The semismooth Newton method for multicomponent reactive transport with minerals

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Abstract

In this article a method is proposed for the efficient simulation of reactive systems or reactive transport problems including (equilibrium) mineral precipitation-dissolution. The difficulty lies in the fact that for larger systems it is usually a priorily not known for which mineral the fluid is saturated and for which it is undersaturated. Currently wide-spread algorithms use some trial-and-error strategy requiring repeated computations, or an approximation of equilibrium precipitation-dissolution by a kinetic description. In this article we propose to formulate the problem as a so-called complementarity problem (CP) and to solve it with the semismooth Newton method, a solution strategy well known in the field of optimization theory. The CP formulation of the mineral reactions is then combined with a reformulation for the full multicomponent reactive transport problem which leads to a reduction of the number of unknowns. The reactive transport problem is tackled in the sense of a one step (global implicit) method.

Keywords: reactive transport, minerals, complementarity problems, semismooth Newton method

1. Introduction

In reactive system where equilibrium precipitation-dissolution reactions are present, often the following difficulty occurs: It is in general not a priori

clear which of the minerals are present in the system and which minerals are completely dissolved. The presence of a mineral means that the fluid is saturated with respect to the corresponding precipitation-dissolution reaction, and if the fluid is undersaturated, then the corresponding mineral is fully dissolved.

In cases where there is some a priori knowledge that all minerals are present, the equilibrium condition can simply be expressed as a system of (nonlinear) algebraic equations which may be solved (together with mass balance equations) by some standard Newton method. However, in practice this knowledge is not available, and standard algorithms try to determine the correct mineral assemblage by some kind of 'trial and error' strategy. In the literature (see Sec. 2.2) the most common approach is to make an assumption as to which of the minerals are present and which are fully dissolved, then compute if the resulting algebraic system has a physically meaningful solution. If not, then the assumption is modified with respect to some heuristic rule, and the procedure with modified assumption is repeated until a physical solution is obtained.

In this article we present the mineral equilibrium conditions as a so-called complementarity condition (CC) which unifies both cases of presence and of full dissolution of a mineral. The benefit of this formulation is that problems containing CCs (so-called complementarity problems, CPs) are well known in the field of optimization theory. In this field, it is a well known strategy to solve CPs with the semismooth Newton method. The intention of this article is the application of this theory and this modern algorithm to the mineral problem. The advantage of this procedure is a reduction in computation time by replacing a sequence of nested Newton iteration by just one level of iterations. When one considers batch problems (closed systems), the question of efficiency of the numerical solution might be not so prominent. However, as soon as we want to solve reactive transport problems (in 2-D or 3-D) with many species, the question of computational efficiency becomes essential.

The article is structured as follows. In Sec. 2.1 we introduce the mineral precipitation-dissolution problem in the setting of a batch problem. We discuss the available solution techniques and we introduce the complementarity formulation and the semismooth Newton algorithm.

In Sec. 3 we couple the reaction system with transport (linear dispersion and advection), and we also generalize our reaction system so that it may contain other equilibrium reactions (aqueous reactions, sorption reactions) or kinetic reactions. The reactive transport system consists of partial and of

ordinary differential equations (PDEs, ODEs) coupled to algebraic equations and CCs. We demonstrate how to eliminate the equilibrium reaction rates from the CP formulation of the problem.

In Sec. 4 we reformulate the system arising from the CP formulation of Sec. 3 using a method described in [17, 18] in order to obtain a stronger reduction of the number of unknowns and equations, compared to the technique of Sec. 3. Some results on the regularity of the system matrix are derived in Sec. 4.3, 4.4, and Appendix A.

Finally, in Sec. 5 we give some numerical results.

2. The mineral problem in a batch situation: The semismooth Newton method and other solution strategies

In this section we want to introduce our algorithm in the context of a reduced complexity situation. In Sec. 2.1 we give the governing equations and in Sec. 2.2 we discuss some solution strategies, including the semismooth Newton method.

2.1. The governing equations

We consider a closed system of $\bar{I}$ minerals $\bar{X}_i$ with concentration vector $\bar{c} = (\bar{c}_1, ..., \bar{c}_{\bar{I}})$ and I aqueous species X_i with concentration vector $c = (c_1, ..., c_I)$, and we assume that all reactions are mineral precipitation-dissolution reactions which are at equilibrium, one for each mineral:

$$\sum_{i=1}^{I} s_{ij} X_i \longleftrightarrow \bar{X}_j, \qquad j = 1, ..., \bar{I},$$
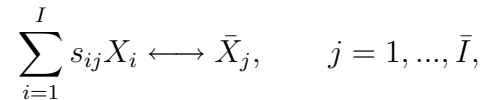
which corresponds to a stoichiometric matrix $S \in \mathbb{R}^{(I+\bar{I}) \times \bar{I}}$,

$$S = \left(\frac{S_1}{-\mathrm{Id}} \right)$$

with Id being a $\bar{I} \times \bar{I}$ identity matrix and $S_1 = (s_{ij})$. The total concentration (cf. [25]), which reads

$$\mathrm{T} = c + S_1 \bar{c} \tag{1}$$

for this shape of matrix S, is usually given.

If it is known that no complete dissolution of minerals takes place, then the equilibrium conditions can be expressed by some algebraic equilibrium

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conditions. For the sake of simplicity we assume that the reactions follow the mass action law with ideal activities for the non-minerals and constant activities (set to unity without loss of generality) for the minerals. Then the equilibrium conditions read

$$\prod_{i=1}^{I} c_i^{s_{ij}} = K_j, \qquad j = 1, ..., \bar{I},$$

or, assuming that all non-mineral concentrations are positive,

$$\sum_{i=1}^{I} s_{ij} \ln c_i = \ln K_j, \qquad j = 1, ..., \bar{I}, \tag{2}$$

where $K_j > 0$ are the equilibrium constants (solubility products). In short,

$$E(c) := \ln K - S_1^T \ln c = 0,$$

where $K := (K_1, ..., K_{\bar{I}})^T$, and where the application of 'ln' is performed componentwise. This condition (2), expressing saturation of the fluid with respect to the corresponding reaction, has only to be fulfilled if the corresponding mineral is present, i.e., when $\bar{c}_j > 0$. In general we cannot exclude the possibility that the fluid is undersaturated and the mineral fully dissolved, i.e.,

$$E_j(c) = \ln K_j - \sum_{i=1}^{I} s_{ij} \ln c_i \geq 0 \quad \text{and} \quad \bar{c}_j = 0.$$

Note that oversaturation ($E_j(c) < 0$) is only possible in kinetic reaction models.

A general unified formulation for the saturated and the undersaturated situation can be expressed as

$$(E_j(c) = 0 \text{ and } \bar{c}_j \geq 0) \text{ or } (E_j(c) \geq 0 \text{ and } \bar{c}_j = 0), \quad j = 1, ..., \bar{I}. \tag{3}$$

An equation of this type, or more generally, of type

$$(f(x) = 0 \text{ and } x \geq 0) \quad \text{or} \quad (f(x) \geq 0 \text{ and } x = 0),$$

is called a complementarity condition [8]. We have to solve the CP consisting of (1) and (3).

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2.2. Motivation: The semismooth Newton method and other solution strategies

A well known solution strategy for problem (1), (3) which is proposed e.g. in [1, 27] and applied e.g. in [7], is to make an assumption as to which subset of minerals is present, and to solve only the corresponding equations from (3) together with (1) by a Newton iteration, then check if the solution is physical. If not (i.e., negative mineral concentrations or oversaturated fluid) then modify the assumption following certain heuristic rules and repeat the computation until a physical solution is obtained. The main disadvantage of this strategy is that instead of one Newton iteration several Newton iterations are required. In particular if we consider reactions coupled to transport using a global implicit approach (one-step method), then the whole computation of a time step has to be done again and again.

For the coupling of mineral reactions to transport, another approach is proposed in [19, 20]: Here the computational domain is divided into subdomains of saturation and of undersaturation with respect to each mineral, and it is proposed to solve the problem with a front tracking algorithm. This approach seems to work well in 1-D problems or in problems where the topology of the subdomain interfaces is known and does not change in time; for system with complex/changing topologies of the subdomains front tracking algorithms are known to be difficult to implement.

Another idea which is used in practice is to approximate the equilibrium conditions by kinetic descriptions of the reactions. However, if we do this using large reaction constants (to meet the fact that equilibrium reactions should be 'fast') we may increase the stiffness of the problem, and if we use moderate rate coefficients, we end up with a rather inaccurate approximation of our problem. Some discussion of this question may be found in [24, 2, 26].

This motivates a search for other approaches. In the field of optimization theory, CPs are often obtained in the form of the first order optimality conditions (Karush-Kuhn-Tucker-)conditions of constrained optimization problems. So in that field of mathematics, we can find well-established, efficient solution strategies, such as the following: The condition (3) is rewritten as

$$E_j(c)\,\bar{c}_j = 0 \quad \text{and} \quad E_j(c) \geq 0 \quad \text{and} \quad \bar{c}_j \geq 0, \quad j = 1, ..., \bar{I}. \qquad (4)$$

Having in mind that we want to apply some Newton-like strategy, it is desirable to eliminate the inequalities in (4). For this, a function $\varphi : \mathbb{R} \times \mathbb{R} \to \mathbb{R}$

with the property

$$\varphi(a, b) = 0 \quad \Leftrightarrow \quad ab = 0 \text{ and } a \geq 0 \text{ and } b \geq 0 \qquad (5)$$

has to be chosen. A function fulfilling (5) is called complementarity function or C-function in the literature. Examples for C-functions are the minimum function $\varphi_{MIN}(a, b) = \min\{a, b\}$ or the Fischer-Burmeister function $\varphi_{FB}(a, b) = a + b - \sqrt{a^2 + b^2}$. Introducing a C-function, condition (4) can be rewritten as

$$\varphi(E_j(c), \bar{c}_j) = 0, \qquad (6)$$

i.e., the inequalities are eliminated, and we can apply a Newton-like strategy to the system (1), (6). However, we have to note that the regularity of a C-function is not as high as it is classically assumed for Newton's method. In fact, the gradient of φ is not everywhere uniquely defined; for the choice $\varphi = \varphi_{MIN}$ we have a set-valued generalized gradient (called the B-subdifferential, see e.g. [8] or [9])

$$\nabla\varphi(a, b) = \begin{cases} \{(1, 0)^T\} & , \ a < b \\ \{(1, 0)^T, (0, 1)^T\} & , \ a = b \\ \{(0, 1)^T\} & , \ a > b \end{cases} \qquad (7)$$

The function φ belongs to the class of so-called strongly semismooth functions. The semismooth Newton method is the application of Newton's method to a semismooth function, where at each Newton step one abitrary element of the B-subdifferential is used instead of the classical Jacobian. It is known that strong semismoothness, together with invertibility of the B-subdifferential, is sufficient for local quadratic convergence. This means that there is a good theoretical justification if we solve the mineral problem with a semismooth algorithm for the CP. A proof of the invertibility of the B-subdifferential for our reactive transport problem is given in Sec. 4.5 and Appendix A. For the definition of (strong) semismoothness and the convergence result see [22, 8].

Let us mention that the semismooth Newton method is not the only technique for solving CPs [9]. In [23], an interior point method is applied to a mineral precipitation-dissolution problem. However, different from Sec. 3-5, a splitting technique is applied to the reactive transport problem in [23], i.e., local problems with CCs being not any more coupled to PDEs are to be solved.

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3. Extension to reactive transport

Of course the idea to express equilibrium conditions with minerals as a CC and to eliminate inequalities in the way of Sec. 2 can also be applied in more complicated settings. In this section we extend the model to transient reactive transport, and we also increase the complexity of the reactive network by allowing different types of reactions. Let us assume we have J_{kin} kinetic reactions and J_{eq} reactions in local equilibrium, i.e., a stoichiometric matrix $S = (S_{\text{eq}}|S_{\text{kin}}) = \left(\begin{array}{c|c} S_{\text{eq}}^1 & S_{\text{kin}}^1 \\ \hline S_{\text{eq}}^2 & S_{\text{kin}}^2 \end{array} \right) \in \mathbb{R}^{(I+\bar{I})\times(J_{\text{eq}}+J_{\text{kin}})}$. For the equilibrium reactions we assume that there are J_{mob} aqueous reactions, J_{sorp} heterogeneous (non-mineral) reactions and J_{min} reactions with minerals, $J_{\text{mob}} + J_{\text{sorp}} + J_{\text{min}} = J_{\text{eq}}$. More precisely, we assume that the stoichiometric matrix has the shape

$$S = \left(\begin{array}{c||c} S_{\text{eq}}^1 & S_{\text{kin}}^1 \\ \hline S_{\text{eq}}^2 & S_{\text{kin}}^2 \end{array} \right) = \left(\begin{array}{c|c|c||c} S_{\text{mob}}^1 & S_{\text{sorp}}^1 & S_{\text{min}}^1 & S_{\text{kin}}^1 \\ \hline 0 & S_{\text{sorp}}^2 & 0 & S_{\text{kin}}^{2,1} \\ \hline 0 & 0 & -\text{Id} & 0 \end{array} \right) \tag{8}$$

where the rows correspond to a sorting of the species starting with mobile ones $c \in \mathbb{R}^I$ (dissolved in the water), then immobile non-mineral (sorbed) species $\bar{c}_{\text{sorp}} \in \mathbb{R}^{\bar{I}_{\text{sorp}}}$ and finally (immobile) mineral species $\bar{c}_{\text{min}} \in \mathbb{R}^{\bar{I}_{\text{min}}}$, $\bar{I}_{\text{sorp}} + \bar{I}_{\text{min}} = \bar{I}$, $\bar{I}_{\text{min}} = J_{\text{min}}$, $\bar{c} = (\bar{c}_{\text{sorp}}, \bar{c}_{\text{min}})$.

For reactive transport problems in porous media with mobile and immobile species and kinetic and equilibrium reactions, the mass balance equations for the species read

$$\begin{pmatrix} \partial_t \theta c + Lc \\ \partial_t \bar{c} \end{pmatrix} = \theta SR = \theta(S_{\text{eq}}R_{\text{eq}} + S_{\text{kin}}R_{\text{kin}}) = \theta \begin{pmatrix} S_{\text{eq}}^1 R_{\text{eq}} + S_{\text{kin}}^1 R_{\text{kin}} \\ S_{\text{eq}}^2 R_{\text{eq}} + S_{\text{kin}}^2 R_{\text{kin}} \end{pmatrix} \tag{9}$$

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

Here L is a linear transport (advection-dispersion) operator with $Lc = (L_1 c_i, ..., L_I c_I)$ and $L_1 = ... = L_I$, $R_{\text{kin}} = R_{\text{kin}}(c, \bar{c})$ is a vector of kinetic rate laws, Q is a vector of J_{eq} equilibrium conditions, which read, if we assume mass action law,

$$Q(c, \bar{c}) = S_{\text{eq}}^{1\,T} \ln c + S_{\text{eq}}^{2\,T} \ln \bar{c} - \ln K_{\text{eq}},$$

and $R_{\text{eq}} \in \mathbb{R}^{J_{\text{eq}}}$ is the vector of equilibrium reactions rates. So (9) is a system of $I + \bar{I} + J_{\text{eq}}$ equations for the unknowns $c, \bar{c}, R_{\text{eq}}$. For the model

under consideration we obtain the mass balance equations

$$
\begin{aligned}
\partial_t \theta c + Lc &= \theta(S_{\text{eq}}^1 R_{\text{eq}} + S_{\text{kin}}^1 R_{\text{kin}}(c, \bar{c}_{\text{sorp}})) \\
&= \theta(S_{\text{mob}}^1 R_{\text{mob}} + S_{\text{sorp}}^1 R_{\text{sorp}} + S_{\text{min}}^1 R_{\text{min}} + S_{\text{kin}}^1 R_{\text{kin}}(c, \bar{c}_{\text{sorp}})) \\
\partial_t \bar{c}_{\text{sorp}} &= \theta(S_{\text{sorp}}^2 R_{\text{sorp}} + S_{\text{kin}}^{2,1} R_{\text{kin}}(c, \bar{c}_{\text{sorp}})) \\
\partial_t \bar{c}_{\text{min}} &= -\theta R_{\text{min}}
\end{aligned}
$$

(10)

where we have split $R_{\text{eq}} = (R_{\text{mob}}, R_{\text{sorp}}, R_{\text{min}})$. Splitting also Q into $Q = (Q_{\text{mob}}, Q_{\text{sorp}})$ and $K_{\text{eq}} = (K_{\text{mob}}, K_{\text{sorp}})$, the equations (10) have to be solved together with the equilibrium conditions

$$
\begin{aligned}
Q_{\text{mob}}(c) &:= S_{\text{mob}}^1{}^T \ln c - \ln K_{\text{mob}} = 0, \\
Q_{\text{sorp}}(c, \bar{c}_{\text{sorp}}) &:= S_{\text{sorp}}^1{}^T \ln c + S_{\text{sorp}}^2{}^T \ln \bar{c}_{\text{sorp}} - \ln K_{\text{sorp}} = 0, \\
\varphi(E(c), \bar{c}_{\text{min}}) &= 0, \quad \text{where } E(c) := \ln K_{\text{min}} - S_{\text{min}}^1{}^T \ln c,
\end{aligned}
$$

(11)

for the aqueous, the sorption, and the mineral reactions, having the equilibrium constants $(K_{\text{mob}}, K_{\text{sorp}}, K_{\text{min}}) \in \mathbb{R}_+^{J_{\text{mob}} + J_{\text{sorp}} + J_{\text{min}}}$. The unknowns are $c, \bar{c}_{\text{sorp}}, \bar{c}_{\text{min}}$ and $R_{\text{eq}} = (R_{\text{mob}}, R_{\text{sorp}}, R_{\text{min}})$. Note that we have already replaced the equilibrium condition of type (3) by the equivalent formulation of type (6). Also note that we have again, just for the sake of simplicity, assumed ideal activities for the mobile and the sorbed species.

