

EFFICIENT AND ACCURATE SIMULATION OF LARGE GENERAL REACTIVE MULTICOMPONENT TRANSPORT PROCESSES IN POROUS MEDIA BY MODEL-PRESERVING DECOUPLING TECHNIQUES

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ABSTRACT

We are proposing a systematic approach for the efficient computation of the transport and reaction of a multi-species multi-reaction system. The objective of this approach is to reformulate the given system of differential or differential-algebraic equations in such a way that the couplings and the nonlinearities are concentrated in a reduced number of equations (if compared to the original formulation), while some linear equations decouple from the system. The resulting system is handled in the spirit of a global implicit approach ('one step method') avoiding operator splitting techniques. The reduction of the problem size proposed in this article helps to limit the large computational costs of numerical simulations for such problems. The reduction mechanism handles problems with mixed mobile/immobile species, homogeneous/heterogeneous kinetic/equilibrium reactions. The gain of cpu time by the reduction mechanism is given for an example problem.

1. INTRODUCTION, MOTIVATION

Detailed modelling of reactive transport processes in the underground often requires the consideration of a large number of reactions and reacting species. A prominent example is natural attenuation, that is the assessment and monitoring of microbially catalysed degradation processes of organic contaminants in the subsurface or aquifer. The reactions often exhibit a wide range of time scales, which advises to model those reactions being much faster than the time scale of the transport processes in a quasistationary manner, i.e., as (algebraically described) equilibrium processes. Additionally, not only mobile species (in solution) appear, but also immobile ones (attached to the porous skeleton). In summary, the resulting system consists of partial differential equations (PDEs), ordinary differential equations (ODEs) and algebraic equations (AEs).

An often used approach to make these large problems feasible is operator splitting, in which transport and reaction become decoupled. This procedure either introduces a further consistency error (in the non-iterative version) which can only be controlled by the time stepping, or applies a fixed point type iteration of unclear convergence properties.

To circumvent these possible disadvantages of operator splitting, we propose, in the spirit of a global implicit approach (GIA), a model-preserving reformulation of the full given PDE-ODE-AE system in such a way that as many unknowns as possible are determined by linear scalar decoupled transport equations or by local AEs. Our reformulation

technique is based on taking linear combinations of the given set of PDEs/ODEs, on the choice of new variables, and on elimination of variables in the sense of a direct substitutional approach (DSA) [Kräutle and Knabner, 2005, Kräutle and Knabner, 2006].

2. THE MODEL

Let us consider I mobile species X_1, \dots, X_I and \bar{I} immobile species $X_{I+1}, \dots, X_{I+\bar{I}}$. Let us denote their time and space dependent concentrations by $\mathbf{c} = (c_1, \dots, c_I)^t$, $\bar{\mathbf{c}} = (\bar{c}_{I+1}, \dots, \bar{c}_{I+\bar{I}})^t$; the mobile c_i are given in moles per fluid volume, the immobile \bar{c}_i in moles per total volume. The mobile species are convected by a given Darcy flow field and are subject to dispersion. Let us assume that the underlying transport operator \mathbf{L} is linear and that it is the same for all mobile species, i.e., $\mathbf{L}(c_1, \dots, c_I)^t = (L_1 c_1, \dots, L_I c_I)^t$ with $L_1 = \dots = L_I$. The J chemical reactions can be written as

$$\sum_{i=1}^I s_{ij} X_i + \sum_{i=I+1}^{I+\bar{I}} s_{ij} \bar{X}_i \xrightarrow{R_j} 0, \quad j = 1, \dots, J,$$

where the stoichiometric coefficients s_{ij} form an $(I+\bar{I}) \times J$ -matrix S and $R_j = R_j(c, \bar{c})$ is the rate expression for reaction j . The $I+\bar{I}$ mass balance equations are

$$\begin{aligned} \frac{d}{dt}(\theta c_i) + L c_i &= \sum_{j=1}^J s_{ij} R_j(c, \bar{c}), & i = 1, \dots, I \\ \frac{d}{dt} \bar{c}_i &= \sum_{j=1}^J s_{ij} R_j(c, \bar{c}), & i = I+1, \dots, I+\bar{I}. \end{aligned} \quad (1)$$

