 1D

In this case, the vector ξ is split in $(\xi_{\mathrm{mob}}, \xi_{\mathrm{sorp}}, \xi_{\mathrm{min}}, \xi_{\mathrm{kin}})$ and the vector $\bar{\xi}$ is split in $(\bar{\xi}_{\mathrm{sorp}}, \bar{\xi}_{\mathrm{min}}, \bar{\xi}_{\mathrm{kin}})$. Additionally, the vector $\bar{\xi}_{\mathrm{sorp}}$ is partitioned in $(\bar{\xi}_{\mathrm{sorp},li}, \bar{\xi}_{\mathrm{sorp},ld})$ analogously to the partitioning of $S_{1,\mathrm{sorp}}$ in Eq. 22.

Analogous to Section 3, we define the additional variables

$$\begin{aligned}
\tilde{\bar{\xi}}_{\mathrm{sorp}} &:= \xi_{\mathrm{sorp}} - \bar{\xi}_{\mathrm{sorp},li} \\
\tilde{\bar{\xi}}_{\mathrm{min}} &:= \xi_{\mathrm{min}} - \bar{\xi}_{\mathrm{min}} - A_{ld}\bar{\xi}_{\mathrm{sorp},ld} \,.
\end{aligned}$$

Here, we get the retransformation

$$\begin{aligned}
c \; &= S_{1,\mathrm{mob}}\xi_{\mathrm{mob}} + S_{1,\mathrm{sorp},li}\tilde{\bar{\xi}}_{\mathrm{sorp}} + S_{1,\mathrm{sorp}}\bar{\xi}_{\mathrm{sorp}} \\
&\quad + S_{1,\mathrm{min}}(\tilde{\bar{\xi}}_{\mathrm{min}} + \bar{\xi}_{\mathrm{min}}) + S^{*}_{1,\mathrm{kin}}\xi_{\mathrm{kin}} + B_1^{\perp}\eta \\
\bar{c}_{\mathrm{nmin}} &= S_{2,\mathrm{sorp}}\bar{\xi}_{\mathrm{sorp}} + \tilde{S}_{2,\mathrm{kin}}\bar{\xi}_{\mathrm{kin}} + \tilde{B}_2^{\perp}\bar{\eta} \\
\bar{c}_{\mathrm{min}} &= \bar{\xi}_{\mathrm{min}} \,.
\end{aligned}$$

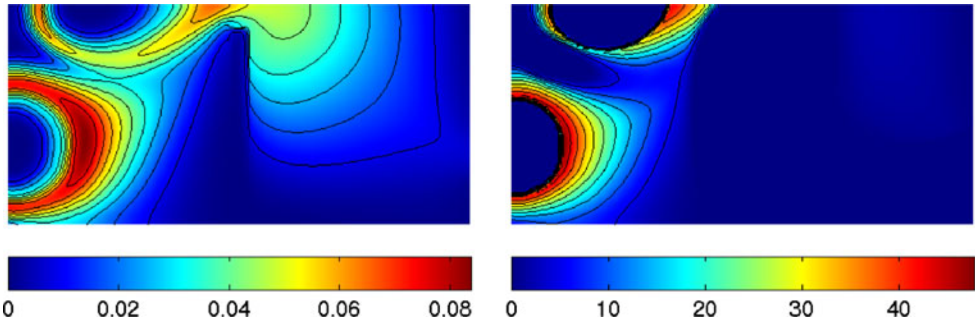
Here, the secondary variables are $\xi_{\mathrm{sec}} := (\xi_{\mathrm{mob}}, \bar{\xi}_{\mathrm{sorp}}, \bar{\xi}_{\mathrm{min}}, \bar{\xi}_{\mathrm{kin}})$. There exists a resolution function for this secondary variable ξ_{sec} as a function of $(\tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}})$. Plugging this resolution function in the nonlinear system leads to the smaller system

