

# NEWTON-KRYLOV METHODS FOR COUPLING TRANSPORT WITH CHEMISTRY IN POROUS MEDIA

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## ABSTRACT

The simulation of multispecies reacting systems in porous media is of importance in several different fields: for computing the near field in nuclear waste simulations, in the treatment of bio-remediation, and in the evaluation of underground water quality.

When looking at a coupled system, the role of chemistry is simply to separate the species into mobile and immobile species (immobile species may come from either sorption or precipitation reactions, and are not subject to transport). In this work, we assume that the medium is saturated, and that surface reactions do not change the porosity.

Multi-species chemistry involves the solution of ordinary differential equations (if the reactions are kinetic) or nonlinear algebraic equations (if we assume local equilibrium). When simulating a coupled system, these equations have to be solved at each (grid) point, and at every time (step), leading to a huge coupled non-linear system. As has been observed several times, it is essential to use efficient numerical methods so as to be able to handle the size of systems occurring in the applications.

If we assume local equilibrium, then the coupled system may be written as a DAE. Since methods and software for solving DAEs have reached a high level of maturity (at least for small index systems, which is the case here), it is natural to try and use this technology. One important issue is the size of the system to be solved, as all chemical species at all grid points are coupled. For any realistic configuration, it will not be possible to form, let alone factor, the Jacobian matrix. A better solution is to use Newton–Krylov methods, where the linear system at each Newton iteration is solved by an iterative method. We can thus keep the fast convergence of Newton’s method, while only requiring Jacobian matrix–vector products, and these can be approximated by finite differences.

We will discuss two methods, based on different choices for the main unknowns:

In the “one level” method, we take as unknowns both the total dissolved and fixed concentrations, but also the concentrations for the component species that are the main unknowns of the chemical problem. This is closely related to the Direct Substitution Approach used by the geochemists. By carefully formulating the problem, we can put it into the DAE framework. At each time step, a single non-linear system has to be solved, and the Jacobian matrix couples both the transport matrix, and the chemistry Jacobian matrix. The method is called one-level as we solve transport and chemistry at the same time. Provided that we can access this Jacobian matrices (and this may not always be possible in practice), this may be less expensive than the two-level methods below.

The second, “two-level” method takes as unknowns only the total dissolved and fixed concentrations. The system to be solved at each time step requires the solution of the chemical sub-problem at each Newton iteration, when evaluating the residual. On the other hand, the Jacobian matrix again involves the transport matrix, as well as the Jacobian of the “chemical solution operator” mapping. This is only known implicitly, and the Jacobian has again to be evaluated by finite differences. Even though this method may be more expensive than the one-level method, its main advantage is to make it possible to treat chemistry as a black-box, even in the Newton–Krylov context. This may be important, as chemical simulators are becoming increasingly sophisticated.

A major issue for both methods will be the choice of a suitable preconditioner.

## 1. INTRODUCTION

The simulation of multispecies reacting systems in porous media is of importance in several different fields: for computing the near field in nuclear waste simulations, in the treatment of bio-remediation, and in the evaluation of underground water quality.

Multi-species chemistry involves the solution of ordinary differential equations (if the reactions are kinetic) or nonlinear algebraic equations (if we assume local equilibrium). When simulating a coupled system, these equations have to be solved at each (grid) point, and at every time (step), leading to a huge coupled non-linear system. As has been observed several times, it is essential to use efficient numerical methods so as to be able to handle the size of systems occurring in the applications.

In this paper, we study different formulations of the coupled reactive transport problem, and we compare a formulation for global coupling with the more traditional operator split approach. As the Jacobian matrix is likely to be very large, we use a Newton–iterative method to solve the non-linear system that occurs at each time step.

We start by a description of the test case that we use for comparison of our implementation of global and sequential approach, followed by the physical model. We then discuss the numerical methods we use, and present numerical results.