Some Newton-like strategy might be directly applied to the system (10)-(11). However, it is common practice to transform the system by eliminating the R_{eq}. There are many different strategies; however, the standard strategy is to find $I + \bar{I} - J_{\text{eq}}$ many linear combinations of the equations of (10) which are void of R_{eq}, see, e.g., [10, 25, 28, 21]. The size of the resulting system then usually is $I + \bar{I}$. We show in the following that this problem size reduction can also be applied when the systems contains CCs. By taking linear combinations of columns of the given S_{eq} and possibly by changing the order of the species within their blocks we can assume without loss of generality the shape

$$
S_{\text{eq}} = \left(
\begin{array}{c|c|c}
\tilde{S}_{\text{mob}}^1 & \tilde{S}_{\text{sorp}}^1 & \tilde{S}_{\text{min}}^1 \\
-\text{Id} & 0 & 0 \\
\hline
0 & \tilde{S}_{\text{sorp}}^2 & 0 \\
0 & -\text{Id} & 0 \\
\hline
0 & 0 & -\text{Id}
\end{array}
\right)
$$

where the columns have as before the size $J_{\mathrm{mob}}, J_{\mathrm{sorp}}, J_{\mathrm{min}}$, resp., and the rows have the size $I - J_{\mathrm{mob}}, J_{\mathrm{mob}}, \bar{I}_{\mathrm{sorp}} - J_{\mathrm{sorp}}, J_{\mathrm{sorp}}, J_{\mathrm{min}}$, resp. For this reformulation, the usual assumption that the columns of S_{eq} are linearly independent, is applied. Obviously the matrix

$$U^T = \left(\begin{array}{ccccc} \mathrm{Id} & \tilde{S}^1_{\mathrm{mob}} & 0 & \tilde{S}^1_{\mathrm{sorp}} & \tilde{S}^1_{\mathrm{min}} \\ 0 & 0 & \mathrm{Id} & \tilde{S}^2_{\mathrm{sorp}} & 0 \end{array} \right)$$

has the property $U^T S_{\mathrm{eq}} = 0$. Hence, a multiplication of the mass balance equations in (9)/(10) by U^T leads to

$$\begin{pmatrix} \partial_t(\theta(c_\alpha + \tilde{S}^1_{\mathrm{mob}} c_\beta) + \tilde{S}^1_{\mathrm{sorp}} \bar{c}_{\mathrm{sorp},\beta} + \tilde{S}^1_{\mathrm{min}} \bar{c}_{\mathrm{min}}) + L(c_\alpha + \tilde{S}^1_{\mathrm{mob}} c_\beta) \\ \partial_t(\bar{c}_{\mathrm{sorp},\alpha} + \tilde{S}^2_{\mathrm{sorp}} \bar{c}_{\mathrm{sorp},\beta}) \end{pmatrix} \qquad (12)$$
$$= \theta \tilde{S}_{\mathrm{kin}} R_{\mathrm{kin}}(c, \bar{c}_{\mathrm{sorp}}),$$

i.e., an elimination of R_{eq}. Here $\tilde{S}_{\mathrm{kin}} = U^T S_{\mathrm{kin}}$, and we split the vectors of unknowns $c = (c_\alpha, c_\beta)$, $\bar{c}_{\mathrm{sorp}} = (\bar{c}_{\mathrm{sorp},\alpha}, \bar{c}_{\mathrm{sorp},\beta})$. Note that $c_\alpha, \bar{c}_{\mathrm{sorp},\alpha}$ are sometimes called primary variables, and $c_\beta, \bar{c}_{\mathrm{sorp},\beta}, \bar{c}_{\mathrm{min}}$ secondary variables. System (12) consists of $I + \bar{I} - J_{\mathrm{eq}}$ mass balance equations, which have to be solved together with the J_{eq} equilibrium conditions

$$\tilde{Q}_{\mathrm{mob}}(c) := (\tilde{S}^1_{\mathrm{mob}})^T \ln c_\alpha - \ln c_\beta - \ln \tilde{K}_{\mathrm{mob}} = 0,$$
$$\tilde{Q}_{\mathrm{sorp}}(c, \bar{c}_{\mathrm{sorp}}) := (\tilde{S}^1_{\mathrm{sorp}})^T \ln c_\alpha + (\tilde{S}^2_{\mathrm{sorp}})^T \ln \bar{c}_{\mathrm{sorp},\alpha} - \ln \bar{c}_{\mathrm{sorp},\beta} - \ln \tilde{K}_{\mathrm{sorp}} = 0,$$
$$\varphi(\tilde{E}(c), \bar{c}_{\mathrm{min}}) = 0, \quad \text{where } \tilde{E}(c) := \ln \tilde{K}_{\mathrm{min}} - (\tilde{S}^1_{\mathrm{min}})^T \ln c_\alpha.$$
$$(13)$$

The size of the system (12)-(13) is $I + \bar{I}$. In general situations, one cannot expect a decoupling of some of the mass balance equation, except in the special case that there are no equilibrium sorption reactions [21]. A way to reduce the size of the system further more would be a substitution of the equilibrium conditions $\tilde{Q}_{\mathrm{mob}}, \tilde{Q}_{\mathrm{sorp}}$, solved for $c_\beta, \bar{c}_{\mathrm{sorp},\beta}$, into the mass balance equations, but this has the drawback of nonlinear coupling terms appearing under the spatial derivatives of L. This motivates the use of the reformulation proposed in the following section which will lead to a smaller number of equations than (12)-(13). We will show how the reformulation can be combined with the complementarity formulation, and we will investigate its performance in that combination.

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4. Application of the complementarity formulation in combination with a size reduction strategy

4.1. The reformulation technique

In [17, 18] a technique was introduced to enable the reformulation of a given reactive transport problem in porous media in such a way that some linear conservative equations decouple so that a nonlinear problem smaller than (12)-(13) remains to be solved. The method allows rather general systems containing mobile and immobile species and kinetic and equilibrium reactions. Compared to other approaches such as [21], this approach does not require any additional assumptions such as the absence of equilibrium sorption reactions. However, in [17, 18] the model did not contain any minerals. The purpose of this section is to demonstrate that the reformulation technique can also be applied when minerals are involved. A model with minerals, but without kinetic and sorption reactions is considered in [4].

We assume that the reactive system has the shape (8). Without loss of generality we can assume that the columns of S_{sorp}^2 are linearly independent (if necessary we take linear combinations of columns of S_{eq} and increase J_{mob} and decrease J_{sorp}). For the sake of simplicity we assume that the columns of S_{eq}^1 are linearly independent (this condition can be weakened). The following transformation is very similar to the one in [17, 18], except that there is an additional block of mineral species and reactions. Therefore we summarize the main steps and refer to [17, 18] for more details. We define S_1^* as the matrix consisting of a maximal set of linear independent columns of matrix $S^1 = (S_{\text{eq}}^1 | S_{\text{kin}}^1)$ containing all columns of S_{eq}^1, and a matrix S_2^* consisting of a maximal set of linear independent columns of $S^2 = (S_{\text{eq}}^2 | S_{\text{kin}}^2)$, containing at least all the (linear independent) nonzero columns of S_{eq}^2. Let J_i^* be the number of columns of S_i^*, $i = 1, 2$ (i.e., $J_{\text{eq}} \leq J_1^* \leq J$, $J_{\text{sorp}} + J_{\text{min}} \leq J_2^* \leq J_{\text{sorp}} + J_{\text{min}} + J_{\text{kin}}$). Since the columns of S_i^* are linearly independent, $((S_i^*)^T S_i^*)^{-1}$ exist, $i = 1, 2$. We find A_i such that $S_i = S_i^* A_i$. (It is $A_i = (S_i^{*T} S_i^*)^{-1} S_i^{*T} S_i$.) For some applications (such as the example in Sec. 5/Appendix B) the columns of S^1 are already linear independent. In this case simply $S_1^* = S^1$ and $A_1 = \text{Id}$, $J_1^* = J$ holds. Furthermore, often S_2^* just coincides with S_2 after the J_{mob} zero columns of the aqueous reactions are dropped. Then $J_2^* = J_{\text{sorp}} + J_{\text{min}} + J_{\text{kin}}$ holds.

Next, we introduce a matrix $U_1 \in \mathbb{R}^{(I - J_1^*) \times I}$ and a matrix $U_2 \in \mathbb{R}^{(\bar{I} - J_2^*) \times \bar{I}}$ such that the columns of U_i are linearly independent and orthogonal to the columns of S_i^*, $i = 1, 2$. This means that $U_i^T S_i^* = 0$. We multiply the PDE

block of (9)/(10) by $(S_1^{*T} S_1^*)^{-1} S_1^{*T}$ and by $(U_1^T U_1)^{-1} U_1^T$, and we multiply the ODE block of (9)/(10) by $(S_2^{*T} S_2^*)^{-1} S_2^{*T}$ and by $(U_2^T U_2)^{-1} U_2^T$. After a substitution

$$\xi = (S_1^{*T} S_1^*)^{-1} S_1^{*T} c \in \mathbb{R}^{J_1^*}, \quad \eta = (U_1^T U_1)^{-1} U_1^T c \in \mathbb{R}^{I - J_1^*}$$
$$\bar{\xi} = (S_2^{*T} S_2^*)^{-1} S_2^{*T} \bar{c} \in \mathbb{R}^{J_2^*}, \quad \bar{\eta} = (U_2^T U_2)^{-1} U_2^T \bar{c} \in \mathbb{R}^{\bar{I} - J_2^*},$$

which can be inverted by

$$\begin{aligned} c &= S_1^* \xi + U_1 \eta \\ \bar{c} &= S_2^* \bar{\xi} + U_2 \bar{\eta}, \end{aligned} \tag{14}$$

we obtain the transformed $I + \bar{I} - J_{\text{eq}}$ mass balance equations

$$\begin{array}{llll}
\partial_t \theta \eta & +L\,\eta & = 0 & (I - J_1^* \text{ eq.}) \\
\partial_t \bar{\eta} & & = 0 & (\bar{I} - J_2^* \text{ eq.}) \\
\partial_t \theta \xi_{\text{kin}} & +L\,\xi_{\text{kin}} \;\; -f_1(\xi, \bar{\xi}) & = 0 & (J_1^* - J_{\text{eq}} \text{ eq.}) \\
\partial_t (\theta \xi_{\text{sorp}} - \bar{\xi}_{\text{sorp}}) & +L\,\xi_{\text{sorp}} \;\; -f_2(\xi, \bar{\xi}) & = 0 & (J_{\text{sorp}} \text{ eq.}) \\
\partial_t (\theta \xi_{\text{min}} - \bar{\xi}_{\text{min}}) & +L\,\xi_{\text{min}} \;\; -f_3(\xi, \bar{\xi}) & = 0 & (J_{\text{min}} \text{ eq.}) \\
\partial_t \bar{\xi}_{\text{kin}} & -f_4(\xi, \bar{\xi}) & = 0 & (J_2^* - J_{\text{sorp}} - J_{\text{min}} \text{ eq.})
\end{array} \tag{15}$$

which have to be solved together with the J_{eq} equilibrium conditions (11), where all $c, \bar{c}$ have to be replaced through (14) by $\xi, \eta, \bar{\xi}, \bar{\eta}$. The terms f_i contain the kinetic rates:

$$\begin{aligned} f_1 &= \theta A_{\text{kin}}^1 R_{\text{kin}}(c, \bar{c}_{\text{sorp}}), \quad f_2 = \theta A_{\text{sorp}} R_{\text{kin}}(c, \bar{c}_{\text{sorp}}), \\ f_3 &= \theta A_{\text{min}} R_{\text{kin}}(c, \bar{c}_{\text{sorp}}), \quad f_4 = \theta A_{\text{kin}}^2 R_{\text{kin}}(c, \bar{c}_{\text{sorp}}), \end{aligned}$$

where the matrices $A_{\text{kin}}^1, A_{\text{kin}}^2, A_{\text{sorp}}, A_{\text{min}}$ can be computed from A_1, A_2. The vectors $\xi \in \mathbb{R}^{J_1^*}$ and $\bar{\xi} \in \mathbb{R}^{J_2^*}$ were split into $\xi = (\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}})$ of size $J_{\text{mob}}, J_{\text{sorp}}, J_{\text{min}}, J_{\text{kin}}^{1'}$ and $\bar{\xi} = (\bar{\xi}_{\text{sorp}}, \bar{\xi}_{\text{min}}, \bar{\xi}_{\text{kin}})$ of size $J_{\text{sorp}}, J_{\text{min}}, J_{\text{kin}}^{2'}$, where we set $J_{\text{kin}}^{1'} = J_1^* - J_{\text{eq}}$, $J_{\text{kin}}^{2'} = J_2^* - J_{\text{sorp}} - J_{\text{min}}$.

Due to the definition of U_i, the columns of U_i span the orthogonal complement space of the columns of S_i, i.e., the formulas (14) describe a decomposition of the mobile species vector c and of the immobile species vector $\bar{c}$ into a direct sum with respect to two orthogonal subspaces of $\mathbb{R}^I$, $\mathbb{R}^{\bar{I}}$, respectively. ξ and η are linear combinations of only mobile entities, and $\bar{\xi}$ and $\bar{\eta}$

are linear combinations of only immobile entities. For later use we give the transformation (14) in terms of the blocks of S_i:

$$
\begin{aligned}
c &= S_1^* \xi + U_1 \eta = S_{\mathrm{mob}}^1 \xi_{\mathrm{mob}} + S_{\mathrm{sorp}}^1 \xi_{\mathrm{sorp}} + S_{\mathrm{min}}^1 \xi_{\mathrm{min}} + S_{\mathrm{kin}}^{1'} \xi_{\mathrm{kin}} + U_1 \eta, \\
\bar{c} = \begin{pmatrix} \bar{c}_{\mathrm{sorp}} \\ \bar{c}_{\mathrm{min}} \end{pmatrix} &= S_2^* \bar{\xi} + U_2 \bar{\eta} = \begin{pmatrix} S_{\mathrm{sorp}}^2 \bar{\xi}_{\mathrm{sorp}} & + S_{\mathrm{kin}}^{2'} \bar{\xi}_{\mathrm{kin}} \\ & -\bar{\xi}_{\mathrm{min}} \end{pmatrix} + U_2 \bar{\eta},
\end{aligned}
$$

$$(16)$$

where $S_{\mathrm{kin}}^{i'}$ contains the columns of S_{kin}^i chosen for the construction of S_i^* from S_i, $i = 1, 2$. In particular, (16) shows that $\bar{\xi}_{\mathrm{min}} = -\bar{c}_{\mathrm{min}}$; for the non-mineral species the transformation is not so simple.