$$\begin{aligned}
&\tilde{\bar{\xi}}_{\mathrm{sorp}} = \xi_{\mathrm{sorp}} - \bar{\xi}_{\mathrm{sorp},li}(\tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}}) \\
&\tilde{\bar{\xi}}_{\mathrm{min}} = \xi_{\mathrm{min}} - \bar{\xi}_{\mathrm{min}}(\tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}}) \\
&\qquad\quad - A_{ld}\bar{\xi}_{\mathrm{sorp},ld}(\tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}}) \\
&\partial_t\tilde{\bar{\xi}}_{\mathrm{sorp}} + \mathscr{L}\xi_{\mathrm{sorp}} \\
&\quad = g_1(\eta, \bar{\eta}, \tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}}, \xi_{\mathrm{sec}}(\tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}})) \\
&\partial_t\tilde{\bar{\xi}}_{\mathrm{min}} + \mathscr{L}\xi_{\mathrm{min}} \\
&\quad = g_2(\eta, \bar{\eta}, \tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}}, \xi_{\mathrm{sec}}(\tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}})) \\
&\partial_t\xi_{\mathrm{kin}} + \mathscr{L}\xi_{\mathrm{kin}} \\
&\quad = g_3(\eta, \bar{\eta}, \tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}}, \xi_{\mathrm{sec}}(\tilde{\bar{\xi}}_{\mathrm{sorp}}, \tilde{\bar{\xi}}_{\mathrm{min}}, \xi_{\mathrm{kin}})) \,.
\end{aligned}$$

To evaluate the resolution function, we have to solve the local problem

$$\begin{aligned}
\partial_t\bar{\xi}_{\mathrm{kin}} &= g_4(\eta, \bar{\eta}, \xi, \bar{\xi}) \\
Q(\eta, \bar{\eta}, \xi, \bar{\xi}_{\mathrm{nmin}}) &= 0 \\
\min\{\bar{\xi}_{\mathrm{min},i}, F_i(\eta, \xi)\} &= 0 \,.
\end{aligned}$$

Fig. 3 Concentration profile at $t = 5010$ for $X5$ (*left*) and for the mineral CP1 (*right*) in 2D



According to Section 3, we use the logarithms of the nonmineral concentrations

$$l := \ln(c), \qquad \bar{l}_{\mathrm{nmin}} := \ln(\bar{c}_{\mathrm{nmin}}),$$

$\bar{c}_{\mathrm{min}}$ and $\bar{\xi}_{\mathrm{kin}}$ as unknowns and add the definition equations of the transformed variables $\eta, \tilde{\xi}_{\mathrm{sorp}}, \tilde{\xi}_{\mathrm{min}}, \xi_{\mathrm{kin}}, \bar{\eta}, \bar{\xi}_{\mathrm{kin}}$ as additional equations. Altogether, in the local problem, we have to solve the nonlinear system[3]

$$\begin{aligned}
\partial_t \bar{\xi}_{\mathrm{kin}} &= g_4(\exp(l), \exp(\bar{l}_{\mathrm{nmin}}), \bar{c}_{\mathrm{min}}) \\
Q(l, \bar{l}_{\mathrm{nmin}}) &= 0 \\
\min\{\bar{\xi}_{\mathrm{min},i}, F_i(l)\} &= 0 \\
\eta &= \left((S_1^{\perp})^T B_1^{\perp}\right)^{-1} (S_1^{\perp})^T \exp(l) \\
\tilde{\xi}_{\mathrm{sorp}} &= \left((B_1^T S_1^*)^{-1} B_1^T \exp(l)\right)_2 \\
&\quad -\left((B_2^T S_2^*)^{-1} B_2^T (\exp(\bar{l}_{\mathrm{nmin}}), \bar{c}_{\mathrm{min}})^T\right)_1 \\
\tilde{\xi}_{\mathrm{min}} &= \left((B_1^T S_1^*)^{-1} B_1^T \exp(l)\right)_3 - \bar{c}_{\mathrm{min}} \\
&\quad -A_{ld}\left((B_2^T S_2^*)^{-1} B_2^T (\exp(\bar{l}_{\mathrm{nmin}}), \bar{c}_{\mathrm{min}})^T\right)_2 \\
\xi_{\mathrm{kin}} &= \left((B_1^T S_1^*)^{-1} B_1^T \exp(l)\right)_4 \\
\bar{\eta} &= \left((S_2^{\perp})^T B_2^{\perp}\right)^{-1} (S_2^{\perp})^T (\exp(\bar{l}_{\mathrm{nmin}}), \bar{c}_{\mathrm{min}})^T \\
\bar{\xi}_{\mathrm{kin}} &= \left((B_2^T S_2^*)^{-1} B_2^T (\exp(\bar{l}_{\mathrm{nmin}}), \bar{c}_{\mathrm{min}})^T\right)_4
\end{aligned}$$