## 2. TEST CASE TRANSPORT AND CATION EXCHANGE

The following example of advective transport in the presence of cation exchanger is adopted as a first test case comparison of both approaches. The example is used in documentation of PHREEQC-2 [Parkhurst and Appelo (1999)] as Example 11. The one-dimensional simulation problem describes a column experiment where the chemical composition of the effluent from a column containing a cation exchanger is simulated. Initially, the column contains a sodium-potassium-nitrate solution in equilibrium with the cation exchanger. The column is then flushed with three pore volumes of calcium chloride solution. Calcium, potassium, and sodium react to equilibrium with the exchanger at all times. The flow and transport parameters used for this example are presented in 1, and the aqueous initial and flushed concentrations are listed in 2. The Cationic Exchange Capacity for the exchanger is 1.1 mmol/l.

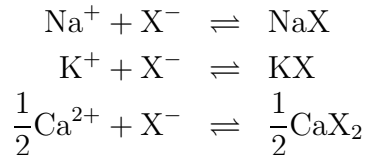
Darcy velocity	$2.78 \cdot 10^{-6}$ m/s
Diffusion coefficient	$5.56 \cdot 10^{-9}$ m <sup>2</sup> /s
Length of column	0.08 m
Mesh size	0.0002 m
Duration of experiment	1 day
Time step	720 s

TABLE 1. Physical parameters

Component	$C_{\text{init}}$	$C_{\text{inflow}}$
Ca	0	$0.6 \cdot 10^{-3}$
Cl	0	$1.2 \cdot 10^{-3}$
K	$2.0 \cdot 10^{-4}$	0
Na	$1.0 \cdot 10^{-3}$	0

TABLE 2. Aqueous concentrations

The chemical reactions for this example can be written as:



$X$  indicates exchange site with a charge -1

### 3. REACTIVE TRANSPORT EQUATIONS

**3.1. Transport model.** We consider  $N_c$  mobile species  $C_1, C_2, \dots, C_{N_c}$  and  $N_s$  sorbed species. The mobile species are convected by a known Darcy flow field  $U$  and are subject to dispersion. If we consider only transport in a single, aqueous phase, then the transport operator  $L$  is linear

$$L(C) = \nabla(U C) - \nabla \cdot (D \nabla C),$$

where  $D$  is the dispersion tensor and  $q$ . We assume that the transport operator is the same for all species, i.e.  $L(C_1, C_2, \dots, C_{N_c}) = (L_1 C_1, L_2 C_2, \dots, L_{N_c} C_{N_c})$ . The transport problem for one species is then written as

$$\frac{\partial C}{\partial t} + L(C) = q, \quad (1)$$

where  $q$  is known source term.

**3.2. Chemical equations.** In our study, we assume a local chemical equilibrium at every point. This leads to a relationship between components and products of chemical reaction: one mass action law for each chemical reaction, and one mass conservation equation for each component (we have used the Morel formalism [Morel and Hering, 1993], where each reaction involves several components that combine to give one product). This leads to a system of algebraic equations

$$\begin{cases} C = c + S^T x \\ W = s + B^T y \\ F = A^T y \\ T = C + F \end{cases} \quad \text{and} \quad \begin{cases} \log x = S \log c + \log K_x \\ \log y = A \log c + B \log s + \log K_y \end{cases} \quad (2)$$

where:

- $c, s$  are the concentrations for aqueous and sorbed component
- $x, y$  are the concentrations for aqueous and sorbed secondary species
- $T$  is the total aqueous concentrations

- $W$  is the total sorbed concentrations
- $K_x, K_y$  are vectors of equilibrium constants
- $A, B, S$  are matrices of stoichiometric coefficients,

and we have also introduced, for each component, its total dissolved concentration  $C$ , and its total sorbed concentration  $F$ .

For the coupled problem, it will be convenient to condense the chemical sub-problem by a function  $\Psi : F = \Psi(T, W)$  means that given  $T$  and  $W$ ,  $F$  we solve the above system of equations for  $c$  and  $s$ , and compute  $F$  as indicated.