$\theta > 0$ denotes the fraction of the mobile fluid-phase volume. We assume that the s_{ij} are constant in space and time. The rates R_j and θ may depend on space and time; however, for the sake of simplicity we assume that θ is constant. The stoichiometric matrix \mathbf{S} consists of an $I \times J$ block \mathbf{S}_1 of stoichiometric coefficients for the mobile species and an $\bar{I} \times J$ block \mathbf{S}_2 of coefficients for the immobile species:

$$\mathbf{S} = \begin{pmatrix} \mathbf{S}_1 \\ \mathbf{S}_2 \end{pmatrix}$$

Using the vector notation $\mathbf{R} = (R_1, \dots, R_J)^t$ we get the compact notation

$$\begin{aligned} \theta \frac{d}{dt} \mathbf{c} + \mathbf{L} \mathbf{c} &= \mathbf{S}_1 \mathbf{R}(c, \bar{c}) \\ \frac{d}{dt} \bar{\mathbf{c}} &= \mathbf{S}_2 \mathbf{R}(c, \bar{c}) \end{aligned} \quad (2)$$

for (1).

If a rate R_j in (1)/(2) is kinetic, then we prescribe the rate R_j as a function of the local concentrations $\mathbf{c}, \bar{\mathbf{c}}$. If a reaction is assumed to be at local equilibrium then a local AE $Q_j = 0$ holds at every point \mathbf{x} of the computational domain at any time; if we assume the law of mass action for the equilibrium reactions, this reads

$$Q_j(c, \bar{c}) := \prod_{i=1}^I c_i^{s_{ij}} \prod_{i=I+1}^{I+\bar{I}} \bar{c}_i^{s_{ij}} - k_j = 0. \quad (3)$$

Here we have assumed ideal activities of all species for the sake of simplicity. Note that if an algebraic equilibrium condition like (3) is assumed, then the corresponding rate term R_j in (1) is *not* an explicit function of the local concentration vector (see, e.g., [Lichtner, 1996], eq. (121), [De Simoni et al., 2005]). The common way to handle the DAE is to eliminate the rates R_j corresponding to equilibrium reactions from the

system (1)/(2). This can be achieved by taking linear combinations of the differential equations. This process leads to the introduction of what is often called components (see, e.g., [Friedly and Rubin, 1992, Saaltink et al., 1998, Molins et al., 2004]).

Let us assume reactions $R_1, \dots, R_{J_{eq}}$ to be in equilibrium and reactions $R_{J_{eq}+1}, \dots, R_J$ to be kinetic, $0 \leq J_{eq} \leq J$. We can split the vector \mathbf{R} into a vector of equilibrium reaction rates \mathbf{R}_{eq} of size J_{eq} , and a vector of kinetic reaction rates \mathbf{R}_{neq} of size $J_{neq} = J - J_{eq}$. Similarly we split the matrices $\mathbf{S}, \mathbf{S}_1, \mathbf{S}_2$ into a block of J_{eq} columns belonging to the equilibrium reactions, and a block of J_{neq} columns for the kinetic reactions:

$$\mathbf{R} = \begin{pmatrix} \mathbf{R}_{eq} \\ \mathbf{R}_{neq} \end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix} \mathbf{S}_1 \\ \mathbf{S}_2 \end{pmatrix} = \left(\begin{array}{c|c} \mathbf{S}_{eq}^1 & \mathbf{S}_{neq}^1 \\ \mathbf{S}_{eq}^2 & \mathbf{S}_{neq}^2 \end{array} \right) = (\mathbf{S}_{eq} \mid \mathbf{S}_{neq}). \quad (4)$$

With this notation, (2) reads

$$\begin{aligned} \theta \frac{d}{dt} \mathbf{c} + \mathbf{Lc} &= \mathbf{S}_{eq}^1 \mathbf{R}_{eq} + \mathbf{S}_{neq}^1 \mathbf{R}_{neq}(\mathbf{c}, \bar{\mathbf{c}}) \\ \frac{d}{dt} \bar{\mathbf{c}} &= \mathbf{S}_{eq}^2 \mathbf{R}_{eq} + \mathbf{S}_{neq}^2 \mathbf{R}_{neq}(\mathbf{c}, \bar{\mathbf{c}}) \end{aligned} \quad (5)$$