with the unknowns $(l, \bar{l}_{\mathrm{nmin}}, \bar{c}_{\mathrm{min}}, \bar{\xi}_{\mathrm{kin}})$. Numerical results for the "hard advective test case" in 1D and 2D are shown in Figs. 2 and 3.

Appendix

In this example, we consider three mobile species denoted with A, B, and C and two immobile species denoted with $\overline{D}$, $\overline{E}$. Hence, the concentration vector for the mobile species is $c = (c_A, c_B, c_C)^T$ and the one for the immobile species is $\bar{c} = (c_{\overline{D}}, c_{\overline{E}})^T$. We consider two equilibrium reactions:

$$\begin{aligned}
A + C &\longleftrightarrow B \\
3A + \overline{E} &\longleftrightarrow B + 2\overline{D}\,.
\end{aligned}$$

Hence, the stoichiometric matrix is

$$S = \left(\begin{array}{cc} -1 & -3 \\ 1 & 1 \\ -1 & 0 \\ \hline 0 & 2 \\ 0 & -1 \end{array}\right).$$

As there are no kinetic reactions in this example, the variables $\xi_{\mathrm{kin}}, \bar{\xi}_{\mathrm{kin}}$ and the equations for this variable do not appear in the following.

For this example, the transformation matrices mentioned in Section 2 can be chosen in the following way:

$$S_1^* = \begin{pmatrix} -1 & -3 \\ 1 & 1 \\ -1 & 0 \end{pmatrix}, \quad S_1^{\perp} = \begin{pmatrix} 1 \\ 3 \\ 2 \end{pmatrix}, \quad B_1 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \\ 1 & 0 \end{pmatrix},$$

$$B_1^{\perp} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix},$$

$$S_2^* = \begin{pmatrix} 2 \\ -1 \end{pmatrix}, \quad S_2^{\perp} = \begin{pmatrix} 1 \\ 2 \end{pmatrix}, \quad B_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

$$B_2^{\perp} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

According to the definitions of the new variables (Eqs. 15 and 18), the unknowns used in the reduction scheme are

$$\begin{aligned}
\eta &= \left((S_1^{\perp})^T B_1^{\perp}\right)^{-1} (S_1^{\perp})^T c = \begin{pmatrix} 1 & 3 & 2 \end{pmatrix} c \\
&= c_A + 3c_B + 2c_C \\
\begin{pmatrix} \xi_{\mathrm{mob}} \\ \xi_{\mathrm{sorp}} \end{pmatrix} &= (B_1^T S_1^*)^{-1} B_1^T c = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 1 \end{pmatrix} c = \begin{pmatrix} -c_C \\ c_B + c_C \end{pmatrix} \\
\bar{\eta} &= \left((S_2^{\perp})^T B_2^{\perp}\right)^{-1} (S_2^{\perp})^T \bar{c} = \begin{pmatrix} 1 & 2 \end{pmatrix} \bar{c} = c_{\overline{D}} + 2c_{\overline{E}} \\
\bar{\xi}_{\mathrm{sorp}} &= (B_2^T S_2^*)^{-1} B_2^T \bar{c} = (0\ -1)\bar{c} = -c_{\overline{E}} \\
\tilde{\xi}_{\mathrm{sorp}} &= \xi_{\mathrm{sorp}} - \bar{\xi}_{\mathrm{sorp}} = c_B + c_C + c_{\overline{E}}\,.
\end{aligned}$$