**3.3. Coupled transport and chemistry.** To obtain the model coupling transport and chemistry, we write one equation like (1) for each species (if the species is immobile, we omit the term  $L(s)$ ), and we combine them using the conservation of mass relations. This leads to an equation

$$\frac{\partial T_j}{\partial t} + L(C_j) = 0 \quad j = 1, \dots, Nc$$

for each component, where

- $T_j$  is the total concentration for component  $j$ ,
- $C_j$  is the total aqueous concentration for component  $j$ .

These two quantities are related by equation (2) above, with  $T_j = C_j + F_j$ .

#### 4. DIFFERENT COUPLING ALGORITHMS

We first discretize the transport equation in time, using the backward Euler method for simplicity :

$$\frac{C^{n+1} - C^n}{\Delta t} + \frac{F^{n+1} - F^n}{\Delta t} + LC^{n+1} = q^{n+1}. \quad (3)$$

Because of diffusion, it is essential to use an implicit algorithm. On the other hand, care must be taken to properly resolve the convective part. At each time step, the system formed by equation (3) (one for each component) and equation (2) (one for each grid point) form a large nonlinear system, whose size is the number of components times the number of grid points. This system has traditionally been solved by a sequential two-steps approach, as reviewed below (cf.[Yeh and Tripathi, 1989]). However, this method suffers from several defects: it may severely restrict the step size to ensure convergence, and its convergence is only first order. Due to its quadratic convergence rate, Newton's method would be an ideal candidate for solving the system. However, we encounter a practical difficulty: Newton's method requires the solution of an linear system with the Jacobian matrix at each iteration step. In realistic situations, it will not be possible to store, much less factor, the Jacobian matrix. As we shall see in the next section, this difficulty can be overcome by resorting to iterative methods to solve the linear system. Before we detail this step, we go back to an explanation of different coupling methods.

**4.1. Sequential approach.** The sequential approach consists of separately solving the chemical equations and the transport equations. More precisely, at each time step, we first solve equation (3) for  $C^{n+1}$ , with  $F^{n+1}$  given for the chemistry substep. We then solve the chemistry system, with  $T^{n+1}$  computed with the previous value for  $C$ , and we possibly iterate the whole procedure. In the geochemical literature, this is known as an

operator splitting approach, but it is more properly a block Gauss-Seidel methods on the coupled system.

**4.2. Direct substitution approach.** This method consists in solving for the individual concentrations of the components, that is *substituting* equations (2) in equation (1) (this can be done explicitly, cf. [Hammond et al. 2005], or implicitly, cf. [Saaltink et al. (1998)], [Erhel (2005)]). It is also possible to reformulate the problem as a differential algebraic system (DAE), and to take advantage of the high quality software available for such problems.

**4.3. Two level global algorithm.** In this approach, we do not directly substitute the chemical equations in the transport equation, but we use the function  $\Psi$  introduced previously to represent the effect of chemistry. Different formulations can be adopted depending on the choice of unknowns. We have chosen to use both the total dissolved and mobile concentrations, and also the total concentrations. After spatial discretization (but still denoting the discrete operator by  $L$ ), our problem can be written as

$$\begin{cases} (I + \Delta t L)C^{n+1} = C^n + \Delta t q^{n+1} - (F^{n+1} - F^n) \\ T^{n+1} = C^{n+1} + F^{n+1} \\ F^{n+1} = \psi(T^{n+1}) \end{cases} \quad (4)$$

## 5. NUMERICAL METHODS

It is impractical to attack the nonlinear system (4) directly. The numerical methods for transport and chemistry are quite different, and it is even possible that simulation codes have been written by different groups. The formulation given above lends itself to an implementation of Newton’s method that allows to keep the two codes separate. The Jacobian may even be formed in block form, provided the individual codes provide their Jacobians (this is obviously easier for transport than for chemistry). Before we detail how we solve the coupled problem, it is worth saying a few words about the chemistry subproblem (the transport step is easier, or at least more common. We have used a simple upwind finite difference for our 1D example).