The main advantage of the formulation (15), (11) lies in the fact that the equations for η and $\bar{\eta}$ are decoupled and linear. Hence, it remains to solve a smaller nonlinear system for $\xi, \bar{\xi}$, when compared to formulation (12)-(13). So in the following we may suppress the equations for $\eta, \bar{\eta}$, and we also suppress any dependence of functions on $\eta, \bar{\eta}$, as we already did for the terms f_i, since $\eta, \bar{\eta}$ can be considered to be known when computing $\xi, \bar{\xi}$.

Comparing with the model in [18], we have basically the same structure, except that we now have two different types of heterogeneous reactions, leading to two blocks of equations and unknowns $\xi_{\mathrm{sorp}}, \bar{\xi}_{\mathrm{sorp}}$ and $\xi_{\mathrm{min}}, \bar{\xi}_{\mathrm{min}}$ instead of only $\xi_{\mathrm{sorp}}, \bar{\xi}_{\mathrm{sorp}}$ in [18].

In the following we discretize the CP (15), (11). For the sake of simplicity we assume that $\theta = 1$ is constant from now on; it is obvious how to proceed with general θ. We apply an implicit discretization in time, let us say, the implicit Euler method, and we apply an arbitrary spatial discretization by finite elements or finite volumes. If finite elements are used, then we apply mass lumping in order to avoid any artificial spatial couplings in the rate terms or the accumulation terms. We apply a scaling with the size of the element/cell such that the mass matrix becomes the identity matrix. We denote the time step size by τ and the discrete version of L by L_h and obtain

the nonlinear system of equations

$$
\begin{aligned}
G_1 &:= \xi_{\text{kin}} &&+ \tau\, L_h \xi_{\text{kin}} &&- \tau f_1(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}}, \bar{\xi}_{\text{sorp}}, \bar{\xi}_{\text{kin}}) - \xi_{\text{kin}}^{old} && = 0 \\
G_2 &:= \xi_{\text{sorp}} - \bar{\xi}_{\text{sorp}} &&+ \tau\, L_h \xi_{\text{sorp}} &&- \tau f_2(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}}, \bar{\xi}_{\text{sorp}}, \bar{\xi}_{\text{kin}}) - \xi_{\text{sorp}}^{old} + \bar{\xi}_{\text{sorp}}^{old} && = 0 \\
G_3 &:= \xi_{\text{min}} - \bar{\xi}_{\text{min}} &&+ \tau L_h \xi_{\text{min}} &&- \tau f_3(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}}, \bar{\xi}_{\text{sorp}}, \bar{\xi}_{\text{kin}}) - \xi_{\text{min}}^{old} + \bar{\xi}_{\text{min}}^{old} && = 0 \\
G_4 &:= \bar{\xi}_{\text{kin}} && &&- \tau f_4(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}}, \bar{\xi}_{\text{sorp}}, \bar{\xi}_{\text{kin}}) - \bar{\xi}_{\text{kin}}^{old} && = 0 \\
G_5 &:= Q_{\text{sorp}}(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}}, \bar{\xi}_{\text{sorp}}, \bar{\xi}_{\text{kin}}) && && && = 0 \\
G_6 &:= -\varphi(E(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}}), -\bar{\xi}_{\text{min}}) && && && = 0 \\
G_7 &:= Q_{\text{mob}}(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}}) && && && = 0
\end{aligned}
$$

$$\tag{17}$$

The superscript 'old' indicates values from the previous time-step. Though all the variables are now discrete, we do not change the notation. The minus sign in front of φ is chosen in order to simplify the proof in Sec. 4.3.

Now, we want to apply a semismooth Newton method. The resulting linearized system reads

$$
J \begin{pmatrix} \Delta \xi_{\text{kin}} \\ \Delta \xi_{\text{sorp}} \\ \Delta \xi_{\text{min}} \\ \Delta \bar{\xi}_{\text{kin}} \\ \Delta \bar{\xi}_{\text{sorp}} \\ \Delta \bar{\xi}_{\text{min}} \\ \Delta \xi_{\text{mob}} \end{pmatrix} = - \begin{pmatrix} G_1 \\ G_2 \\ G_3 \\ G_4 \\ G_5 \\ G_6 \\ G_7 \end{pmatrix}
\tag{18}
$$

for the Newton update, where the block matrix J is given in Table 1, left part, where φ_a, φ_b denote the partial derivatives of φ and $\Lambda(x)$ denotes a diagonal matrix with entries from a vector x.

4.2. Choice of the CP function and further size reduction

The usage of the reformulation techniques in Sec. 4.1 and in Sec. 3 is driven by the intention to reduce the size of the system to be solved at each time step. Pursuing this maxim, we want to reduce the size of the linear system (18) by a specific choice of the complementarity function φ and by exploiting the special structure of the linear system.

As already noted in [16], the choice of the Fischer-Burmeister function $\varphi = \varphi_{FB}$ leads to entries in the Jacobian (Table 1, left part) which are close to zero, but not equal zero, when a or b is close to zero. When the Newton iteration converges, then always at least one of the arguments $a = E_i(c)$

$$\left(\begin{array}{ccc|cc|c|c}
\mathrm{Id}+\tau L_h-\frac{\tau\,\partial f_1}{\partial\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_1}{\partial\xi_{\mathrm{sorp}}} & -\frac{\tau\,\partial f_1}{\partial\xi_{\mathrm{min}}} & -\frac{\tau\,\partial f_1}{\partial\bar\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_1}{\partial\bar\xi_{\mathrm{sorp}}} & 0 & -\frac{\tau\,\partial f_1}{\partial\xi_{\mathrm{mob}}} \\[2mm]
-\frac{\tau\,\partial f_2}{\partial\xi_{\mathrm{kin}}} & \mathrm{Id}+\tau L_h-\frac{\tau\,\partial f_2}{\partial\xi_{\mathrm{sorp}}} & -\frac{\tau\,\partial f_2}{\partial\xi_{\mathrm{min}}} & -\frac{\tau\,\partial f_2}{\partial\bar\xi_{\mathrm{kin}}} & -\mathrm{Id}-\frac{\tau\,\partial f_2}{\partial\bar\xi_{\mathrm{sorp}}} & 0 & -\frac{\tau\,\partial f_2}{\partial\xi_{\mathrm{mob}}} \\[2mm]
-\frac{\tau\,\partial f_3}{\partial\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_3}{\partial\xi_{\mathrm{sorp}}} & \mathrm{Id}+\tau L_h-\frac{\tau\,\partial f_3}{\partial\xi_{\mathrm{min}}} & -\frac{\tau\,\partial f_3}{\partial\bar\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_3}{\partial\bar\xi_{\mathrm{sorp}}} & -\mathrm{Id} & -\frac{\tau\,\partial f_3}{\partial\xi_{\mathrm{mob}}} \\[2mm]
-\frac{\tau\,\partial f_4}{\partial\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_4}{\partial\xi_{\mathrm{sorp}}} & -\frac{\tau\,\partial f_4}{\partial\xi_{\mathrm{min}}} & \mathrm{Id}-\frac{\tau\,\partial f_4}{\partial\bar\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_4}{\partial\bar\xi_{\mathrm{sorp}}} & 0 & -\frac{\tau\,\partial f_4}{\partial\xi_{\mathrm{mob}}} \\[2mm]
\frac{\partial Q_{\mathrm{sorp}}}{\partial\xi_{\mathrm{kin}}} & \frac{\partial Q_{\mathrm{sorp}}}{\partial\xi_{\mathrm{sorp}}} & \frac{\partial Q_{\mathrm{sorp}}}{\partial\xi_{\mathrm{min}}} & \frac{\partial Q_{\mathrm{sorp}}}{\partial\bar\xi_{\mathrm{kin}}} & \frac{\partial Q_{\mathrm{sorp}}}{\partial\bar\xi_{\mathrm{sorp}}} & 0 & \frac{\partial Q_{\mathrm{sorp}}}{\partial\xi_{\mathrm{mob}}} \\[2mm]
-\Lambda(\varphi_a)\frac{\partial E}{\partial\xi_{\mathrm{kin}}} & -\Lambda(\varphi_a)\frac{\partial E}{\partial\xi_{\mathrm{sorp}}} & -\Lambda(\varphi_a)\frac{\partial E}{\partial\xi_{\mathrm{min}}} & 0 & 0 & \Lambda(\varphi_b) & -\Lambda(\varphi_a)\frac{\partial E}{\partial\xi_{\mathrm{mob}}} \\[2mm]
\frac{\partial Q_{\mathrm{mob}}}{\partial\xi_{\mathrm{kin}}} & \frac{\partial Q_{\mathrm{mob}}}{\partial\xi_{\mathrm{sorp}}} & \frac{\partial Q_{\mathrm{mob}}}{\partial\xi_{\mathrm{min}}} & 0 & 0 & 0 & \frac{\partial Q_{\mathrm{mob}}}{\partial\xi_{\mathrm{mob}}}
\end{array}\right)$$

$$\left(\begin{array}{ccc|cc|c|cc}
\mathrm{Id}+\tau L_h-\frac{\tau\,\partial f_1}{\partial\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_1}{\partial\xi_{\mathrm{sorp}}} & -\frac{\tau\,\partial f_1}{\partial\xi_{\mathrm{min}}^{\mathcal{A}}} & -\frac{\tau\,\partial f_1}{\partial\bar\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_1}{\partial\bar\xi_{\mathrm{sorp}}} & 0 & -\frac{\tau\,\partial f_1}{\partial\xi_{\mathrm{min}}^{\mathcal{I}}} & -\frac{\tau\,\partial f_1}{\partial\xi_{\mathrm{mob}}} \\[2mm]
-\frac{\tau\,\partial f_2}{\partial\xi_{\mathrm{kin}}} & \mathrm{Id}+\tau L_h-\frac{\tau\,\partial f_2}{\partial\xi_{\mathrm{sorp}}} & -\frac{\tau\,\partial f_2}{\partial\xi_{\mathrm{min}}^{\mathcal{A}}} & -\frac{\tau\,\partial f_2}{\partial\bar\xi_{\mathrm{kin}}} & -\mathrm{Id}-\frac{\tau\,\partial f_2}{\partial\bar\xi_{\mathrm{sorp}}} & 0 & -\frac{\tau\,\partial f_2}{\partial\xi_{\mathrm{min}}^{\mathcal{I}}} & -\frac{\tau\,\partial f_2}{\partial\xi_{\mathrm{mob}}} \\[2mm]
-\frac{\tau\,\partial f_3}{\partial\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_3}{\partial\xi_{\mathrm{sorp}}} & \begin{smallmatrix}\mathrm{Id}_{\mathcal{A}}+\tau L_h^{\mathcal{A}\mathcal{A}}-\frac{\tau\,\partial f_{3\,\mathcal{A}}}{\partial\xi_{\mathrm{min}}^{\mathcal{A}}} \\ \tau L_h^{\mathcal{I}\mathcal{A}}-\frac{\tau\,\partial f_{3\,\mathcal{I}}}{\partial\xi_{\mathrm{min}}^{\mathcal{A}}}\end{smallmatrix} & -\frac{\tau\,\partial f_3}{\partial\bar\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_3}{\partial\bar\xi_{\mathrm{sorp}}} & \begin{smallmatrix}-\mathrm{Id}_{\mathcal{A}} & 0 \\ 0 & -\mathrm{Id}_{\mathcal{I}}\end{smallmatrix} & \begin{smallmatrix}\tau L_h^{\mathcal{A}\mathcal{I}}-\frac{\tau\,\partial f_{3\,\mathcal{A}}}{\partial\xi_{\mathrm{min}}^{\mathcal{I}}} \\ \mathrm{Id}_{\mathcal{I}}+\tau L_h^{\mathcal{I}\mathcal{I}}-\frac{\tau\,\partial f_{3\,\mathcal{I}}}{\partial\xi_{\mathrm{min}}^{\mathcal{I}}}\end{smallmatrix} & -\frac{\tau\,\partial f_3}{\partial\xi_{\mathrm{mob}}} \\[4mm]
-\frac{\tau\,\partial f_4}{\partial\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_4}{\partial\xi_{\mathrm{sorp}}} & -\frac{\tau\,\partial f_4}{\partial\xi_{\mathrm{min}}^{\mathcal{A}}} & \mathrm{Id}-\frac{\tau\,\partial f_4}{\partial\bar\xi_{\mathrm{kin}}} & -\frac{\tau\,\partial f_4}{\partial\bar\xi_{\mathrm{sorp}}} & 0 & -\frac{\tau\,\partial f_4}{\partial\xi_{\mathrm{min}}^{\mathcal{I}}} & -\frac{\tau\,\partial f_4}{\partial\xi_{\mathrm{mob}}} \\[2mm]
\frac{\partial Q_{\mathrm{sorp}}}{\partial\xi_{\mathrm{kin}}} & \frac{\partial Q_{\mathrm{sorp}}}{\partial\xi_{\mathrm{sorp}}} & \frac{\partial Q_{\mathrm{sorp}}}{\partial\xi_{\mathrm{min}}^{\mathcal{A}}} & \frac{\partial Q_{\mathrm{sorp}}}{\partial\bar\xi_{\mathrm{kin}}} & \frac{\partial Q_{\mathrm{sorp}}}{\partial\bar\xi_{\mathrm{sorp}}} & 0 & \frac{\partial Q_{\mathrm{sorp}}}{\partial\xi_{\mathrm{min}}^{\mathcal{I}}} & \frac{\partial Q_{\mathrm{sorp}}}{\partial\xi_{\mathrm{mob}}} \\[2mm]
\begin{smallmatrix}0 \\ \frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\mathrm{kin}}}\end{smallmatrix} & \begin{smallmatrix}0 \\ \frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\mathrm{sorp}}}\end{smallmatrix} & \begin{smallmatrix}0 \\ \frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\mathrm{min}}^{\mathcal{A}}}\end{smallmatrix} & 0 & 0 & \begin{smallmatrix}\mathrm{Id}_{\mathcal{A}} & 0 \\ 0 & 0\end{smallmatrix} & \begin{smallmatrix}0 \\ \frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\mathrm{min}}^{\mathcal{I}}}\end{smallmatrix} & \begin{smallmatrix}0 \\ \frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\mathrm{mob}}}\end{smallmatrix} \\[4mm]
\frac{\partial Q_{\mathrm{mob}}}{\partial\xi_{\mathrm{kin}}} & \frac{\partial Q_{\mathrm{mob}}}{\partial\xi_{\mathrm{sorp}}} & \frac{\partial Q_{\mathrm{mob}}}{\partial\xi_{\mathrm{min}}^{\mathcal{A}}} & 0 & 0 & 0 & \frac{\partial Q_{\mathrm{mob}}}{\partial\xi_{\mathrm{min}}^{\mathcal{I}}} & \frac{\partial Q_{\mathrm{mob}}}{\partial\xi_{\mathrm{mob}}}
\end{array}\right)$$

Table 1: Left part: Matrix J from (18). Right part: Matrix J from (20).

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or $b = \bar{c}_{\min,i}$ approaches zero, so we have almost zero entries even on the diagonal of the system, while in the same columns/rows of the system, other entries may be much larger. In order to avoid the possibility that this effect may deteriorate the condition number of the system when approaching the solution, we proceed as follows: We choose the minimum function $\varphi = \varphi_{MIN}$ since this complementarity function does not show this effect, cf. (7). Next we partition the set of degrees of freedom:

Let us denote the set of m spatial discretization points by Ω_h. The variables $\xi_{\min}$ and $\bar{\xi}_{\min}$ consist of $J_{\min} \times m$ degrees of freedom each. We partition the set $M := \{1, ..., J_{\min}\} \times \Omega_h$ into

$$\begin{aligned} \mathcal{A} &:= \{(i, x_k) \in \{1, ..., J_{\min}\} \times \Omega_h \mid E_i(c(x_k)) > \bar{c}_{\min,i}(x_k)\} \\ \mathcal{I} &:= \{(i, x_k) \in \{1, ..., J_{\min}\} \times \Omega_h \mid E_i(c(x_k)) \leq \bar{c}_{\min,i}(x_k)\} \end{aligned} \tag{19}$$

$\mathcal{A}$ is the set of *active* degrees of freedom in the sense of an active set method.