For this example, the retransformation (Eq. 19) reads

$$\begin{aligned}
c_A &= -\xi_{\mathrm{mob}} - 3\tilde{\xi}_{\mathrm{sorp}} + \eta - 3\bar{\xi}_{\mathrm{sorp}} \\
c_B &= \xi_{\mathrm{mob}} + \tilde{\xi}_{\mathrm{sorp}} + \bar{\xi}_{\mathrm{sorp}} \\
c_C &= -\xi_{\mathrm{mob}} \\
c_{\overline{D}} &= 2\bar{\xi}_{\mathrm{sorp}} + \bar{\eta} \\
c_{\overline{E}} &= -\bar{\xi}_{\mathrm{sorp}}
\end{aligned}$$

---

[3] Because of the special structure of S_2^*, the transformed variables $\bar{\eta}$, $\bar{\xi}_{\mathrm{kin}}$ and the last summands in the equations for $\tilde{\xi}_{\mathrm{sorp}}$ and $\tilde{\xi}_{\mathrm{min}}$ do not depend on $\bar{c}_{\mathrm{min}}$.

For the considered chemical reactions the original system of Eqs. 1–3 is

$$\begin{array}{lll}
(I) & \partial_t c_A + \mathscr{L} c_A & = -R_{\mathrm{eq},1} - 3R_{\mathrm{eq},2} \\
(II) & \partial_t c_B + \mathscr{L} c_B & = R_{\mathrm{eq},1} + R_{\mathrm{eq},2} \\
(III) & \partial_t c_C + \mathscr{L} c_C & = -R_{\mathrm{eq},1} \\
(IV) & \partial_t c_{\overline{D}} & = 2R_{\mathrm{eq},2} \\
(V) & \partial_t c_{\overline{E}} & = -R_{\mathrm{eq},2}
\end{array}$$

$$\begin{aligned}
-\ln(c_A) + \ln(c_B) - \ln(c_C) + k_{\mathrm{mob}} &= 0 \\
-3\ln(c_A) + \ln(c_B) + 2\ln(c_{\overline{D}}) - \ln(c_{\overline{E}}) + k_{\mathrm{sorp}} &= 0\,.
\end{aligned}$$

Multiplication of the PDE block by $\left((S_1^\perp)^T B_1^\perp\right)^{-1}(S_1^\perp)^T$ and by $(B_1^T S_1^*)^{-1} B_1^T$, and multiplication of the ODE block by $\left((S_2^\perp)^T B_2^\perp\right)^{-1}(S_2^\perp)^T$ and by $(B_2^T S_2^*)^{-1} B_2^T$, gives

$$\begin{array}{lll}
(I)+3(II)+2(III): & \partial_t(c_A+3c_B+2c_C)+\mathscr{L}(c_A+3c_B+2c_C) & = 0 \\
-(III): & \partial_t(-c_C)+\mathscr{L}(-c_C) & = R_{\mathrm{eq},1} \\
(II)+(III): & \partial_t(c_B+c_C)+\mathscr{L}(c_B+c_C) & = R_{\mathrm{eq},2} \\
(IV)+2(V): & \partial_t(c_{\overline{D}}+2c_{\overline{E}}) & = 0 \\
-(V): & \partial_t(-c_{\overline{E}}) & = R_{\mathrm{eq},2}
\end{array}$$

$$\begin{aligned}
-\ln(c_A) + \ln(c_B) - \ln(c_C) + k_{\mathrm{mob}} &= 0 \\
-3\ln(c_A) + \ln(c_B) + 2\ln(c_{\overline{D}}) - \ln(c_{\overline{E}}) + k_{\mathrm{sorp}} &= 0\,.
\end{aligned}$$