**5.1. Chemistry.** As we have seen before the chemical problem can be written as:

$$\begin{cases} T = c + S^T x + A^T y \\ W = s + B^T y \\ \log x = S \log c + \log K_x \\ \log y = A \log c + B \log s + \log K_y \end{cases}$$

$T$  is determined by the transport equation, and for simplicity we assume that  $W$  is constant (in our case, it is simply the Cationic Exchange Capacity of the exchanger).

Due to the wildly different orders of magnitude of the concentrations that are commonly encountered, we have reformulated the chemical problem by using as main unknowns the logarithms of the concentrations. This has the added advantage that concentrations are automatically positive, and has become the standard way to solve the problem [van der Lee (1993)]. As is well known, Newton’s is not always convergent, and especially for a code that is designed to be used in coupling applications, it is essential to ensure that the solver “always” works. We have found that using a globalized version

of Newton’s method (using a line search, cf. [Kelley (1995)]) was effective in making the algorithm converge from an arbitrary initial guess.

**5.2. Algorithm for the coupled problem: Newton–Krylov method.** As mentioned above, it is impractical to solve the coupled problem (4) by the classical Newton’s method, due to the size of the Jacobian. A possible solution is provided by the Newton–Krylov method (see [Kelley (1995)], [Knoll and Keyes 2004] and [Hammond et al. 2005], to which our work is closely related), where the linear system that arises at each step of Newton’s method is solved by an *iterative* method (of Krylov type). The main advantage of this type of method is that the full Jacobian is not needed, one just needs to be able to compute the product of the Jacobian with a vector. As this is a directional derivative, this leads to the Jacobian free methods, where this product is approximated by finite differences. However, in our particular case, it is possible to compute the needed directional derivative exactly, provided we can obtain the Jacobian of the chemical subproblem. This is both cheaper and more accurate.

The Jacobian matrix has a natural block structure, and it is natural to exploit it when computing the matrix–vector product: if we number the unknowns as  $(C, T, F)$ , the Jacobian is

$$J = \begin{pmatrix} I & 0 & \mathcal{L} \\ I & -I & -I \\ 0 & \Psi'(T) & -I \end{pmatrix},$$

where  $\mathcal{L} = \text{diag}(L, L, \dots, L)$  and  $\Psi'(T)$  is the Jacobian of  $\Psi$ , that also has a block structure (though it is not block diagonal, as the unknowns have been number per species). The Jacobian matrix–vector product can be computed block by block. Within the first block, the computation is done species by species, and within the last block, kit is done grid point by grid point. This gives a natural parallelism to the method, without sacrificing the fast convergence rate of Newton’s method.

The Krylov method is used to solve the linear system  $J\delta x^k = -f(x^k)$ . An initial linear residual  $r_0$  is defined, given an initial guess  $\delta x_0$  (is typically zero), for the Newton correction,

$$r_0 = -f(x) - J\delta x_0$$

Let  $j$  the Krylov iteration index, the  $j$ th iteration minimizes  $\|J\delta x_j + f(x)\|_2$   $\delta x_j$  is drawn from the subspace spanned by Krylov vectors,  $\{r_0, Jr_0, J^2r_0, \dots, J^{j-1}r_0\}$ , and can be written as

$$\delta x_j = \delta x_0 + \sum_{i=0}^{j-1} \beta_i J^i r_0$$

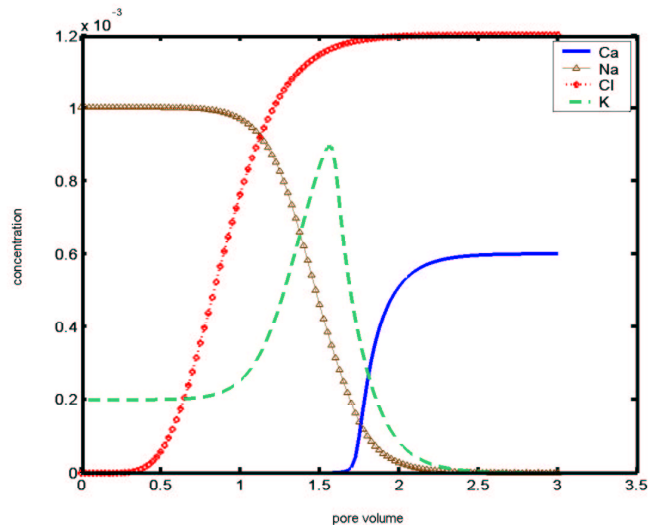
where the scalars  $\beta_i$  are computed so as to minimize the residual (see [Kelley (1995)] for details and an account of the theoretical justifications, that show how accurately the inner linear system should be solved depending on the outer iterations). It is also necessary to globalize the algorithm, and this can be done just as in the “classical” Newton’s method.