and the AEs (3) for $j = 1, \dots, J_{eq}$ can be expressed by the equivalent formulation

$$\hat{\mathbf{Q}}_{eq}(\mathbf{c}, \bar{\mathbf{c}}) := \mathbf{S}_{eq}^t \ln \begin{pmatrix} \mathbf{c} \\ \bar{\mathbf{c}} \end{pmatrix} - \mathbf{K} = \mathbf{S}_{eq}^1{}^t \ln \mathbf{c} + \mathbf{S}_{eq}^2{}^t \ln \bar{\mathbf{c}} - \mathbf{K} = \mathbf{0} \quad (6)$$

where \mathbf{K} is the vector of equilibrium constants $\mathbf{K} = (\ln(k_1), \dots, \ln(k_{J_{eq}}))^t$, and \ln (the natural logarithm) applied to a vector with entries $c_i > 0$ is short for the vector with the entries $\ln c_i$.

The well known way to handle system (5) together with (3) or (6) is to form linear combinations of the equations in (5) in such a way that the unknown reaction terms \mathbf{R}_{eq} vanish. The forming of linear combinations of equations can be expressed by multiplying (2) with certain matrices (e.g., [Lichtner, 1996, Saaltink et al., 1998, Molins et al., 2004, Kräutle and Knabner, 2005]). A main difference between different reduction methods lies in the choice of these matrices. This choice strongly influences whether (or under which conditions) the aim of a partial decoupling of equations can be reached in the resulting system.

3. THE MODEL-PRESERVING A PRIORI DECOUPLING TECHNIQUE

3.1. The transformation for the case of all reactions being kinetic. Let us recall the basic idea of the transformation by [Kräutle and Knabner, 2005], Sec. 4.1.

The first step of the decoupling method is to transform the two blocks of (2) separately: Let J_1, J_2 be the number of linearly independent columns in the matrix $\mathbf{S}_1, \mathbf{S}_2$, respectively. For $\mathbf{S}_i, i = 1, 2$, we define \mathbf{S}_i^* as a matrix consisting of a maximum system of linearly independent columns of \mathbf{S}_i and \mathbf{A}_i such that

$$\mathbf{S}_i = \mathbf{S}_i^* \mathbf{A}_i \quad (7)$$

holds. \mathbf{A}_1 is a matrix of size $J_1 \times J$ and \mathbf{A}_2 of size $J_2 \times J$. For \mathbf{S}_i^* we define $\mathbf{S}_i^{*\top}$ consisting of a maximum set of linearly independent columns that are orthogonal to each column of \mathbf{S}_i^* . By using (7) in (2) and then multiplication of each block of (2) by $(\mathbf{S}_i^{*\top} \mathbf{S}_i^*)^{-1} \mathbf{S}_i^{*t}$ and

by $(\mathbf{S}_1^{\top t} \mathbf{S}_1^{\top})^{-1} \mathbf{S}_1^{\top t}$, we derive the following four blocks:

$$\begin{aligned}
(\mathbf{S}_1^{\top t} \mathbf{S}_1^{\top})^{-1} \mathbf{S}_1^{\top t} (\theta \frac{d}{dt} \mathbf{c} + \mathbf{L} \mathbf{c}) &= \mathbf{0} \\
(\mathbf{S}_2^{\top t} \mathbf{S}_2^{\top})^{-1} \mathbf{S}_2^{\top t} \frac{d}{dt} \bar{\mathbf{c}} &= \mathbf{0} \\
(\mathbf{S}_1^{*t} \mathbf{S}_1^*)^{-1} \mathbf{S}_1^{*t} (\theta \frac{d}{dt} \mathbf{c} + \mathbf{L} \mathbf{c}) &= \mathbf{A}_1 \mathbf{R}(\mathbf{c}, \bar{\mathbf{c}}) \\
(\mathbf{S}_2^{*t} \mathbf{S}_2^*)^{-1} \mathbf{S}_2^{*t} \frac{d}{dt} \bar{\mathbf{c}} &= \mathbf{A}_2 \mathbf{R}(\mathbf{c}, \bar{\mathbf{c}})
\end{aligned} \tag{8}$$

This manipulation corresponds to the forming of linear combinations within each of the two blocks of equations in (2). The number of equations in (8) is the same as the number of equations in (2) or (5). Hence, the reduction is still to come.