Writing this system of equations in the new variables gives

$$\begin{aligned}
\partial_t\eta + \mathscr{L}\eta &= 0 \\
\partial_t\xi_{\mathrm{mob}} + \mathscr{L}\xi_{\mathrm{mob}} &= R_{\mathrm{eq},1} \\
\partial_t\xi_{\mathrm{sorp}} + \mathscr{L}\xi_{\mathrm{sorp}} &= \partial_t\bar{\xi}_{\mathrm{sorp}} \\
\partial_t\bar{\eta} &= 0 \\
\partial_t\bar{\xi}_{\mathrm{sorp}} &= R_{\mathrm{eq},2}
\end{aligned}$$

$$\begin{aligned}
-\ln(-\xi_{\mathrm{mob}} - 3\tilde{\xi}_{\mathrm{sorp}} + \eta - 3\bar{\xi}_{\mathrm{sorp}}) + \ln(\xi_{\mathrm{mob}} + \tilde{\xi}_{\mathrm{sorp}} + \bar{\xi}_{\mathrm{sorp}}) - \ln(-\xi_{\mathrm{mob}}) + k_{\mathrm{mob}} &= 0 \\
-3\ln(-\xi_{\mathrm{mob}} - 3\tilde{\xi}_{\mathrm{sorp}} + \eta - 3\bar{\xi}_{\mathrm{sorp}}) + \ln(\xi_{\mathrm{mob}} + \tilde{\xi}_{\mathrm{sorp}} + \bar{\xi}_{\mathrm{sorp}}) & \\
+ 2\ln(2\bar{\xi}_{\mathrm{sorp}} + \bar{\eta}) - \ln(-\bar{\xi}_{\mathrm{sorp}}) + k_{\mathrm{sorp}} &= 0\,.
\end{aligned}$$

The rates $R_{\mathrm{eq},1}$, $R_{\mathrm{eq},2}$ appear only once in the system. So these two equations can be left out. The equation for η and that for $\bar{\eta}$ decouple and can be solved independently of the rest of the system. According to Section 2, there is a resolution function $(\xi_{\mathrm{mob}}, \bar{\xi}_{\mathrm{sorp}})(\tilde{\xi}_{\mathrm{sorp}})$, which resolves the two equilibrium conditions. Using this and the definition of the variable $\tilde{\xi}_{\mathrm{sorp}}$, one gets the nonlinear system of equations used in the reduction scheme (compare Eq. 20)

$$\begin{aligned}
\partial_t\tilde{\xi}_{\mathrm{sorp}} + \mathscr{L}\xi_{\mathrm{sorp}} &= 0 \\
\tilde{\xi}_{\mathrm{sorp}} &= \xi_{\mathrm{sorp}} - \bar{\xi}_{\mathrm{sorp}}(\tilde{\xi}_{\mathrm{sorp}}),
\end{aligned}$$

with $\bar{\xi}_{\mathrm{sorp}}(\tilde{\xi}_{\mathrm{sorp}})$ the solution of

$$\begin{aligned}
-\ln(-\xi_{\mathrm{mob}} - 3\tilde{\xi}_{\mathrm{sorp}} + \eta - 3\bar{\xi}_{\mathrm{sorp}}) + \ln(\xi_{\mathrm{mob}} + \tilde{\xi}_{\mathrm{sorp}} + \bar{\xi}_{\mathrm{sorp}}) - \ln(-\xi_{\mathrm{mob}}) + k_{\mathrm{mob}} &= 0 \\
-3\ln(-\xi_{\mathrm{mob}} - 3\tilde{\xi}_{\mathrm{sorp}} + \eta - 3\bar{\xi}_{\mathrm{sorp}}) + \ln(\xi_{\mathrm{mob}} + \tilde{\xi}_{\mathrm{sorp}} + \bar{\xi}_{\mathrm{sorp}}) & \\
+ 2\ln(2\bar{\xi}_{\mathrm{sorp}} + \bar{\eta}) - \ln(-\bar{\xi}_{\mathrm{sorp}}) + k_{\mathrm{sorp}} &= 0\,.
\end{aligned}$$