In our application, we found that Newton- iterative method was more robust than Newton’s method based on a direct solution of the linear system, in the sense that it is less sensitive to the both grid size and chemistry.

## 6. NUMERICAL RESULTS

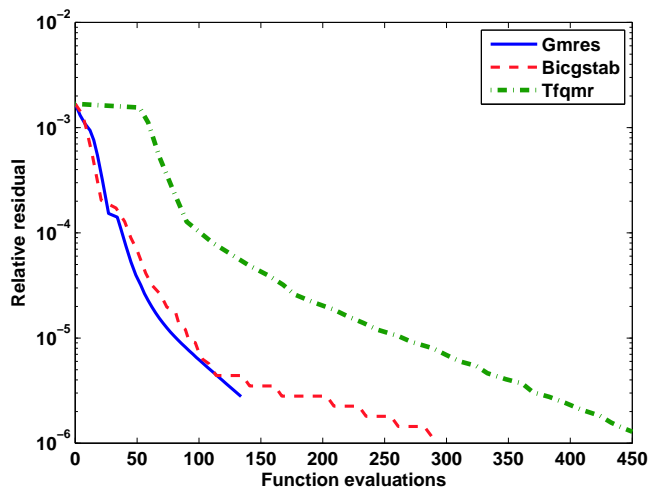
In this part we apply both the sequential method and the two-level method to the test case described in section 2 and compare both computational demands and the accuracy of the solution. The results obtained by the both approaches are analogous, they are shown in the same figure below, and they are similar to the results in [Parkhurst and Appelo (1999)].

The figure to the right shows elution curves, that is the evolution of the concentration of the various species at the end of the column, as a function of time. The sorbed potassium and sodium ions are successively replaced by calcium. Because potassium exchanges more strongly than sodium (as indicated by a larger value of  $\log K$  in the exchange reaction), sodium is released first, followed by potassium. Finally when all of concentration has been released, the concentration of calcium increases to its steady-state value, the potassium is displaced from the exchanger and the concentration in solution increases to balance the  $\text{Cl}^-$  concentration.



Experimental results show that the sequential approach require less CPU time then the global approach for a small number of nodes and a simple chemical problem such as the one considered here, but for larger grids the global approach seems to be the most appropriate, faster than the sequential one, because of the use of an iterative method and a good choice of the preconditioner will accelerate the convergence and reduce the CPU time of the global approach.

We also look at the efficiency of the Newton-Krylov method. We plot the nonlinear residual versus the number of function calls, for a typical time step. Note that this includes the function evaluations needed for the linear GMRES iterations. As expected, when we compare different linear solvers, GMRES required fewer calls than other solvers BICGSTAB, TFQMR, but the cost of one iteration is more expensive for GMRES.



## 7. CONCLUSIONS – PERSPECTIVES

The preliminary results we have shown are promising: it is possible to solve efficiently geochemical problems using a Newton–Krylov method. This investigation is just beginning, and there remains several issues that need to be addressed.

- the first is to run test cases on more demanding configurations, where we expect the method to show its full potential.
- it will then certainly be necessary to explore the question of how to precondition the Jacobian, to reduce the number of Krylov iterations. A natural avenue is to reuse the operator splitting methods, as proposed by [Hammond et al. 2005].
- A more difficult problem will be to take into account precipitation–dissolution phenomena in the chemical model. As the models are non-differentiable, this makes it more difficult to employ Newton’s method.

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