Restricted to one species i we can define the set of active/inactive degrees of freedom

$$\begin{aligned} \mathcal{A}_i &:= \{x_k \in \Omega_h \mid (i, x_k) \in \mathcal{A}\}, \\ \mathcal{I}_i &:= \{x_k \in \Omega_h \mid (i, x_k) \in \mathcal{I}\}, \end{aligned}$$

$i = 1, ..., J_{\min}$.

Let us emphasize that this partition into active and inactive degrees of freedom due to condition (19) is based on the evaluation of the current Newton iterate and is renewed after each Newton step. So for the choice $\varphi = \varphi_{MIN}$, the index set illustrates which of the two cases holds:

$$\varphi(E_i(c), \bar{c}_{\min,i}) = \begin{cases} \bar{c}_{\min,i}, & x \in \mathcal{A}_i \\ E_i(c), & x \in \mathcal{I}_i \end{cases}$$

The Semismooth Newton method with φ_{MIN} as a CP-function can thus be regarded as an active set strategy, a fact that has been stated in [16] and in [12]. Now we decompose the vector $\bar{\xi}_{\min} \in \mathbb{R}^{|M|}$ into a vector $\bar{\xi}_{\min}^{\mathcal{I}}$ living on $\mathcal{I}$ and a vector $\bar{\xi}_{\min}^{\mathcal{A}}$ living on $\mathcal{A}$. The same decomposition is applied to vector $\xi_{\min}$. By reordering the entries of vector $\bar{\xi}_{\min}$, starting with the 'active' components and then proceeding with the inactive, we can write

$$\bar{\xi}_{\min} = \begin{pmatrix} \bar{\xi}_{\min}^{\mathcal{A}} \\ \bar{\xi}_{\min}^{\mathcal{I}} \end{pmatrix}, \quad \xi_{\min} = \begin{pmatrix} \xi_{\min}^{\mathcal{A}} \\ \xi_{\min}^{\mathcal{I}} \end{pmatrix}.$$

The same reordering can be applied to the equations. The rows within the third and within the sixth set of equations of the linear system (18) reordered,

starting with those equations acting on active nodes, followed by those equations acting on inactive nodes. That means that we decompose f_3, $L_h \xi_{\min}$, G_3, G_6, E into the components $f_{3\mathcal{A}}$, $L_h^{\mathcal{A}} \xi_{\min}$, $G_{3\mathcal{A}}$, $G_{6\mathcal{A}}$, $E_{\mathcal{A}}$, and $f_{3\mathcal{I}}$, $L_h^{\mathcal{I}} \xi_{\min}$, $G_{3\mathcal{I}}$, $G_{6\mathcal{I}}$, $E_{\mathcal{I}}$:

$$ f_3 = \begin{pmatrix} f_{3\mathcal{A}} \\ f_{3\mathcal{I}} \end{pmatrix}, \quad L_h \xi_{\min} = \begin{pmatrix} L_h^{\mathcal{A}} \xi_{\min} \\ L_h^{\mathcal{I}} \xi_{\min} \end{pmatrix}, \quad E = \begin{pmatrix} E_{\mathcal{A}} \\ E_{\mathcal{I}} \end{pmatrix}, \quad S_{\min}^1 = (S_{\min\mathcal{A}}^1 | S_{\min\mathcal{I}}^1), $$

etc. The discrete differential operators can be split into a part acting on the variables with $\mathcal{A}$-subscript and a part acting on the variables with $\mathcal{I}$-subscript:

$$ \begin{aligned} L_h^{\mathcal{A}} \xi_{\min} &= L_h^{\mathcal{A}\mathcal{A}} \xi_{\min}^{\mathcal{A}} + L_h^{\mathcal{A}\mathcal{I}} \xi_{\min}^{\mathcal{I}}, \\ L_h^{\mathcal{I}} \xi_{\min} &= L_h^{\mathcal{I}\mathcal{A}} \xi_{\min}^{\mathcal{A}} + L_h^{\mathcal{I}\mathcal{I}} \xi_{\min}^{\mathcal{I}} \end{aligned} $$

With these definitions and restructuring, exploiting (7), the linear system (18) reads

$$ J \begin{pmatrix} \Delta \xi_{\mathrm{kin}} \\ \Delta \xi_{\mathrm{sorp}} \\ \Delta \xi_{\min}^{\mathcal{A}} \\ \Delta \bar{\xi}_{\mathrm{kin}} \\ \Delta \bar{\xi}_{\mathrm{sorp}} \\ \Delta \bar{\xi}_{\min}^{\mathcal{A}} \\ \Delta \bar{\xi}_{\min}^{\mathcal{I}} \\ \Delta \xi_{\min}^{\mathcal{I}} \\ \Delta \xi_{\mathrm{mob}} \end{pmatrix} = - \begin{pmatrix} G_1 \\ G_2 \\ G_{3\mathcal{A}} \\ G_{3\mathcal{I}} \\ G_4 \\ G_5 \\ \bar{\xi}_{\min}^{\mathcal{A}} \\ -E_{\mathcal{I}} \\ G_7 \end{pmatrix} \tag{20} $$

where J is displayed in Table 1, right part. Note that, for later use, we moved the $\Delta \xi_{\min}^{\mathcal{I}}$ part of the vector of unknowns to the lower part of that vector, which obviously requires a shift of the corresponding columns of the matrix of Table 1. We emphasize that the zeros in this matrix and one of the $\mathrm{Id}_{\mathcal{A}}$-blocks are due to the specific choice $\varphi = \varphi_{MIN}$ for the C-function. The presence of these blocks can be exploited to decouple some equations: The upper part of the sixth block of equations simply reads

$$ \Delta \bar{\xi}_{\min}^{\mathcal{A}} = -\bar{\xi}_{\min}^{\mathcal{A}}, $$

where on the right-hand side the *old* Newton iterate is meant; subscripts denoting the Newton iterates are suppressed here and in the following. Hence,

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the update for the variable $\bar{\xi}_{\min}^{\mathcal{A}}$ just reads

$$\bar{\xi}_{\min}^{\mathcal{A}} := 0, \tag{21}$$

i.e., active mineral degrees of freedom are directly set to zero within a Newton step. Hence, the linear system (20) can be diminished by these equations/unknowns. Another decoupling is possible since the unknowns $\Delta \bar{\xi}_{\min}^{\mathcal{I}}$ only occur in the lower part of the third block of equations. This block of equations can be written as

$$
\begin{aligned}
\Delta \bar{\xi}_{\min}^{\mathcal{I}} = \ & -G_{3\mathcal{I}} \\
& -\tau \frac{\partial f_{3\mathcal{I}}}{\partial \xi_{\text{kin}}} \Delta \xi_{\text{kin}} - \tau \frac{\partial f_{3\mathcal{I}}}{\partial \xi_{\text{sorp}}} \Delta \xi_{\text{sorp}} + \left(\text{Id}_{\mathcal{I}} + \tau L_h^{\mathcal{I}} - \tau \frac{\partial f_{3\mathcal{I}}}{\partial \xi_{\min}} \right) \Delta \xi_{\min} \\
& -\tau \frac{\partial f_{3\mathcal{I}}}{\partial \bar{\xi}_{\text{kin}}} \Delta \bar{\xi}_{\text{kin}} - \tau \frac{\partial f_{3\mathcal{I}}}{\partial \bar{\xi}_{\text{sorp}}} \Delta \bar{\xi}_{\text{sorp}} - \tau \frac{\partial f_{3I}}{\partial \xi_{\text{mob}}} \Delta \xi_{\text{mob}}.
\end{aligned}
$$

This block of equations can be solved a posteriori after the rest of the system has been solved for the other unknowns. That means that the mineral concentrations (in the linear problem) are expressed as a function of the non-mineral concentrations.

After these two decouplings the remaining linear system reads

$$
J \begin{pmatrix} \Delta \xi_{\text{kin}} \\ \Delta \xi_{\text{sorp}} \\ \Delta \xi_{\min}^{\mathcal{A}} \\ \hline \Delta \bar{\xi}_{\text{kin}} \\ \Delta \bar{\xi}_{\text{sorp}} \\ \Delta \xi_{\min}^{\mathcal{I}} \\ \Delta \xi_{\text{mob}} \end{pmatrix} = - \begin{pmatrix} G_1 \\ G_2 \\ G_{3\mathcal{A}} \\ \hline G_4 \\ G_5 \\ -E_{\mathcal{I}} \\ G_7 \end{pmatrix} \tag{22}
$$

with system matrix J as it is displayed in Table 2.

The lower right part of the system matrix does not contain any spatial couplings. Hence, a Schur complement technique can be applied to this system, which requires only the solution of *local* problems. It is worthwile to check if a proof of solvability of the local problem can be found. This is done in the following section.

4.3. Schur complement technique, solvability of the local equations

As already done in [18], appendix, for the system without minerals, we want to investigate the solvability of the local problem in the extended model

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$$\begin{pmatrix}
\mathrm{Id}+\tau L_h-\tau\frac{\partial f_1}{\partial\xi_{\text{kin}}} & -\tau\frac{\partial f_1}{\partial\xi_{\text{sorp}}} & -\tau\frac{\partial f_1}{\partial\xi_{\text{min}}^{\mathcal{A}}} & -\tau\frac{\partial f_1}{\partial\bar\xi_{\text{kin}}} & -\tau\frac{\partial f_1}{\partial\bar\xi_{\text{sorp}}} & -\tau\frac{\partial f_1}{\partial\xi_{\text{min}}^{\mathcal{I}}} & -\tau\frac{\partial f_1}{\partial\xi_{\text{mob}}} \\[4pt]
-\tau\frac{\partial f_2}{\partial\xi_{\text{kin}}} & \mathrm{Id}+\tau L_h-\tau\frac{\partial f_2}{\partial\xi_{\text{sorp}}} & -\tau\frac{\partial f_2}{\partial\xi_{\text{min}}^{\mathcal{A}}} & -\tau\frac{\partial f_2}{\partial\bar\xi_{\text{kin}}} & -\mathrm{Id}-\tau\frac{\partial f_2}{\partial\bar\xi_{\text{sorp}}} & -\tau\frac{\partial f_2}{\partial\xi_{\text{min}}^{\mathcal{I}}} & -\tau\frac{\partial f_2}{\partial\xi_{\text{mob}}} \\[4pt]
-\tau\frac{\partial f_{3\,\mathcal{A}}}{\partial\xi_{\text{kin}}} & -\tau\frac{\partial f_{3\,\mathcal{A}}}{\partial\xi_{\text{sorp}}} & \mathrm{Id}_{\mathcal{A}}+\tau L_h^{\mathcal{A}\mathcal{A}}-\tau\frac{\partial f_{3\,\mathcal{A}}}{\partial\xi_{\text{min}}^{\mathcal{A}}} & -\tau\frac{\partial f_{3\,\mathcal{A}}}{\partial\bar\xi_{\text{kin}}} & -\tau\frac{\partial f_{3\,\mathcal{A}}}{\partial\bar\xi_{\text{sorp}}} & \tau L_h^{\mathcal{A}\mathcal{I}}-\tau\frac{\partial f_{3\,\mathcal{A}}}{\partial\xi_{\text{min}}^{\mathcal{I}}} & -\tau\frac{\partial f_{3\,\mathcal{A}}}{\partial\xi_{\text{mob}}} \\[4pt]
-\tau\frac{\partial f_4}{\partial\xi_{\text{kin}}} & -\tau\frac{\partial f_4}{\partial\xi_{\text{sorp}}} & -\tau\frac{\partial f_4}{\partial\xi_{\text{min}}^{\mathcal{A}}} & \mathrm{Id}-\tau\frac{\partial f_4}{\partial\bar\xi_{\text{kin}}} & -\tau\frac{\partial f_4}{\partial\bar\xi_{\text{sorp}}} & -\tau\frac{\partial f_4}{\partial\xi_{\text{min}}^{\mathcal{I}}} & -\tau\frac{\partial f_4}{\partial\xi_{\text{mob}}} \\[4pt]
\frac{\partial Q_{\text{sorp}}}{\partial\xi_{\text{kin}}} & \frac{\partial Q_{\text{sorp}}}{\partial\xi_{\text{sorp}}} & \frac{\partial Q_{\text{sorp}}}{\partial\xi_{\text{min}}^{\mathcal{A}}} & \frac{\partial Q_{\text{sorp}}}{\partial\bar\xi_{\text{kin}}} & \frac{\partial Q_{\text{sorp}}}{\partial\bar\xi_{\text{sorp}}} & \frac{\partial Q_{\text{sorp}}}{\partial\xi_{\text{min}}^{\mathcal{I}}} & \frac{\partial Q_{\text{sorp}}}{\partial\xi_{\text{mob}}} \\[4pt]
\frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\text{kin}}} & \frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\text{sorp}}} & \frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\text{min}}^{\mathcal{A}}} & 0 & 0 & \frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\text{min}}^{\mathcal{I}}} & \frac{-\partial E_{\mathcal{I}}}{\partial\xi_{\text{mob}}} \\[4pt]
\frac{\partial Q_{\text{mob}}}{\partial\xi_{\text{kin}}} & \frac{\partial Q_{\text{mob}}}{\partial\xi_{\text{sorp}}} & \frac{\partial Q_{\text{mob}}}{\partial\xi_{\text{min}}^{\mathcal{A}}} & 0 & 0 & \frac{\partial Q_{\text{mob}}}{\partial\xi_{\text{min}}^{\mathcal{I}}} & \frac{\partial Q_{\text{mob}}}{\partial\xi_{\text{mob}}}
\end{pmatrix}$$

Table 2: Linear system (22) after decoupling of a posteriori equations.

containing minerals. Let us write system (22) as

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} \Delta\xi_{\text{glob}} \\ \Delta\xi_{\text{loc}} \end{pmatrix} = \begin{pmatrix} \mathcal{G}_{\text{glob}} \\ \mathcal{G}_{\text{loc}} \end{pmatrix} \tag{23}$$

with

$$\Delta\xi_{\text{glob}} := \begin{pmatrix} \Delta\xi_{\text{kin}} \\ \Delta\xi_{\text{sorp}} \\ \Delta\xi_{\text{min}}^{\mathcal{A}} \end{pmatrix}, \quad \Delta\xi_{\text{loc}} := \begin{pmatrix} \Delta\bar{\xi}_{\text{kin}} \\ \Delta\bar{\xi}_{\text{sorp}} \\ \Delta\xi_{\text{min}}^{\mathcal{I}} \\ \Delta\xi_{\text{mob}} \end{pmatrix}, \quad \mathcal{G}_{\text{glob}} := \begin{pmatrix} G_1 \\ G_2 \\ G_{3\mathcal{A}} \end{pmatrix}, \quad \mathcal{G}_{\text{loc}} := \begin{pmatrix} G_4 \\ G_5 \\ -E_{\mathcal{I}} \\ G_7 \end{pmatrix},$$

and (cf. Table 2)

$$D = \begin{pmatrix} \text{Id} - \frac{\tau\,\partial f_4}{\partial\bar{\xi}_{\text{kin}}} & -\frac{\tau\,\partial f_4}{\partial\bar{\xi}_{\text{sorp}}} & -\frac{\tau\,\partial f_4}{\partial\xi_{\text{min}}^{\mathcal{I}}} & -\frac{\tau\,\partial f_4}{\partial\xi_{\text{mob}}} \\ \frac{\partial Q_{\text{sorp}}}{\partial\bar{\xi}_{\text{kin}}} & \frac{\partial Q_{\text{sorp}}}{\partial\bar{\xi}_{\text{sorp}}} & \frac{\partial Q_{\text{sorp}}}{\partial\xi_{\text{min}}^{\mathcal{I}}} & \frac{\partial Q_{\text{sorp}}}{\partial\xi_{\text{mob}}} \\ 0 & 0 & -\frac{\partial E_{\mathcal{I}}}{\partial\xi_{\text{min}}^{\mathcal{I}}} & -\frac{\partial E_{\mathcal{I}}}{\partial\xi_{\text{mob}}} \\ 0 & 0 & \frac{\partial Q_{\text{mob}}}{\partial\xi_{\text{min}}^{\mathcal{I}}} & \frac{\partial Q_{\text{mob}}}{\partial\xi_{\text{mob}}} \end{pmatrix}. \tag{24}$$

The size of the square matrix D, and as well the size of the corresponding vector of 'local' unknowns $\Delta\xi_{\text{loc}}$, is $m \cdot (J_{\text{kin}}^{2'} + J_{\text{sorp}} + J_{\text{mob}}) + \sum_{i=1}^{m} J_{\text{min},i}^{\mathcal{I}}$, where m is the number of mesh points and $J_{\text{min},i}^{\mathcal{I}}$ is the number of inactive (i.e., 'present') minerals at mesh point x_i. Due to the lack of spatial derivaties there are no couplings between the mesh points. Hence, by sorting the unknowns and equations with respect to the mesh points, the matrix D has a block-diagonal structure $D = \text{diag}(D_1, ..., D_m)$, consisting of $i = 1, ..., m$ square blocks D_i of size $J_{\text{kin}}^{2'} + J_{\text{sorp}} + J_{\text{mob}} + J_{\text{min},i}^{\mathcal{I}}$, i.e., the block sizes are less than or equal to the number of reactions. An inversion of D requires only the inversion of the small local blocks D_i. If we know that the block matrix D is invertible, then it is possible and reasonable to solve the smaller system (Schur complement system)

$$(A - BD^{-1}C)\,\Delta\xi_{\text{glob}} = \mathcal{G}_{\text{glob}} - BD^{-1}\mathcal{G}_{\text{loc}} \tag{25}$$

and get $\Delta\xi_{\text{loc}}$ by $\Delta\xi_{\text{loc}} = D^{-1}(\mathcal{G}_{\text{loc}} - C\,\Delta\xi_{\text{glob}})$. In [4] a numerical experiment displayed a condition number of system (25) being more than one thousand times lower than the condition number of the system (22)/(23) (even if a

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diagonal scaling is applied to (22)/(23)). Hence, the efficiency of iterative solvers is increased, thus motivating the Schur approach.