Since the matrices and the differential operators in system (8) commute, we can substitute

$$\begin{aligned}
\boldsymbol{\eta} &= (\mathbf{S}_1^{\top t} \mathbf{S}_1^{\top})^{-1} \mathbf{S}_1^{\top t} \mathbf{c}, & \boldsymbol{\xi} &= (\mathbf{S}_1^{*t} \mathbf{S}_1^*)^{-1} \mathbf{S}_1^{*t} \mathbf{c}, \\
\bar{\boldsymbol{\eta}} &= (\mathbf{S}_2^{\top t} \mathbf{S}_2^{\top})^{-1} \mathbf{S}_2^{\top t} \bar{\mathbf{c}}, & \bar{\boldsymbol{\xi}} &= (\mathbf{S}_2^{*t} \mathbf{S}_2^*)^{-1} \mathbf{S}_2^{*t} \bar{\mathbf{c}}.
\end{aligned} \tag{9}$$

The inversion of relation (9) reads

$$\mathbf{c} = \mathbf{S}_1^* \boldsymbol{\xi} + \mathbf{S}_1^{\top} \boldsymbol{\eta}, \quad \bar{\mathbf{c}} = \mathbf{S}_2^* \bar{\boldsymbol{\xi}} + \mathbf{S}_2^{\top} \bar{\boldsymbol{\eta}}. \tag{10}$$

The vectors $(\boldsymbol{\xi}, \boldsymbol{\eta}) \in \mathbb{R}^I$, $(\bar{\boldsymbol{\xi}}, \bar{\boldsymbol{\eta}}) \in \mathbb{R}^{\bar{I}}$ are representations of the vectors \mathbf{c} , $\bar{\mathbf{c}}$, respectively, with respect to another basis. $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$ are linear combinations of only mobile species, and $\bar{\boldsymbol{\xi}}$, $\bar{\boldsymbol{\eta}}$ are linear combinations of only immobile species. Equations (10) represent the decomposition of a vector in \mathbb{R}^I ($\mathbb{R}^{\bar{I}}$, resp.) with respect to two orthogonal subspaces.

System (8) becomes

$$\begin{aligned}
\theta \frac{d}{dt} \boldsymbol{\eta} + \mathbf{L} \boldsymbol{\eta} &= \mathbf{0} & (I - J_1 \text{ eqs.}) \\
\frac{d}{dt} \bar{\boldsymbol{\eta}} &= \mathbf{0} & (\bar{I} - J_2 \text{ eqs.}) \\
\theta \frac{d}{dt} \boldsymbol{\xi} + \mathbf{L} \boldsymbol{\xi} &= \mathbf{A}_1 \mathbf{R} \left(\begin{array}{c} \mathbf{S}_1^* \boldsymbol{\xi} + \mathbf{S}_1^{\top} \boldsymbol{\eta} \\ \mathbf{S}_2^* \bar{\boldsymbol{\xi}} + \mathbf{S}_2^{\top} \bar{\boldsymbol{\eta}} \end{array} \right) & (J_1 \text{ eqs.}) \\
\frac{d}{dt} \bar{\boldsymbol{\xi}} &= \mathbf{A}_2 \mathbf{R} \left(\begin{array}{c} \mathbf{S}_1^* \boldsymbol{\xi} + \mathbf{S}_1^{\top} \boldsymbol{\eta} \\ \mathbf{S}_2^* \bar{\boldsymbol{\xi}} + \mathbf{S}_2^{\top} \bar{\boldsymbol{\eta}} \end{array} \right) & (J_2 \text{ eqs.})
\end{aligned} \tag{11}$$

The advantage of (11) compared to other possible formulations is that the 'reaction invariants', i.e., the equations for the components $\boldsymbol{\eta}$ and $\bar{\boldsymbol{\eta}}$ are decoupled from the equations for $\boldsymbol{\xi}$, $\bar{\boldsymbol{\xi}}$. This is caused by the fact that our components $\boldsymbol{\eta}$, $\bar{\boldsymbol{\eta}}$ do not consist of mixed linear combinations of mobile and immobile species, as it is usually the case for example for the canonical formulation (e.g., [Lichtner, 1985, Lichtner, 1996]). Note that the decoupled equations for $\boldsymbol{\eta}$ are linear and scalar which makes their solution rather fast. The components $\bar{\boldsymbol{\eta}}$ are even constant throughout the whole simulation. The evolution of both of these quantities is completely determined by the initial and boundary values for \mathbf{c} , $\bar{\mathbf{c}}$ and is independent of the reactions. The $\boldsymbol{\xi}$, $\bar{\boldsymbol{\xi}}$ differ from the classical definition of 'reaction extents', since on the right hand sides of the corresponding equations, linear combinations of reaction rates occur.