That is equivalent to $\bar{\xi}_{\text{sorp}}(\tilde{\xi}_{\text{sorp}}) = -\exp(l_{\overline{E}})$ where $(l_A, l_B, l_C, l_{\overline{D}}, l_{\overline{E}})$ is the solution of (compare Eq. 21)

$$\begin{aligned}
-l_A + l_B - l_C + k_{\text{mob}} &= 0\\
-3l_A + l_B + 2l_{\overline{D}} - l_{\overline{E}} + k_{\text{sorp}} &= 0\\
\eta &= \exp(l_A) + 3\exp(l_B)\\
&\quad +2\exp(l_C)\\
\tilde{\xi}_{\text{sorp}} &= \exp(l_B) + \exp(l_C)\\
&\quad +\exp(l_{\overline{E}})\\
\bar{\eta} &= \exp(l_{\overline{D}}) + 2\exp(l_{\overline{E}})\,.
\end{aligned}$$

One can resolve the equilibrium conditions for l_C, $l_{\overline{E}}$ and plug this in the other equations. Then we have $\bar{\xi}_{\text{sorp}}(\tilde{\xi}_{\text{sorp}}) = -\exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})$ where $(l_A, l_B, l_{\overline{D}})$ is the solution of

$$\begin{aligned}
\eta &= \exp(l_A) + 3\exp(l_B) + 2\exp(-l_A + l_B + k_{\text{mob}})\\
\tilde{\xi}_{\text{sorp}} &= \exp(l_B) + \exp(-l_A + l_B + k_{\text{mob}})\\
&\quad +\exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})\\
\bar{\eta} &= \exp(l_{\overline{D}}) + 2\exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})\,.
\end{aligned}$$

In the Morel tableau the variables

$$\begin{aligned}
T_1 &= c_A - c_C - 3c_{\overline{E}}\\
T_2 &= c_B + c_C + c_{\overline{E}}\\
T_S &= c_{\overline{D}} + 2c_{\overline{E}}\\
T_{M,1} &= c_A - c_C\\
T_{M,2} &= c_B + c_C\\
T_{F,1} &= -3c_{\overline{E}}\\
T_{F,2} &= c_{\overline{E}}
\end{aligned}$$

are used (see Section 2). Using the Morel tableau, two different formulations are possible. The TC formulation for this example is

$$\begin{aligned}
\partial_t T_1 + \mathscr{L} T_{M,1} &= 0\\
\partial_t T_2 + \mathscr{L} T_{M,2} &= 0\\
\partial_t T_S &= 0\\
T_{M,1} &= \exp(l_A) - \exp(-l_A + l_B + k_{\text{mob}})\\
T_{M,2} &= \exp(l_B) + \exp(-l_A + l_B + k_{\text{mob}})\\
T_1 &= \exp(l_A) - \exp(-l_A + l_B + k_{\text{mob}})\\
&\quad -3\exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})\\
T_2 &= \exp(l_B) + \exp(-l_A + l_B + k_{\text{mob}})\\
&\quad +\exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})\\
T_S &= \exp(l_{\overline{D}}) + 2\exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})
\end{aligned}$$

and the CC formulation for this example is

$$\begin{aligned}
\partial_t T_{M,1} + \partial_t T_{F,1} + \mathscr{L} T_{M,1} &= 0\\
\partial_t T_{M,2} + \partial_t T_{F,2} + \mathscr{L} T_{M,2} &= 0\\
\partial_t T_S &= 0\\
T_{F,1} &= -3\exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})\\
T_{F,2} &= \exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})\\
T_{M,1} + T_{F,1} &= \exp(l_A) - \exp(-l_A + l_B + k_{\text{mob}}) - 3\exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})\\
T_{M,2} + T_{F,2} &= \exp(l_B) + \exp(-l_A + l_B + k_{\text{mob}}) + \exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})\\
T_S &= \exp(l_{\overline{D}}) + 2\exp(-3l_A + l_B + 2l_{\overline{D}} + k_{\text{sorp}})\,.
\end{aligned}$$

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