For the invertibility of D we can state the following theoretical result:

Theorem. If the discrete values of all non-minerals c_i, $\bar{c}_{\mathrm{sorp},i}$ are strictly positive at each mesh point, if R_{kin} is continuous and if the time step size $\tau > 0$ is sufficiently small, then the matrix D is regular, i.e., problem (22)/(23) is equivalent to the (smaller, and better conditioned) problem (25). If $J_{\mathrm{kin}}^{2'} = 0$ (which in particular holds if all reactions are equilibrium reactions), then the statement even holds for arbitrarily large $\tau > 0$.

Proof. As explained above, it is sufficient to prove the regularity of each local block D_i of D. To keep the notation simple, we will omit the subscript i from now on und denote the local matrix at an arbitrary mesh point just by D. Using (11) and (16) we obtain

$$
D \;=\; D(\tau) = \left(
\begin{array}{cc||cc}
\mathrm{Id} - O(\tau) & O(\tau) & O(\tau) & O(\tau) \\
{S_{\mathrm{sorp}}^2}^T \tilde{\Lambda} S_{\mathrm{kin}}^{2'} & {S_{\mathrm{sorp}}^2}^T \tilde{\Lambda} S_{\mathrm{sorp}}^2 & {S_{\mathrm{sorp}}^1}^T \Lambda S_{\mathrm{min}\mathcal{I}}^1 & {S_{\mathrm{sorp}}^1}^T \Lambda S_{\mathrm{mob}}^1 \\ \hline\hline
0 & 0 & {S_{\mathrm{min}\mathcal{I}}^1}^T \Lambda S_{\mathrm{min}\mathcal{I}}^1 & {S_{\mathrm{min}\mathcal{I}}^1}^T \Lambda S_{\mathrm{mob}}^1 \\
0 & 0 & {S_{\mathrm{mob}}^1}^T \Lambda S_{\mathrm{min}\mathcal{I}}^1 & {S_{\mathrm{mob}}^1}^T \Lambda S_{\mathrm{mob}}^1
\end{array}
\right)
$$

$$
=: \left(\begin{array}{c|c} D_{11} & D_{12} \\ \hline 0 & D_{22} \end{array} \right)
\tag{26}
$$

with $\tilde{\Lambda} := \mathrm{diag}(1/\bar{c}_{\mathrm{sorp},i}) \in \mathbb{R}^{\bar{I}_{\mathrm{sorp}} \times \bar{I}_{\mathrm{sorp}}}$ and $\Lambda = \mathrm{diag}(1/c_i) \in \mathbb{R}^{I \times I}$.

It is sufficient to prove the regularity of the blocks D_{11} and D_{22}. We can write

$$
D_{22} = (S_{\mathrm{min}\mathcal{I}}^1 | S_{\mathrm{mob}}^1)^T \, \Lambda \, (S_{\mathrm{min}\mathcal{I}}^1 | S_{\mathrm{mob}}^1).
$$

Due to the assumption of linear independence of the columns of matrix $(S_{\mathrm{min}\mathcal{I}}^1 | S_{\mathrm{mob}}^1)$ and the positivity of the c_i, matrix D_{22} is symmetric positive definite. The entries of D_{11} depend continuously on the time step size τ, and for $\tau = 0$ matrix D_{11} becomes

$$
D_{11}(0) = \left(\begin{array}{c|c} \mathrm{Id} & 0 \\ \hline {S_{\mathrm{sorp}}^2}^T \tilde{\Lambda} S_{\mathrm{kin}}^{2'} & {S_{\mathrm{sorp}}^2}^T \tilde{\Lambda} S_{\mathrm{sorp}}^2 \end{array} \right)
$$

Matrix $D_{11}(0)$ is obviously regular, since its lower right block is symmetric positive definite. Then there is a neighbourhood around $D_{11}(0)$ where

all matrices are regular. Since the matrix depends continuously on τ, for sufficiently small τ, D_{11} is regular.

The τ-depending terms in D_{11} are nonexistent, if $J_{\text{kin}}^{2'} = 0$. In this case, the regularity holds for arbitrarily large time steps.

Note that the practical solution of the local problem at each mesh point can be split into two even smaller problems, exploiting the block structure, by solving problems related to the blocks D_{22}, D_{11}.

4.4. The structure of the global system

From the previous section we know that we can solve the smaller linear system (25) instead of the larger system (22)/(23), since the 'local' matrix D is invertible. The question may be posed if we can find out anything about the invertibility of the matrix (25) and hence, of matrix (22)/(23). Note that the invertibility of the matrix is of course required for the applicability of the semismooth Newton method, see end of Sec. 2.2. While the term A in (25) is basically the discretization of standard advection-diffusion equations, it is not a priorily clear which effect the additional term $-BD^{-1}C$, coming from the local equations, has on the whole system. Note that while for standard advection-diffuction equations, the system matrix approaches the identity matrix when $\tau \to 0$ (for $h = \text{const}$, or for $\tau = o(h^2)$), this is not the case for problems including 'infinitely fast' equilibrium reactions, i.e., for the term $-BD^{-1}C$ in our case. In particular is seems reasonable to investigate the structure of the system for the limit case $\tau = 0$ in order to find out about the system for sufficiently small $\tau > 0$. We state the following facts:

Let the current Newton iterate of the global problem be such that the corresponding concentration values in terms of c, $\bar{c}_{\text{sorp}}$, $\bar{c}_{\text{min}}$ lies in $\mathbb{R}_+^{I + \bar{I}_{\text{sorp}}} \times \mathbb{R}^{\bar{I}_{\text{min}}}$ at each of the $m \in \mathbb{N}$ mesh points. Then the system matrix of the global problem, after the local equations have been eliminated, (25), has the structure

$$\mathcal{J}_{\text{glob}} = \mathcal{J}_{\text{glob}}(\tau) = \text{Id} + \mathcal{J}_{\text{equil}} + \tau\,\mathcal{J}_{\text{transp}} + \tau\mathcal{J}_{\text{bdry}} + \tau\,\mathcal{J}_{\text{kinet}}$$

where $\mathcal{J}_{\text{transp}}$ contains the transport terms L_h, where $\mathcal{J}_{\text{bdry}}$ contains the terms containing $L_h^{\mathcal{AI}}$, where $\mathcal{J}_{\text{kinet}}$ contains terms from kinetic reactions. The τ-independent part, i.e., the system matrix in the limit case $\tau = 0$, (coming from the accumulation term and the equilibrium reactions) has the structure

$$\mathcal{J}_{\text{glob}}(0) = \text{Id} + \mathcal{J}_{\text{equil}} \tag{27}$$

where $\mathcal{J}_{\text{equil}}$ is a matrix which has a complete system of eigenvectors (i.e., can be diagonalized) with only nonnegative eigenvalues. As a consequence, $\mathcal{J}_{\text{glob}}(0)$ has a complete system of eigenvectors with strictly positive eigenvalues, i.e., is regular. With a continuity argument it follows that $\mathcal{J}_{\text{glob}}(\tau)$ is invertible for sufficiently small $\tau > 0$.

The proof of this property is more demanding than for the local matrix in Sec. 4.3 and is postponed in the Appendix A. Let us remark that this theoretical result is a promising, but not yet satisfactory result and will require further investigations. From a practical point of view not only the existence of a positive τ, but also some concrete values for a τ for which the Jacobian is regular is desirable. Note that $\mathcal{J}_{\text{transp}}$ contains terms of order τ/h^2 due to the discretization of a diffusion/dispersion term, so the given argument that the τ-depending terms become small works for $\tau = o(h^2)$, while in practical computations with global implicit methods usually larger time steps are used.

4.5. A variant: Elimination on the nonlinear level

In Sec. 4.2, 4.3 local equations were eliminated from the linearized system of equations. A variant of this idea is to reduce the size of the nonlinear system. The motivation for this variant is that most of the nonlinearities are moved from global to local problems at each mesh point; see end of this section.

The nonlinear discrete system (17) reads, after choosing $\varphi = \varphi_{MIN}$ and after the splitting of the degrees of freedom of Sec. 4.2 is applied,

$$
\begin{aligned}
G_1 &:= \xi_{\text{kin}} && +\tau\, L_h \xi_{\text{kin}} && -\tau f_1 - \xi_{\text{kin}}^{old} && = 0 \\
G_2 &:= \xi_{\text{sorp}} - \bar{\xi}_{\text{sorp}} +\tau\, L_h \xi_{\text{sorp}} && -\tau f_2 - \xi_{\text{sorp}}^{old} + \bar{\xi}_{\text{sorp}}^{old} && = 0 \\
G_{3\mathcal{A}} &:= \xi_{\text{min}}^{\mathcal{A}} - \bar{\xi}_{\text{min}}^{\mathcal{A}} +\tau L_h^{\mathcal{A}\mathcal{A}} \xi_{\text{min}}^{\mathcal{A}} + L_h^{\mathcal{A}\mathcal{I}} \xi_{\text{min}}^{\mathcal{I}} -\tau f_3^{\mathcal{A}} - \xi_{\text{min}}^{old} + \bar{\xi}_{\text{min}}^{old} && = 0 \\
G_{3\mathcal{I}} &:= \xi_{\text{min}}^{\mathcal{I}} - \bar{\xi}_{\text{min}}^{\mathcal{I}} +\tau L_h^{\mathcal{I}\mathcal{A}} \xi_{\text{min}}^{\mathcal{A}} + L_h^{\mathcal{I}\mathcal{I}} \xi_{\text{min}}^{\mathcal{I}} -\tau f_3^{\mathcal{I}} - \xi_{\text{min}}^{old} + \bar{\xi}_{\text{min}}^{old} && = 0 \\
G_4 &:= \bar{\xi}_{\text{kin}} && -\tau f_4 - \bar{\xi}_{\text{kin}}^{old} && = 0 \quad (28) \\
G_5 &:= Q_{\text{sorp}}(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}}, \bar{\xi}_{\text{sorp}}, \bar{\xi}_{\text{kin}}) && = 0 \\
G_{6\mathcal{A}} &:= \bar{\xi}_{\text{min}}^{\mathcal{A}} && = 0 \\
G_{6\mathcal{I}} &:= -E_{\mathcal{I}}(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}})) && = 0 \\
G_7 &:= Q_{\text{mob}}(\xi_{\text{mob}}, \xi_{\text{sorp}}, \xi_{\text{min}}, \xi_{\text{kin}}) && = 0
\end{aligned}
$$

The (decoupled) equations for η, $\bar{\eta}$ were omitted again as well as any dependence of functions on these variables. the f_i are functions of ξ_{mob}, ξ_{sorp}, ξ_{min}, ξ_{kin}, $\bar{\xi}_{\text{sorp}}$, $\bar{\xi}_{\text{kin}}$ (arguments are omitted in (28)). The decomposition of

the degrees of freedom $\xi_{\min}$, $\bar{\xi}_{\min}$ and the discrete equations $\mathcal{G}_3$, $\mathcal{G}_6$ has been performed based on the evaluation of the variables of the current Newton iteration; a subscript indicating the Newton iterate is suppressed. As in Sec. 4.2, the equation $G_{6_\mathcal{A}}$ allows the elimination of the unknown $\bar{\xi}^{\mathcal{A}}_{\min}$ from the system, and the equation $G_{3_\mathcal{I}}$ can be used for an a posteriori computation of $\bar{\xi}^{\mathcal{I}}_{\min}$, since this unknown does not occur in any of the other equations. Hence, we obtain the nonlinear system

$$
\begin{array}{lll}
\text{(i)} & \xi_{\text{kin}} \quad\quad +\tau\,L_h\xi_{\text{kin}} \quad\quad\quad\quad\quad\quad -\tau f_1 - \xi^{old}_{\text{kin}} & = 0 \\
\text{(ii)} & \xi_{\text{sorp}} - \bar{\xi}_{\text{sorp}} + \tau\,L_h\xi_{\text{sorp}} \quad\quad\quad\quad -\tau f_2 - \xi^{old}_{\text{sorp}} + \bar{\xi}^{old}_{\text{sorp}} & = 0 \\
\text{(iii)} & \xi^{\mathcal{A}}_{\min} \quad\quad +\tau L_h^{\mathcal{A}\mathcal{A}}\xi^{\mathcal{A}}_{\min} + \tau L_h^{\mathcal{A}\mathcal{I}}\xi^{\mathcal{I}}_{\min} - \tau f_3^{\mathcal{A}} - \xi^{old\,\mathcal{A}}_{\min} + \bar{\xi}^{old\,\mathcal{A}}_{\min} & = 0 \\
\text{(iv)} & \bar{\xi}_{\text{kin}} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad -\tau f_4 - \bar{\xi}^{old}_{\text{kin}} & = 0 \\
\text{(v)} & Q_{\text{mob}}(\xi_{\text{mob}},\xi_{\text{sorp}},\xi_{\min},\xi_{\text{kin}}) & = 0 \\
\text{(vi)} & Q_{\text{sorp}}(\xi_{\text{mob}},\xi_{\text{sorp}},\xi_{\min},\xi_{\text{kin}},\bar{\xi}_{\text{sorp}},\bar{\xi}_{\text{kin}}) & = 0 \\
\text{(vii)} & -E_{\mathcal{I}}(\xi_{\text{mob}},\xi_{\text{sorp}},\xi_{\min},\xi_{\text{kin}}) & = 0
\end{array}
\tag{29}
$$

with the decoupled equations

$$
\bar{\xi}^{\mathcal{I}}_{\min} = \xi_{\min} + \tau L_h^{\mathcal{I}}\xi_{\min} - \tau f_{3_\mathcal{I}} - \xi^{old,\mathcal{I}}_{\min} + \bar{\xi}^{old,\mathcal{I}}_{\min},
$$
$$
\bar{\xi}^{\mathcal{A}}_{\min} = 0.
$$

The ODE (iv) and the algebraic equations (v)-(vii) are local equations. As in [18], a reduction of the problem size can be achieved by solving the local equation with respect to local unknowns $\xi_{\text{loc}} = (\xi_{\text{mob}}, \xi^{\mathcal{I}}_{\min}, \bar{\xi}_{\text{sorp}}, \bar{\xi}_{\text{kin}})$ and by eliminating these unknowns from the remaining equations. The algorithmic treatment leads to a local Newton iteration for the local unknowns nested in the global Newton iteration for the global unknowns $\xi_{\text{glob}} = (\xi_{\text{kin}}, \xi_{\text{sorp}}, \xi^{\mathcal{A}}_{\min})$, since the solution of the local equations with respect to the local variables, for a given set of global variables, cannot be given explicitely. The possibility to solve the local equations w.r.t. to ξ_{loc}, or more precisely, the existence of a solving function, is guaranteed by the implicit function theorem, provided that the Jacobian of the local equations w.r.t. ξ_{loc} is invertible. Note that the structure of this matrix is exactly the same as in (26). Hence, the proof in Sec. 4.3 also guarantees the existence of the solving function. Note that also the structure of the global Jacobian is exactly the same as the one considered in Sec. 4.4 and in the appendix; all results apply also in the case of elimination on the nonlinear level.