The number of remaining coupled nonlinear equations for representation (11) is $J_1 + J_2$. If all reactions are kinetic, then the formulation (11) could directly be used for simulation. However, it is possible to further reduce the system size: After discretization in time, the last block in (11) consists of local AEs for $\bar{\boldsymbol{\xi}}$. These equations can be solved for $\bar{\boldsymbol{\xi}}$ and

substituted in the right hand side of the third block in (11). This reduces the number of remaining coupled nonlinear PDEs to J_1 .

3.2. The general algorithm capable of handling (homogeneous and heterogeneous) equilibrium reactions. If some of the reactions are assumed to be at equilibrium (formulation (5) together with (6)), then formulation (11) cannot be used directly. It is necessary to eliminate the equilibrium rates \mathbf{R}_{eq} from $I+\bar{I}-J_{eq}$ equations from system (11) and use the remaining equations together with the J_{eq} equilibrium conditions (6). The way how to eliminate the equilibrium reactions from the system (11) such that the component equations for $\boldsymbol{\eta}$, $\bar{\boldsymbol{\eta}}$ remain decoupled will be summarized in this section. The details can be found in [Kräutle and Knabner, 2006], Sec. 3.3.

We assume a certain ordering of the equilibrium reactions: We start with J_{mob} equilibrium reactions in the mobile phase, then J_{sorp} heterogeneous equilibrium reactions (such as equilibrium sorption), and finally J_{imm} equilibrium reactions in the immobile phase; $J_{mob} + J_{sorp} + J_{imm} = J_{eq}$. This leads to a certain block structure of $\mathbf{S}_{eq}^1, \mathbf{S}_{eq}^2$. Similarly, we split the vectors $\boldsymbol{\xi}$, $\bar{\boldsymbol{\xi}}$ into the subvectors $\boldsymbol{\xi} = (\boldsymbol{\xi}_{mob}, \boldsymbol{\xi}_{sorp}, \boldsymbol{\xi}_{neq})$, $\bar{\boldsymbol{\xi}} = (\bar{\boldsymbol{\xi}}_{sorp}, \bar{\boldsymbol{\xi}}_{imm}, \bar{\boldsymbol{\xi}}_{neq})$ of size $J_{mob}, J_{sorp}, J_{neq}^1; J_{sorp}, J_{imm}, J_{neq}^2$. Then, we follow the proceeding of Sec. 3.1 and arrive at formulation (11). The block structure we assumed for $\mathbf{S}_{eq}^1, \mathbf{S}_{eq}^2$ results in a certain block structure for the matrices $\mathbf{A}_1, \mathbf{A}_2$. Formulation (11), when expressed using the structuring of $\mathbf{S}_1, \mathbf{S}_2, \mathbf{A}_1, \mathbf{A}_2, \boldsymbol{\xi}, \bar{\boldsymbol{\xi}}$ reveals that the rates of the mobile homogeneous and the rates of the immobile homogeneous equilibrium reactions occur exactly once in this system, while each heterogeneous equilibrium reactions occurs exactly twice in this system; one occurrence in the $\boldsymbol{\xi}$ -block of (11), and one occurrence in the $\bar{\boldsymbol{\xi}}$ -block of (11). In order to eliminate the unknown equilibrium reaction rates from $J_{mob} + J_{sorp} + J_{imm} = J_{eq}$ of the equations, we take the difference between equations from the $\boldsymbol{\xi}$ -block and from the $\bar{\boldsymbol{\xi}}$ -block of (11) in such a way that the second occurrence of any equilibrium rate is eliminated. By this, every equilibrium reaction rate R_{eq}^j , $j = 1, \dots, J_{eq}$ is contained in the right hand side of exactly one PDE or ODE of (11). This is essential, since it allows us to omit these J_{eq} PDEs/ODEs and replace each of them by the corresponding algebraic equilibrium condition. The PDE-ODE-AE system then reads:

$$\begin{aligned}
\text{(i)} \quad & \theta \frac{d}{dt} \boldsymbol{\eta} + \mathbf{L} \boldsymbol{\eta} = \mathbf{0} & (I - J_1 \text{ eqs.}) \\
\text{(ii)} \quad & \frac{d}{dt} \bar{\boldsymbol{\eta}} = \mathbf{0} & (\bar{I} - J_2 \text{ eqs.}) \\
\text{(iii)} \quad & \hat{\mathbf{Q}}_{eq}(\mathbf{c}, \bar{\mathbf{c}}) = \mathbf{0} & (J_{eq} \text{ eqs.}) \\
\text{(iv)} \quad & \frac{d}{dt} \bar{\boldsymbol{\xi}}_{neq} = \mathbf{A}_{neq}^2 \mathbf{R}_{neq}(\mathbf{c}, \bar{\mathbf{c}}) & (J_{neq}^{2'} \text{ eqs.}) \\
\text{(v)} \quad & \frac{d}{dt} (\theta \boldsymbol{\xi}_{sorp} - \bar{\boldsymbol{\xi}}_{sorp}) + \mathbf{L} \boldsymbol{\xi}_{sorp} = \mathbf{A}_{sorp} \mathbf{R}_{neq}(\mathbf{c}, \bar{\mathbf{c}}) & (J_{sorp} \text{ eqs.}) \\
\text{(vi)} \quad & \theta \frac{d}{dt} \boldsymbol{\xi}_{neq} + \mathbf{L} \boldsymbol{\xi}_{neq} = \mathbf{A}_{neq}^1 \mathbf{R}_{neq}(\mathbf{c}, \bar{\mathbf{c}}) & (J_{neq}^{1'} \text{ eqs.})
\end{aligned} \tag{12}$$

where $\mathbf{A}_{neq}^1, \mathbf{A}_{neq}^2, \mathbf{A}_{sorp}$ are matrices (subblocks) derived from $\mathbf{A}_1, \mathbf{A}_2$. Using (10) and the block structure of $\mathbf{S}_1, \mathbf{S}_2$, the system is closed by the relations

$$\begin{aligned}
\mathbf{c} &= \mathbf{S}_1^* \boldsymbol{\xi} + \mathbf{S}_1^\top \boldsymbol{\eta} = \mathbf{S}_{mob}^1 \boldsymbol{\xi}_{mob} + \mathbf{S}_{sorp}^1 \boldsymbol{\xi}_{sorp} + \mathbf{S}_{neq}^{1'} \boldsymbol{\xi}_{neq} + \mathbf{S}_1^\top \boldsymbol{\eta}, \\
\bar{\mathbf{c}} &= \mathbf{S}_2^* \bar{\boldsymbol{\xi}} + \mathbf{S}_2^\top \bar{\boldsymbol{\eta}} = \mathbf{S}_{sorp}^2 \bar{\boldsymbol{\xi}}_{sorp} + \mathbf{S}_{imm}^2 \bar{\boldsymbol{\xi}}_{imm} + \mathbf{S}_{neq}^{2'} \bar{\boldsymbol{\xi}}_{neq} + \mathbf{S}_2^\top \bar{\boldsymbol{\eta}};
\end{aligned} \tag{13}$$

$\mathbf{S}_{mob}^1, \mathbf{S}_{sorp}^1, \mathbf{S}_{neq}^{1'}, \mathbf{S}_{sorp}^2, \mathbf{S}_{imm}^2, \mathbf{S}_{neq}^{2'}$ are subblocks of $\mathbf{S}_1, \mathbf{S}_2$.