The motivation for the substitution on the lonlinear level is that most of the nonlinearities are now handled in local subproblems. On the local

level, nonlinearities are more efficient to be solved than on the global, since the computations at the mesh points are independent of each other. So for simulations where the reactions are concentrated to certain reaction fronts there are usually many mesh points where not much computation is required, while at other mesh points several iterations are required; on a global level this situation would require many solves over the whole domain. However, from the theoretical point of view, some aspects of the variant of Sec. 4.4 might be more difficult to investigate, since the nonlinear system (29) (even its size) for which the Newton step is performed, varies from Newton step to Newton step.

The remaining global nonlinear discrete problem reads

$$
\begin{aligned}
\xi_{\text{kin}} \qquad\qquad +\tau\, L_h \xi_{\text{kin}} - \tau f_1(\xi_{\text{glob}}, \xi_{\text{loc}}(\xi_{\text{glob}})) - \xi_{\text{kin}}^{old} \qquad\qquad\qquad &= 0 \\
\xi_{\text{sorp}} - \bar{\xi}_{\text{sorp}}(\xi_{\text{glob}}) + \tau\, L_h \xi_{\text{sorp}} - \tau f_2(\xi_{\text{glob}}, \xi_{\text{loc}}(\xi_{\text{glob}})) - \xi_{\text{sorp}}^{old} + \bar{\xi}_{\text{sorp}}^{old} \qquad &= 0 \\
\xi_{\text{min}}^{\mathcal{A}} \quad + \tau L_h^{\mathcal{A}\mathcal{A}} \xi_{\text{min}}^{\mathcal{A}} - \tau f_3^{\mathcal{A}}(\xi_{\text{glob}}, \xi_{\text{loc}}(\xi_{\text{glob}})) - \xi_{\text{min}}^{old\,\mathcal{A}} + \bar{\xi}_{\text{min}}^{old\,\mathcal{A}} + \tau L_h^{\mathcal{A}\mathcal{I}} \xi_{\text{min}}^{\mathcal{I}}(\xi_{\text{glob}}) &= 0
\end{aligned}
$$

5. A numerical application

5.1. The problem setting

In order to demonstrate that the proposed algorithms works in practice we have chosen a reactive transport problem with several minerals, displaying precipitation-dissolution fronts and changes of topology of the subdomains of total dissolution (i.e., of the sets $\mathcal{A}_i$).

We use the following generic simplified set of chemical reactions that contains a principal mechanism which may take place in subsurface CO_2 storage sites:

$$
\begin{aligned}
CO_2{}^{(aq)} + H_2O &\xleftrightarrow{R_1} HCO_3^- + H^+ \\
\text{Calcite} + H^+ &\xleftrightarrow{R_2} Ca^{2+} + HCO_3^- \\
M_S + 3\,H^+ &\xleftrightarrow{R_3} Me^{3+} + SiO_2{}^{(aq)} \\
M_C + 2\,H^+ &\xleftrightarrow{R_4} Me^{3+} + HCO_3^- \\[4pt]
Z^+ + H^+ &\xleftrightarrow{R_5} Z^0 + Ca^{2+} \\
Z^- + H_2O &\xleftrightarrow{R_6} Z^0 + Ion^{2-} + H^+
\end{aligned}
\tag{30}
$$
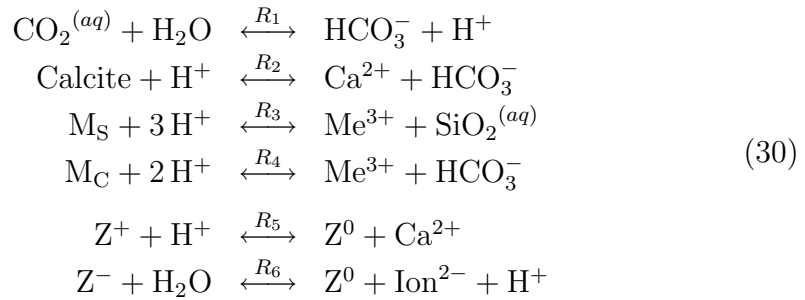
It consists of three minerals (calcite and M_C are carbonates, M_S is a silicate), three surface species Z^0, Z^+, Z^-, seven aqueous reacting species plus H_2O and one conservative tracer. We assume that R_1 to R_4 are at local equilibrium

and that the sorption reactions R_5, R_6 are kinetic. R_2, R_3, R_4 are mineral precipitation-dissulution reactions which are expressed by complementarity conditions. All six reaction are assumed to follow the law of mass action. We assume that the CO_2 is dissolved in the ground water and that there is no gas phase present. The first two reactions allow a transition of the carbon into HCO_3^- (mobile) and calcite (mineral). These reactions affect (and are affected by) the pH, i.e., the concentration of H^+. The silicate M_S, present in the initial state, dissolves at high H^+-concentrations. Thereby, it releases metal ions Me^{3+}. These ions can initiate the precipitation of the carbonate M_C, storing the carbon. In order to demonstrate the capability of combining different types of reactions, we assume the presence of sorpion places Z^0, Z^+, Z^- concentrated in one layer of the computational domain.

The problem, including the concentrations and the reaction constants chosen for this simulation, is fully generic. The most interesting point in this model is that, due to the way the Me^{3+} ions are incorporated, the dissolution of one mineral can cause an immediate precipitation of another mineral (i.e., the dissolution front of one mineral coincides with the precipitation front of another mineral).

The parameters are given in dimensionless form. The computational domain is $\Omega = (0,10) \times (0,6)$, the length of the time interval is $T = 400$, the transport operator is $L_i c_i = -\nabla \cdot (\mathcal{D}\nabla c_i - qc_i)$, the Darcy velocity is $q = (0.015, 0)^T$, the water content $\theta = 0.3$, (i.e., pore velocity $|q|/\theta = 0.05$), the dispersion tensor is according to Bear-Scheidegger $\mathcal{D} = \beta_t |q| \operatorname{Id} + \frac{\beta_l - \beta_t}{|q|} qq^T$, with longitudinal/transversal dispersion length $(\beta_l, \beta_t) = (0.3, 0.03)$. The equilibrium constant of the first reaction is $K_1 = 0.1$, where the activity of H_2O is already incorporated; i.e., $c_{H^+} c_{HCO_3^-}/c_{CO_2} = 0.1$. The solubility products of the three mineral reactions are $K_2 = 100$, $K_3 = 10$, $K_4 = 1.25$; i.e., $c_{Ca^{2+}} c_{HCO_3^-}/c_{H^+} = 100$ (if $c_{Calcite} > 0$), etc.; the forward and the backward rate coefficient of the two kinetic reactions are equal to 0.003333.

The initial values and the Dirichlet boundary values at the inflow boundary are given in Table B.4. The minerals M_S and calcite are present in certain layers D_2 and D_3-D_5 (see Fig. B.4), and the sorption places are concentrated in the layer D_4. In the part B_1 of the left boundary, the CO_2 enriched water enters, in the part B_2 of the boundary, the boundary values equal the initial values. At the rest of the boundary, homogeneous Neumann boundary conditions are applied. All initial and boundary values are in compliance with the equilibrium conditions.
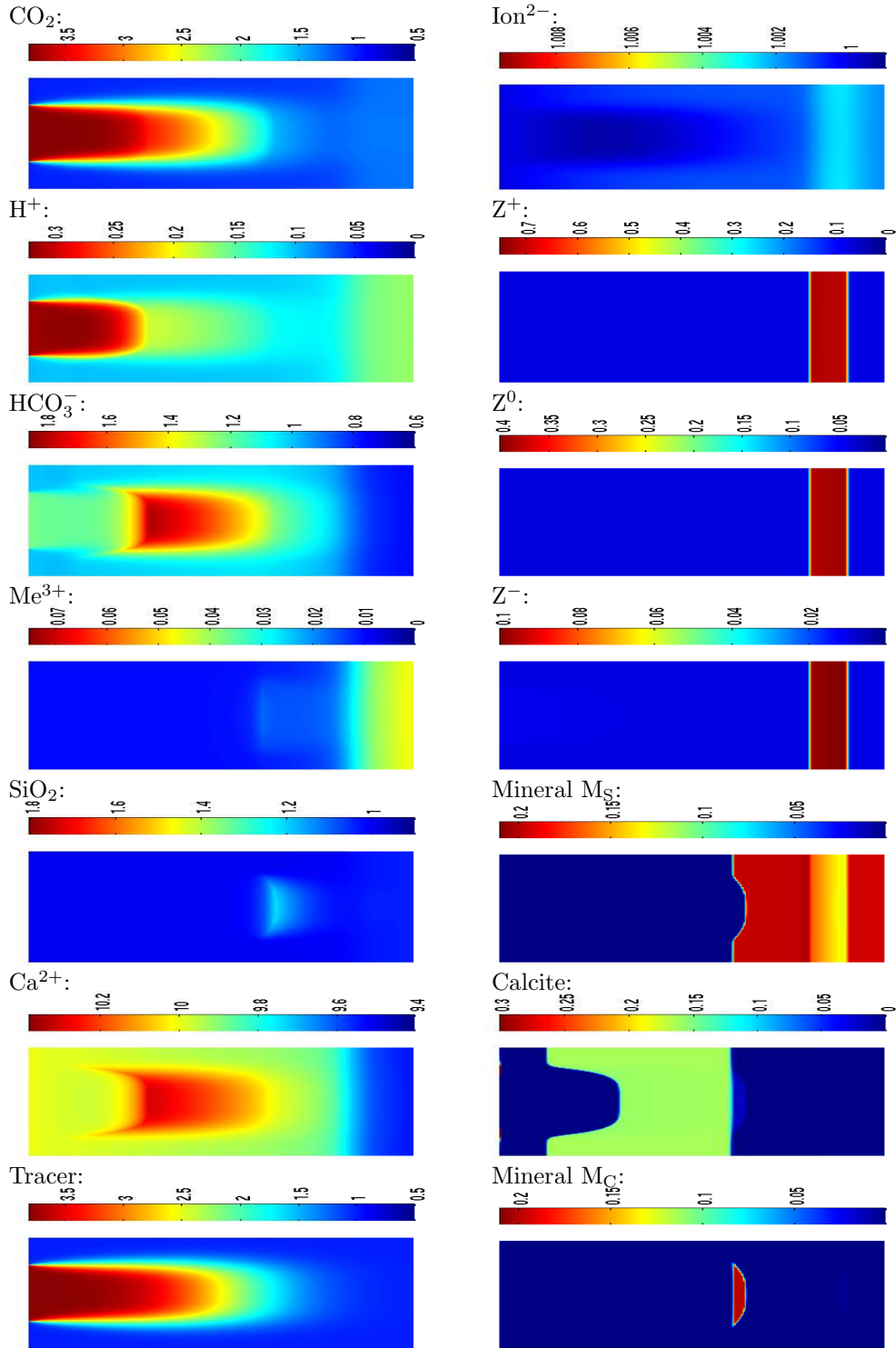
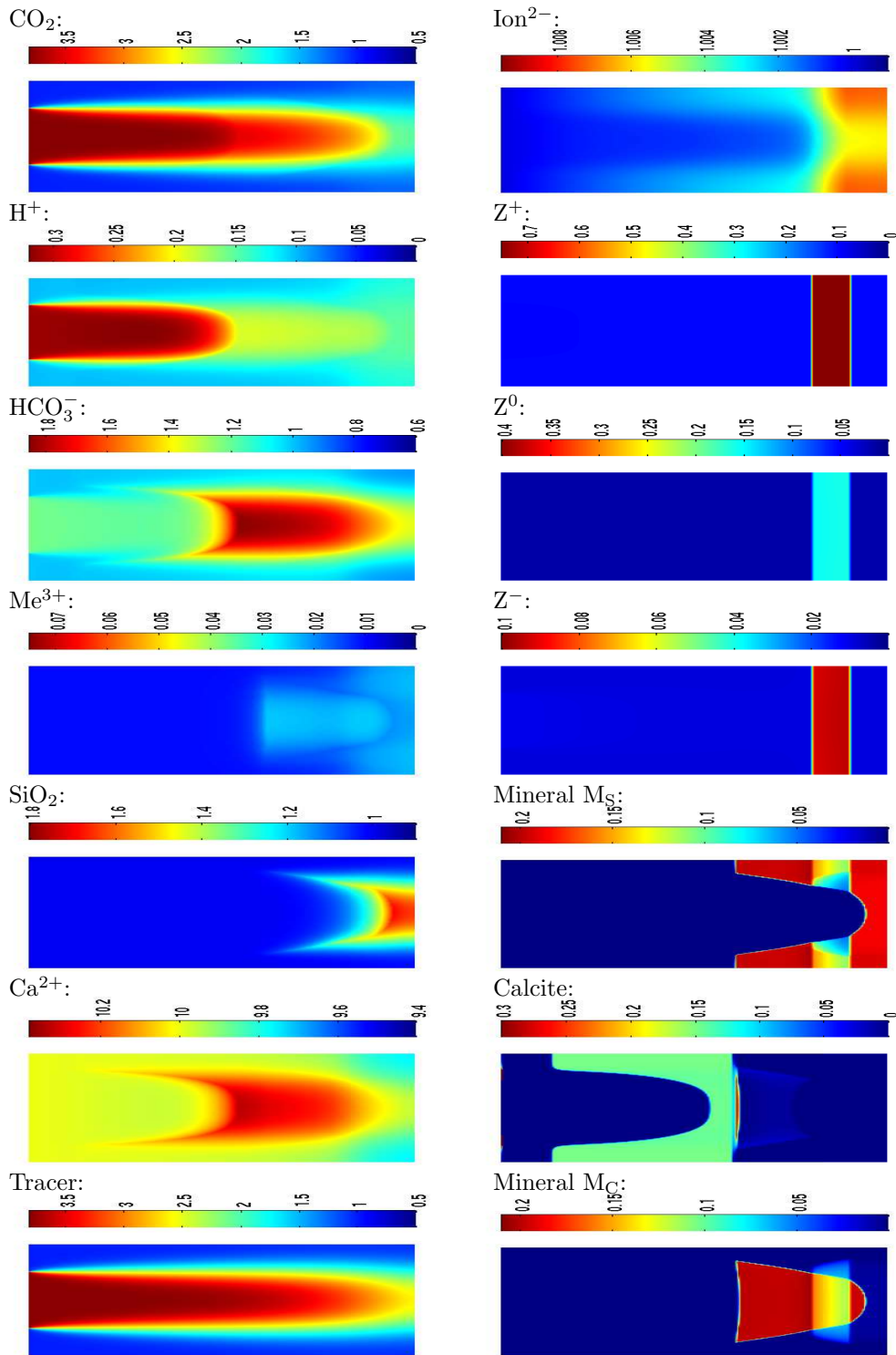Figure 1: Time $t = 100$. (The graphics are compressed by a factor of ≈ 2 in vertical direction.)

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CO$_2$:

Ion^{2-}:

H$^+$:

Z$^+$:

HCO$_3^-$:

Z^0:

Me^{3+}:

Z$^-$:

SiO$_2$:

Mineral M$_S$:

Ca^{2+}:

Calcite:

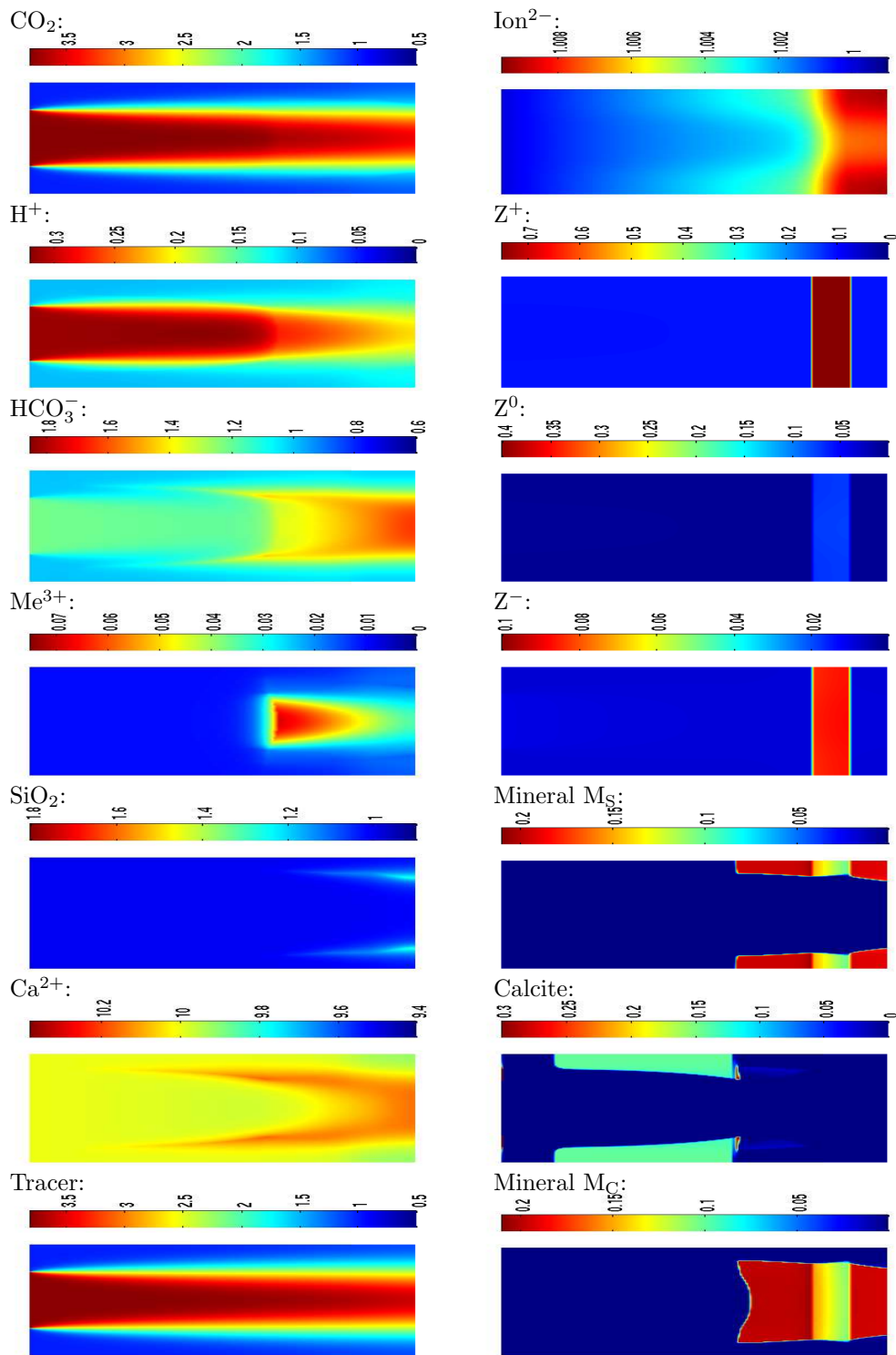Tracer:

Mineral M$_C$:

Figure 2: Time $t = 200$.

27

Figure 3: Time $t = 300$.

28

The stoichiometric matrix (8) for the system (30) is given in Appendix B.

5.2. Numerical results and discussion

We apply the reduction method of Sec. 4.5, i.e., the local equations are eliminated on the nonlinear level. Note that the versions without elimination and with elimination on the linear level (Sec. 4.3) are applied in [4]. We obtain $I - J_1^* = 8 - 6 = 2$ decoupled linear scalar PDEs for the η_i, $\bar{I} - J_2^* = 6 - 5 = 1$ constant $\bar{\eta}_i$, and a remaining nonlinear system consisting of $J_{\text{kin}} = 2$ discretized PDEs for the $\xi_{\text{kin},i}$ and $J_{\text{min}} = 3$ PDEs for $\xi_{\text{min},i}^{\mathcal{A}}$, each living on the active domain of the corresponding mineral $\bar{\xi}_{\text{min},i}$; the local problems have a size between $J_{\text{mob}} + J_{\text{sorp}} + J_{\text{kin}}^{2'} = 1 + 0 + 2 = 3$ and $J_{\text{mob}} + J_{\text{sorp}} + J_{\text{min}} + J_{\text{kin}}^{2'} = 1 + 0 + 3 + 2 = 6$, depending on the number of minerals present.

Figs. 1-3 show the computational results for time step size $\tau = 0.1$, corresponding to 4000 time steps with the implicit Euler method, and a P1 finite element discretization with 48,000 triangles, corresponding to about 24,321 mesh points and a mesh size of about $h = 0.05$, i.e., about 340,000 degrees of freedom in terms of the concentrations c_i, $\bar{c}_i$ on the mesh points per time step. The code was implemented by J. Hoffmann using the software platform M++ (Meshes, multigrid and more). The CO_2 entering the domain from the left affects the pH, which leads to a dissolution of calcite and a release of Ca^{2+} and HCO_3^- (Fig. 1). The increasing HCO_3^- concentration triggers the dissolution of M_S and the precipitation of M_C (Figs. 1-3). In the layer with the sorption places, slowly some Z^- turns into Z^0 and Z^0 into Z^+, releasing small amounts of Ion^{2-} and H^+.

The figures show that the propagation of the fronts, in particular of the precipitation-dissolution front between M_S and M_C, is reproduced well by the complementarity based Semismooth Newton code. Also the discontinuities of the mineral concentrations are handled in a stable and robust way.

We use a stopping criterion with $\epsilon_{\text{nonlin}} = 10^{-8}$ for the L^2-norm of the residual for the nonlinear problem and $\epsilon_{\text{lin}} = 10^{-10}$ for the iterative linear solver GMRES(100) with Jacobi preconditioner, and $\epsilon_{\text{loc}} = 10^{-12}$ for the local Newton iterations. Though rather severe stopping criteria are applied, only a moderate number of Newton steps for the global problem of 3.61 per time step (average over the time steps) are required (Table 3, row 1). The number of nested local Newton steps is given per mesh point per global Newton step. This number, 0.77, is extraordinary small, since in each time step there are

Table 3: Performance data.

triangles	time step	glob. Newton steps	loc. Newton steps	cpu time (min)
48,000	0.1	3.61	0.77	768
12,000	0.1	2.99	0.87	128
12,000	0.2	3.36	0.88	102
12,000	0.4	4.05	0.84	45
4,196	0.4	3.60	0.93	13.1
1,024	0.4	3.07	1.03	2.75

parts of the computational domain where the system is already in equilibrium, at least after one or two global Newton steps have been performed. The whole simulation required less than 13 hours on an average notebook computer. In order to give an impression of the potential dependence of the number of Newton steps and the cpu time on the discretization, we give some results for different discretization parameters in the table. For a decreasing time step, the number of global Newton steps decreases. This is caused by the fact that the initial value for the Newton iteration, i.e., the value of the previous time step, is of course closer to the solution then. Note that, since there are equilibrium reactions, the principal part of the time step solution operator does not approach the identity operator (cf. (27)), as it would be the case for a pure kinetic problem, so the impact of the nonlinearity is not significantly decreasing for $\tau \to 0$. Concerning a finer spatial mesh, we see a rather moderate increase of the number of Newton steps when τ is fixed. To answer the question thoroughly whether the number of Newton steps can be bounded independendly of $h \to 0$, further investigations, either by extended numerical tests or by theoretical investigations such as in [13], would be required. The average number of local iteration steps per global iteration step is reduced by refining the mesh. This may be explained by the fact that the fraction of grid points close to reaction interfaces becomes smaller then.

The question of global convergence is not addressed in this paper. However, it is well known that even for (local) speciation problems without any minerals involved, the convergence of a method when no good starting point is known (which is usually the case when large time steps are used and/or concentrations vary over many magnitudes) is delicate; see, e.g., [7]. Popular strategies to improve robustness are line search or chemically allowed intervals. For the local Newton iteration the Armijo line search rule was implemented, and for the global Newton iteration componentwise cut-offs are

used to avoid the quitting of the positive range for non-mineral concentrations. Beyond that, globalization strategies specially adapted to semismooth methods and their theoretical investigation can be found in [11, 15].

Finally, let us emphasize here that the proposed method does not involve any slow fixed-point type iterations (which are typical for iterative splitting methods). Direct efficiency comparisons of the reformulation method with other numerical geoscientific codes are given in [6] for the MoMaS benchmark problem on reactive transport [3, 5].

Appendix A. Proof of the regularity results of Sec. 4.4

Theorem. Let the current Newton iterate of the global problem (25) be positive ('physical') in the sense that the corresponding value in terms of c, $\bar{c}_{\text{sorp}}$, $\bar{c}_{\text{min}}$ lies in $\mathbb{R}_+^{I+\bar{I}_{\text{sorp}}} \times \mathbb{R}^{\bar{I}_{\text{min}}}$ at each of the $m \in \mathbb{N}$ mesh points.

(a) Then the Jacobian of the global problem, after the local equations have been eliminated, (25), has the structure

$$\mathcal{J}_{\text{glob}} = \text{Id} + \mathcal{J}_{\text{equil}} + \tau\, \mathcal{J}_{\text{transp}} + \tau \mathcal{J}_{\text{bdry}} + \tau\, \mathcal{J}_{\text{kinet}}$$
$$\in \mathbb{R}^{(mJ_{\text{kin}}^{1'}+mJ_{\text{sorp}}+|\mathcal{A}|)\times(mJ_{\text{kin}}^{1'}+mJ_{\text{sorp}}+|\mathcal{A}|)}$$

where[1] the τ-independent part $\mathcal{J}_{\text{equil}}$ has the structure

$$\mathcal{J}_{\text{equil}} = \left(\begin{array}{c|c|c} 0 & 0 & 0 \\ \hline U_1 & U_2 & U_3 \\ \hline 0 & 0 & 0 \end{array} \right),$$

and where

$$\mathcal{J}_{\text{transp}} = \left(\begin{array}{c|c|c} L_h & 0 & 0 \\ \hline 0 & L_h & 0 \\ \hline 0 & 0 & L_h^{\mathcal{A}\mathcal{A}} \end{array} \right), \quad \mathcal{J}_{\text{bdry}} = \left(\begin{array}{c|c|c} 0 & 0 & 0 \\ \hline 0 & 0 & 0 \\ \hline L_h^{\mathcal{A}\mathcal{I}} V_1 & L_h^{\mathcal{A}\mathcal{I}} V_2 & L_h^{\mathcal{A}\mathcal{I}} V_3 \end{array} \right)$$

with the blocks

$$U_1 = H_0\, S_{\text{sorp}}^{1}{}^{T} \Lambda^{1/2} P_{(\Lambda^{1/2}(S_{\text{min}\mathcal{I}}^1|S_{\text{mob}}^1))^\perp} \Lambda^{1/2} S_{\text{kin}}^{1'} \in \mathbb{R}^{(mJ_{\text{sorp}})\times(mJ_{\text{kin}}^{1'})},$$

$$U_2 = H_0\, S_{\text{sorp}}^{1}{}^{T} \Lambda^{1/2} P_{(\Lambda^{1/2}(S_{\text{min}\mathcal{I}}^1|S_{\text{mob}}^1))^\perp} \Lambda^{1/2} S_{\text{sorp}}^{1} \in \mathbb{R}^{(mJ_{\text{sorp}})\times(mJ_{\text{sorp}})},$$

$$U_3 = H_0\, S_{\text{sorp}}^{1}{}^{T} \Lambda^{1/2} P_{(\Lambda^{1/2}(S_{\text{min}\mathcal{I}}^1|S_{\text{mob}}^1))^\perp} \Lambda^{1/2} S_{\text{min}\mathcal{A}}^{1} \in \mathbb{R}^{(mJ_{\text{sorp}})\times|\mathcal{A}|},$$

---

[1]$\mathcal{J}_{\text{kinet}}$ may depend on τ due to the substitution of the local solving function, but only as $O(1)$ for $\tau \to 0$.

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where P_X, for a matrix X with maximal column rank, is the orthogonal projection onto the space spanned by the columns of X; $P_X = X(X^T X)^{-1} X^T$, $P_{X^\perp} = \mathrm{Id} - P_X$. H_0 is the positive definite matrix

$$H_0 = (S_{\mathrm{sorp}}^2{}^T \tilde{\Lambda} S_{\mathrm{sorp}}^2)^{-1},$$

and Λ, $\tilde{\Lambda}$ are defined as in the proof of the Theorem in Sec. 4.3.

(b) Matrix U_2 has a full system of eigenvectors with eigenvalues all being strictly positive, and the Jacobian in the limit case $\tau = 0$, (27), has a complete system of eigenvectors with eigenvalues all greater than or equal to one, and is nonsingular, hence. Matrix $\mathrm{Id} + J_{\mathrm{equil}}$, i.e., the matrix J_{glob} in the limit case $\tau = 0$, is therefore invertible.

(c) Matrices V_1, V_2, V_3 can be expressed as

$$(V_1|V_2|V_3) = H_1^{-1} H_2 \left(S_{\mathrm{kin}}^1 | S_{\mathrm{sorp}}^1 | S_{\mathrm{min}\mathcal{A}}^1\right)$$

with

$$
\begin{aligned}
H_1 &:= S_{\mathrm{min}\mathcal{I}}^1{}^T \Lambda^{1/2} P_{(\Lambda^{1/2} S_{\mathrm{mob}}^1)^\top} \Lambda^{1/2} S_{\mathrm{min}\mathcal{I}}^1 \\
H_2 &:= [S_{\mathrm{min}\mathcal{I}}^1{}^T - S_{\mathrm{min}\mathcal{I}}^1{}^T \Lambda S_{\mathrm{mob}}^1 (S_{\mathrm{mob}}^1{}^T \Lambda S_{\mathrm{mob}}^1)^{-1} S_{\mathrm{mob}}^1{}^T] \Lambda \\
&= S_{\mathrm{min}\mathcal{I}}^1{}^T \Lambda^{1/2} [\mathrm{Id} - \Lambda^{1/2} S_{\mathrm{mob}}^1 (S_{\mathrm{mob}}^1{}^T \Lambda S_{\mathrm{mob}}^1)^{-1} S_{\mathrm{mob}}^1{}^T \Lambda^{1/2}] \Lambda^{1/2} \\
&= S_{\mathrm{min}\mathcal{I}}^1{}^T \Lambda^{1/2} P_{(\Lambda^{1/2} S_{\mathrm{mob}}^1)^\top} \Lambda^{1/2}.
\end{aligned}
$$

Proof.