The system (12) consists of the *decoupled* linear problems (i) for $\boldsymbol{\eta}$, a block of 'local' problems (iii), (iv), and a system of PDEs (v), (vi). The character of equation (v) is that of a 'generalized equilibrium sorption process'. To reduce the problem size once more, the blocks of local equations (iii), (iv) can (after discretization in time) be solved for the unknowns $\boldsymbol{\xi}_{mob}$, $\bar{\boldsymbol{\xi}}_{sorp}$, $\bar{\boldsymbol{\xi}}_{immob}$ and $\bar{\boldsymbol{\xi}}_{neq}$ and substituted into the remaining PDEs (v), (vi) in the sense of a DSA. The choice to solve (iii), (iv) for $\boldsymbol{\xi}_{sec} := (\boldsymbol{\xi}_{mob}, \bar{\boldsymbol{\xi}}_{sorp}, \bar{\boldsymbol{\xi}}_{immob}, \bar{\boldsymbol{\xi}}_{neq})$ corresponds to the segregation of the so-called *secondary dependent* variables from the *primary* variables $\boldsymbol{\xi}_{prim} := (\boldsymbol{\xi}_{sorp}, \boldsymbol{\xi}_{neq})$. So for our method, this distinction is not done for the original unknowns c_i, \bar{c}_i , as it is done, e.g., by [Lichtner, 1996, Molins et al., 2004], but for the new unknowns $\xi_i, \bar{\xi}_i$. The remaining nonlinearly coupled system has the structure

$$\begin{aligned} \frac{d}{dt}(\theta \boldsymbol{\xi}_{sorp} - \bar{\boldsymbol{\xi}}_{sorp}(\boldsymbol{\xi}_{sorp}, \boldsymbol{\xi}_{neq})) + \mathbf{L}\boldsymbol{\xi}_{sorp} &= \mathbf{f}_1(\boldsymbol{\xi}_{sorp}, \boldsymbol{\xi}_{neq}) \\ \frac{d}{dt}\theta \boldsymbol{\xi}_{neq} + \mathbf{L}\boldsymbol{\xi}_{neq} &= \mathbf{f}_2(\boldsymbol{\xi}_{sorp}, \boldsymbol{\xi}_{neq}). \end{aligned} \quad (14)$$

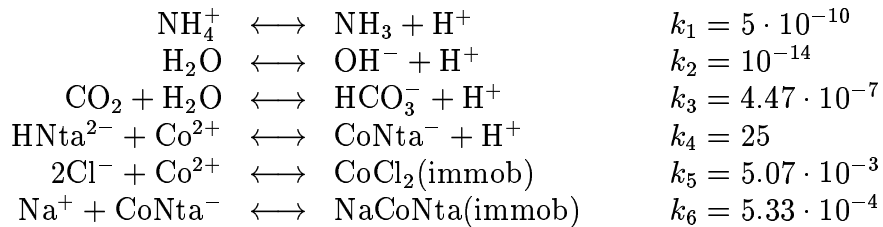
Note that (different from many other reformulations using DSA techniques), the introduction of the resolution functions for $\boldsymbol{\xi}_{mob}, \bar{\boldsymbol{\xi}}_{sorp}, \bar{\boldsymbol{\xi}}_{immob}, \bar{\boldsymbol{\xi}}_{neq}$ in (v), (vi) does not take place under the transport operator. Hence the sparsity pattern for the linear problems arising from the discretization of (12) is more convenient for efficient numerical solution with iterative linear solvers. See [Kräutle and Knabner, 2005], Sec. 3.4, for a more detailed discussion of the sparsity pattern.

The existence of the resolution functions of (iii), (iv) can be proved under the assumption of mass action law for the equilibrium reactions and a time step size $\tau > 0$ not too large [Kräutle and Knabner, 2006]. The size of remaining coupled nonlinear problem (14) is $J_{sorp} + J_{neq}'$, which is less than or equal to $J_{sorp} + J_{neq}$, which is again less than or equal to the total number of reactions J , and J is less than or equal to the size $I + \bar{I}$ of the original problem (1)/(2). See also Section 5 in [Kräutle and Knabner, 2006] Sections 3.5 and 5, for the realization of the Newton solver for the reduced problem, and for a comparison of our reduction scheme to classical formulations and to [Molins et al., 2004].