Part (i). Computation of U_1, U_2, U_3:

For later use we state that for the inversion of a block matrix with square regular blocks M_{11}, M_{22} the following formulas hold:

$$
\begin{pmatrix} M_{11} & M_{12} \\ 0 & M_{22} \end{pmatrix}^{-1} = \begin{pmatrix} M_{11}^{-1} & -M_{11}^{-1} M_{12} M_{22}^{-1} \\ 0 & M_{22}^{-1} \end{pmatrix} \tag{A.1}
$$

$$
\begin{pmatrix} M_{11} & 0 \\ M_{21} & M_{22} \end{pmatrix}^{-1} = \begin{pmatrix} M_{11}^{-1} & 0 \\ -M_{22}^{-1} M_{21} M_{11}^{-1} & M_{22}^{-1} \end{pmatrix} \tag{A.2}
$$

The system $(22)/(23)$ (see Table 2) can be written as

$$
\left[\left(\begin{array}{ccc|cccc}
\mathrm{Id} + \tau L_h & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \mathrm{Id} + \tau L_h & 0 & 0 & -\mathrm{Id} & 0 & 0 \\
0 & 0 & \mathrm{Id}_\mathcal{A} + \tau L_h^{\mathcal{A}\mathcal{A}} & 0 & 0 & 0 & 0 \\
\hline
\multicolumn{3}{c|}{C} & \multicolumn{4}{c}{D}
\end{array} \right) \right.
$$

$$+\tau \left(\begin{array}{c|c} 0 & \begin{array}{c|c|c|c} 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \\ \hline 0 & 0 & L_h^{\mathcal{AI}} & 0 \end{array} \\ \hline 0 & 0 \end{array} \right) + \text{kinetic terms} \Bigg] \left(\begin{array}{c} \Delta\xi_{\text{kin}} \\ \Delta\xi_{\text{sorp}} \\ \Delta\xi_{\text{min}}^{\mathcal{A}} \\ \hline \Delta\bar{\xi}_{\text{kin}} \\ \Delta\bar{\xi}_{\text{sorp}} \\ \Delta\xi_{\text{min}}^{\mathcal{I}} \\ \Delta\xi_{\text{mob}} \end{array} \right) = \text{r.h.s.}$$

where the kinetic terms (containing derivatives of $f_1, ..., f_4$) are $O(\tau)$. We rewrite this system as

$$(\text{Id} + \tau L_h)\, \Delta\xi_{\text{glob}} - \left(\begin{array}{c} 0 \\ \Delta\bar{\xi}_{\text{sorp}} \\ 0 \end{array} \right) + \tau \left(\begin{array}{c} 0 \\ 0 \\ L_h^{\mathcal{AI}} \Delta\xi_{\text{min}}^{\mathcal{I}} \end{array} \right) + \text{kin.terms} = \text{r.h.s.} \quad (A.3)$$

$$C\, \Delta\xi_{\text{glob}} + D\, \Delta\xi_{\text{loc}} + \text{kin.terms} = \text{r.h.s.} \quad (A.4)$$

where $\Delta\xi_{\text{glob}} = (\Delta\xi_{\text{kin}}, \Delta\xi_{\text{sorp}}, \Delta\xi_{\text{min}}^{\mathcal{A}})$, $\Delta\xi_{\text{loc}} = (\Delta\bar{\xi}_{\text{kin}}, \Delta\bar{\xi}_{\text{sorp}}, \Delta\xi_{\text{min}}^{\mathcal{I}}, \Delta\xi_{\text{mob}})$. Looking up C and D in Table 2 and using (11) and (16) we find

$$C = \left(\begin{array}{c} 0 \\ \hline (S_{\text{sorp}}^1 | S_{\text{min}\mathcal{I}}^1 | S_{\text{mob}}^1)^T \Lambda (S_{\text{kin}}^{1'} | S_{\text{sorp}}^1 | S_{\text{min}\mathcal{A}}^1) \end{array} \right),$$

$$D = \left(\begin{array}{cc|cc} \text{Id} & 0 & 0 & 0 \\ \hline S_{\text{sorp}}^{2\ T} \tilde{\Lambda} S_{\text{kin}}^{2'} & S_{\text{sorp}}^{2\ T} \tilde{\Lambda} S_{\text{sorp}}^2 & S_{\text{sorp}}^{1\ T} \Lambda S_{\text{min},\mathcal{I}}^1 & S_{\text{sorp}}^{1\ T} \Lambda S_{\text{mob}}^1 \\ \hline 0 & & (S_{\text{min}\mathcal{I}}^1 | S_{\text{mob}}^1)^T \Lambda (S_{\text{min}\mathcal{I}}^1 | S_{\text{mob}}^1) \end{array} \right).$$

$$(A.5)$$

In order to obtain the Schur complement system (25), we have to solve (A.4) for $\Delta\xi_{\text{loc}}$ and substitute its components $\Delta\bar{\xi}_{\text{sorp}}$, $\Delta\xi_{\text{min}}^{\mathcal{I}}$ in (A.3). We get

$$\Delta\xi_{\text{loc}} = -D^{-1} C \Delta\xi_{\text{glob}} + O(\tau) + \text{r.h.s.}$$

$$= -\left(\begin{array}{c|c} D_{11}^{-1} & -D_{11}^{-1} D_{12} D_{22}^{-1} \\ \hline 0 & D_{22}^{-1} \end{array} \right) C\, \Delta\xi_{\text{glob}} + \text{term} \quad (A.6)$$

where we have applied the inversion formula (A.1) to D, and where the 'term' contains the $O(\tau)$ terms and the terms independent of the unknowns. From the vector equation (A.6) we drop the lower components and get

$$\left(\begin{array}{c} \Delta\bar{\xi}_{\text{kin}} \\ \Delta\bar{\xi}_{\text{sorp}} \end{array} \right) = D_{11}^{-1} \left(-\text{Id} | D_{12} D_{22}^{-1} \right) C\, \Delta\xi_{\text{glob}} + \text{term}. \quad (A.7)$$

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We obtain the inverse of D_{11}, the upper left block in (A.5), by formula (A.2):

$$D_{11}^{-1} = \left(\begin{array}{c|c} \text{Id} & 0 \\ \hline S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{kin}}^{2'} & S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{sorp}}^{2} \end{array} \right)^{-1} = \left(\begin{array}{c|c} \text{Id} & 0 \\ \hline -(S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{sorp}}^{2})^{-1}\, S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{kin}}^{2'} & (S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{sorp}}^{2})^{-1} \end{array} \right)$$
$$\text{(A.8)}$$

We substitute D_{11}^{-1} in (A.7) and drop the upper part of the vector equation. We get

$$\Delta\bar{\xi}_{\text{sorp}} = (S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{sorp}}^{2})^{-1}\,(\,-S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{kin}}^{2'}|\text{Id})\,(-\text{Id}|D_{12}D_{22}^{-1})\,C\,\Delta\xi_{\text{glob}} + \text{term}$$

where by exploiting first the structure of D_{12} and then of C (cf. (A.5))

$$(-S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{kin}}^{2'}|\text{Id})\,(-\text{Id}|D_{12}D_{22}^{-1})\,C$$

$$= (-S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{kin}}^{2'}|\text{Id}) \left(\begin{array}{c|c||c|c} -\text{Id} & 0 & 0 & 0 \\ \hline 0 & -\text{Id} & S_{\text{sorp}}^{1}{}^{T}\Lambda S_{\min,\mathcal{I}}^{1}D_{22}^{-1} & S_{\text{sorp}}^{1}{}^{T}\Lambda S_{\text{mob}}^{1}D_{22}^{-1} \end{array} \right) C$$

$$= (\,S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{kin}}^{2'}|-\text{Id}|S_{\text{sorp}}^{1}{}^{T}\Lambda S_{\min,\mathcal{I}}^{1}D_{22}^{-1}|S_{\text{sorp}}^{1}{}^{T}\Lambda S_{\text{mob}}^{1}D_{22}^{-1}\,)\,C$$

$$= (-\text{Id}\,|S_{\text{sorp}}^{1}{}^{T}\Lambda S_{\min,\mathcal{I}}^{1}D_{22}^{-1}|S_{\text{sorp}}^{1}{}^{T}\Lambda S_{\text{mob}}^{1}D_{22}^{-1}\,)\,(S_{\text{sorp}}^{1}|S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1})^{T}\Lambda\,(S_{\text{kin}}^{1'}|S_{\text{sorp}}^{1}|S_{\min\mathcal{A}}^{1})$$

$$= \left[-S_{\text{sorp}}^{1}{}^{T} + S_{\text{sorp}}^{1}{}^{T}\Lambda(S_{\min,\mathcal{I}}^{1}|S_{\text{mob}}^{1})\,D_{22}^{-1}\,(S_{\min,\mathcal{I}}^{1}|S_{\text{mob}}^{1})^{T} \right]\,\Lambda\,(S_{\text{kin}}^{1'}|S_{\text{sorp}}^{1}|S_{\min\mathcal{A}}^{1})$$

$$= -S_{\text{sorp}}^{1}{}^{T}\Lambda^{1/2}\left[\text{Id} - \Lambda^{1/2}(S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1})D_{22}^{-1}(S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1})^{T}\Lambda^{1/2} \right]\,\Lambda^{1/2}\,(S_{\text{kin}}^{1'}|S_{\text{sorp}}^{1}|S_{\min\mathcal{A}}^{1})$$

$$= -S_{\text{sorp}}^{1}{}^{T}\Lambda^{1/2}\,P_{(\Lambda^{1/2}(S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1}))^{\perp}}\Lambda^{1/2}\,(S_{\text{kin}}^{1'}|S_{\text{sorp}}^{1}|S_{\min\mathcal{A}}^{1})$$

holds. The desired structure of the U_i follows by substituting $\Delta\bar{\xi}_{\text{sorp}}$ in (A.3).
Part (ii). We prove that U_2 is a product of two symmetric positive definite matrices:
Matrix $S_{\text{sorp}}^{2}{}^{T}\tilde{\Lambda}S_{\text{sorp}}^{2}$ is symmetric positiv definite, since the columns of S_{sorp}^{2} are linearly independend and $\tilde{\Lambda}$ is a diagonal matrix with positive entries. Hence, also its inverse, H_0, is symmetric positive definite. The other factor of U_2, $W := S_{\text{sorp}}^{1}{}^{T}\Lambda^{1/2}P_{(\Lambda^{1/2}(S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1}))^{\perp}}\Lambda^{1/2}S_{\text{sorp}}^{1}$, is obviously symmetric positive semidefinite, since any orthogonal projection is semidefinite.

By exploiting the linear independence of the columns of $(S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1}|S_{\text{sorp}}^{1})$, the existence of a zero eigenvalue of W can be excluded: Let x be a member of the nullspace of W. By introducing $y = \Lambda^{1/2}S_{\text{sorp}}^{1}x$ we obtain $0 = \langle Wx, x \rangle = \langle P_{(\Lambda^{1/2}(S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1}))^{\perp}}y, y \rangle = \langle P_{(\Lambda^{1/2}(S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1}))^{\perp}}y, P_{(\Lambda^{1/2}(S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1}))^{\perp}}y \rangle$ where the property $P = P^2 = P^{T}P$ of orthogonal projections was used in the last step. So the norm of $P_{(\Lambda^{1/2}(S_{\min\mathcal{I}}^{1}|S_{\text{mob}}^{1}))^{\perp}}y$ must be zero, i.e., y lies in the

nullspace of $P_{(\Lambda^{1/2}(S^1_{\min\mathcal{I}}|S^1_{\mathrm{mob}}))^\perp}$. Therefore y is a member of the range of matrix $\Lambda^{1/2}(S^1_{\min\mathcal{I}}|S^1_{\mathrm{mob}})$. On the other hand, by its definition, y lies in the range of $\Lambda^{1/2}S^1_{\mathrm{sorp}}$. Since the columns of $(S^1_{\min\mathcal{I}}|S^1_{\mathrm{mob}}|S^1_{\mathrm{sorp}})$ are assumed to be linearly independent, we obtain $y = 0$. Therefore $S^1_{\mathrm{sorp}}x = 0$, which results in $x = 0$ since the columns of S^1_{sorp} are linearely independent. As a result, W must be strictly positive definite.

Part (iii). From (ii) we know that matrix $H_0^{1/2}WH_0^{1/2}$ is symmetric positive definite, and $U_2 = H_0W$ is similar to this matrix. Therefore U_2 has a complete basis of eigenvectors with eigenvalues strictly positive. Hence $\mathcal{J}_{\mathrm{equil}}$ has a complete basis of eigenvectors (consisting of the eigenvector basis of U_2, extended by zeros, and a basis of the nullspace of J_{equil}) with eigenvalues all being nonnegative. Therefore all eigenvalues of $\mathrm{Id} + \mathcal{J}_{\mathrm{equil}}$ are estimated from below by one.

Part (iv). The formulas for the matrices V_1, V_2, V_3 can be derived in a similar way as the U_i by dropping the upper components instead of the lower ones in (A.6) to obtain a formula for $\Delta\xi^{\mathcal{I}}_{\min}$ which is then substituted in (A.3).

Appendix B. Stoichiometric matrix, initial and boundary values of the numerical simulation

The matrix (8) for the problem (30) reads (the sorption blocks are lacking):

$$
S = \left(\begin{array}{c|c|c||c}
S^1_{\mathrm{mob}} & S^1_{\mathrm{sorp}} & S^1_{\min} & S^1_{\mathrm{kin}} \\
\hline
0 & S^2_{\mathrm{sorp}} & 0 & S^{2,1}_{\mathrm{kin}} \\
\hline
0 & 0 & -\mathrm{Id} & 0
\end{array}\right) =
\left(\begin{array}{c|ccc||cc}
-1 & 0 & 0 & 0 & 0 & 0 \\
1 & -3 & -1 & -2 & 1 & -1 \\
1 & 0 & 1 & 1 & 0 & 0 \\
0 & 1 & 0 & 1 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 \\
\hline
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & -1 & -1 \\
0 & 0 & 0 & 0 & 0 & 1 \\
\hline
0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0
\end{array}\right)
$$

The dimensions are $I = 8$, $\bar{I} = 6$, $J_1^* = \mathrm{rank}(S^1) = 6$ (hence $S_1^* = S^1$), $J_2^* = \mathrm{rank}(S^2) = 5$, $J_{\mathrm{mob}} = 1$, $J_{\mathrm{sorp}} = 0$, $J_{\min} = 3$, $J_{\mathrm{kin}} = 2$, $J_{\mathrm{eq}} = J_{\mathrm{mob}} + J_{\mathrm{sorp}} + J_{\min} = 4$, $J_{\mathrm{kin}}^{1'} = J_1^* - J_{\mathrm{eq}} = 2$, $J_{\mathrm{kin}}^{2'} = J_2^* - J_{\mathrm{sorp}} - J_{\min} = 2$.

Table B.4: Initial values in the layers $D_1, ..., D_5$ (see Fig. B.4) and Dirichlet boundary values at the inflow boundary B_1, B_2.

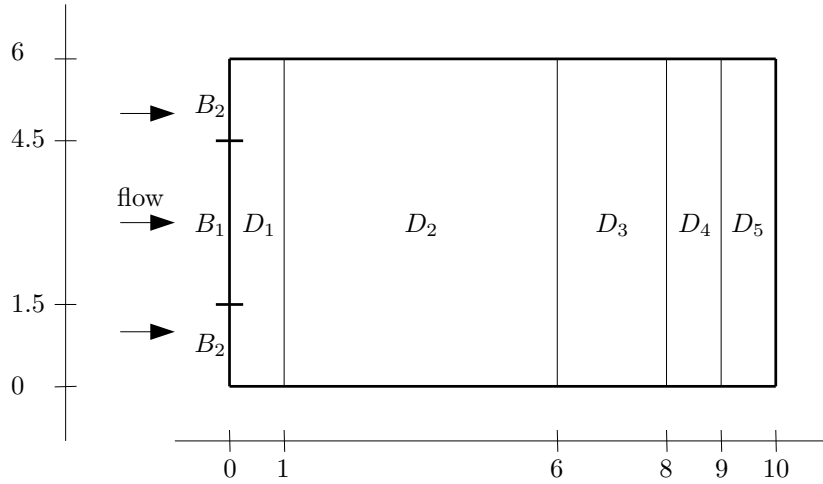| Species		initial value			boundary value	
		all zones $D_1, ..., D_5$:			bdry B_1:	bdry B_2:
c_1	CO_2	1			3.7870	1
c_2	H^+	0.1			0.3124	0.1
c_3	HCO_3^-	1			1.2120	1
c_4	Me^{3+}	0.01			0.01	
c_5	SiO_2	1			1	
c_6	Ca^{2+}	10			10	
c_7	tracer	1			3.787	1
c_8	Ion^{2-}	1			1	
		D_1, D_2, D_3:	D_4:	D_5:		
$\bar{c}_1$	Z^+	0.01	0.1	0.01		
$\bar{c}_2$	Z^0	0.1	1	0.1		
$\bar{c}_3$	Z^-	0.01	0.1	0.01		
		D_1:	D_2:	D_3, D_4, D_5:		
$\bar{c}_4$	M_S	0	0	0.2		
$\bar{c}_5$	calcite	0	0.2	0		
$\bar{c}_6$	M_C	0	0	0		

Figure B.4: Zoning of the computational domain.

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