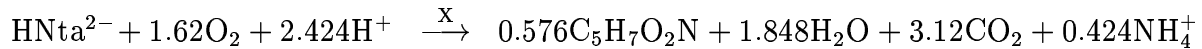
4. A NUMERICAL EXAMPLE

In order to verify the computational efficiency we applied our reduction method to several multicomponent transport reaction problems. We noticed that for all problems we considered, the number of remaining coupled PDEs was smaller than for the standard formulation in [Lichtner, 1985]. Besides a consideration of efficiency based on the size of the system, we performed computational test for several scenarios [Hoffmann, 2005]. In these tests, we compared the cpu time required with the reduction technique to program runs using the original formulation (1) (with equilibrium reactions modelled by kinetic reactions with large reaction coefficients). Let us mention the following test case:

We are considering the reaction network consisting of the six equilibrium reactions



and one kinetic biodegradation reaction



catalyzed by the biospecies X . The stoichiometry covers the main features of the Example 15 in [Parkhurst and Appelo, 1999] which was considered by Tebes-Steven and Valocchi in 1997. The fifth and the sixth reaction are mineral precipitation/dissolution reactions; however, we assume a mass-transfer limited process (diffusive transport from the bulk solution to stagnant water in contact with the mineral surface) [Tebes-Stevens, 2005] leading to mass action like law $c_{\text{Cl}^-}^2 - c_{\text{Co}^{2+}} c_{\text{CoCl}_2}^{-1} = k_5$ (for the fifth reaction). For the biodegradation reaction we assume the Monod model. We assume that the species H_2O , Cl^- , Na^+ are not significantly affected by the reactions and constant throughout the simulation; hence the corresponding concentrations/activities are incorporated into the equilibrium constants. See [Hoffmann, 2005] for the specific scenario (initial and boundary values, Monod parameters etc.).

The following table shows the cpu time required for simulations for a 2145 and for a 8385 node discretization of the computational domain. For both, test runs with the reduced and with the nonreduced scheme were performed. A cpu time reduction by a factor of four which is increasing for finer meshes can be observed.

	2145 nodes:		8385 nodes:	
	reduced	nonreduced	reduced	nonreduced
cpu time for				
assembling	10:28.87min	26:15.19min	42:09.14min	1:44:28.39h
local problems	3:17.58min	-	12:56.52min	-
linear solver	7:51.10min	56:18.38min	1:21:54.52h	7:53:24.47h
total cpu time	21:49.03min	1:23:38.00h	2:17:45.00h	9:42:05.00h
relative cpu time	26.1%	100%	23.7%	100%
average Newton steps	3.041	3.42975	3.025	3.40496
average local Newton steps	1.71019	-	1.72147	-

TABLE 1. Comparison of reduced and nonreduced scheme. Cpu times for 2145 and for 8385 node discretization.

5. SUMMARY AND OUTLOOK

We have proposed a new reduction scheme for multicomponent reactive transport problems, which is able to handle coupled mobile and immobile species and mixed equilibrium and kinetic reactions. The basic philosophy is to figure out how much the size of the nonlinear system of differential equations can be reduced *without* using splitting techniques or imposing restrictions on the stoichiometry.

A special property of the scheme is that even within those equations which remain coupled, these coupling terms do not occur under the transport operator, which would cause many nonzero entries in the Jacobian. The sparsity of the system matrix can be exploited if iterative linear solver are used. Under rather general conditions, assuming mass action law for the equilibrium reactions, the applicability of the reduction method

and the existence of the resolution functions can be guaranteed. Application to problems including minerals are possible as long as the mineral concentrations do not vanish.

The number of coupled PDEs for the canonical formulation (e.g., [Lichtner, 1996]) is the number of species minus the number of equilibrium reactions $I + \bar{I} - J_{eq}$. For [Molins et al., 2004], the resulting size is in general only slightly smaller unless splitting techniques are applied. The number of coupled nonlinear PDEs for our reduction scheme lies between J_{sorp} and $J_{sorp} + J_{neq}$, where J_{sorp} is the number of heterogeneous equilibrium reactions and J_{neq} is the number of kinetic reactions. For most stoichiometric examples, the number of remaining PDEs seems to be smaller than for the other mentioned formulations; however, there might be counterexamples. Comparisons of our GIA in terms of efficiency to methods using splitting techniques were not the subject of this article; results can be expected to depend strongly on the specific problem under consideration.

Future work will consider the full generalization of the reduction scheme to situations where constant activity species (minerals) that vanish/reappear are present in parts of the computational domain. Note that the transformation into a formulation corresponding to (12) is still valid in this situation, only the additional size reduction by elimination of certain variables (formulation (14)) has to be adapted to this case.

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