Solving Partial Differential Algebraic Equations and reactive transport models

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Note

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Abstract

In some scientific applications, such as groundwater studies, several processes are represented by coupled models. For example, a density-driven flow model couples the flow equations with the transport of salt. A reactive transport model couples transport equations of pollutants with chemical equations. The coupled model can combine partial differential equations with algebraic equations, in a so-called PDAE system, which is in general nonlinear. A classical approach is to follow a method of lines, where space is first discretized, leading to a semi-discrete differential algebraic system (DAE). Then time is discretized by a scheme tuned for DAE, such that each time step requires solving a nonlinear system of equations. In some decoupled approaches, a fixed-point technique is used. However, a Newton method converges faster in general and is more efficient, even though each iteration is more CPU-intensive. In this paper, we deal with reactive transport models and show how a Newton method can be used efficiently. Numerical experiments illustrate the efficiency of a substitution technique. Moreover, it appears that using logarithms in the chemistry equations lead to ill conditioned matrices and increase the computational cost.

Keywords : PDAE, Newton, fixed-point, domain decomposition.

1 Introduction

Underground media both provide natural resources and potential sites for waste storage. On one hand, permeable geological layers bear resources like water or oil. On the other hand, less pervious sites are considered for containing nuclear waste and more recently CO_2. Examples of applications concern freshwater supply, remediation of mine drainage, waste geological disposal. These opposed objectives reveal first the large differences in hydrogeological conditions echoing the heterogeneity of the subsurface environment. The opposed resource and storage objectives also reveal a wide panel of chemical interactions. The fate of contaminants in aquifers is controlled by acido-basic reactions, oxydo-reduction reactions, precipitation-dissolution of minerals and chemical sorption [16].

Numerical simulations are essential for studying the fate of contaminants in aquifers and are a first step towards the determination of upscaling rules. Also, risk assessment and resources management rely on numerical simulations at large scale [2], [41]. Chemical reactions must be coupled with advection and dispersion when modeling the contamination of aquifers. Reactive transport models face a real challenge in simulating accurately sharp fronts and their evolution in space and time. These numerical difficulties require adaptive discrete schemes and advanced computational tools. On the physical side, the transport model of mobile species includes the advection, diffusion and dispersion processes. On the chemical side, models handle kinetic reactions and thermodynamic equilibrium, including fluid-rock interactions and reactions in solution. Transport and chemistry models are coupled through the immobile species, inducing a reactive transport model which is a global system of nonlinear Partial Differential Algebraic Equations (PDAE).

Several methods have been designed for solving this system of PDAE. Most approaches can be described with a method of lines, where space is first discretized to yield a semi-discrete system of Differential Algebraic Equations (DAE), which is then discretized in time [20]. A unified framework is proposed in [13] to describe the different approaches.

A Sequential Non Iterative Approach (SNIA) uses in general an explicit Euler scheme, where a chemistry solver is interfaced with a transport solver ; for example, PHREEQC is coupled with HST3D in PHAST [32], and SPECY [8]. A Sequential Iterative Approach (SIA) uses in general an implicit Euler scheme, which is stable and does not require a small time step, unlike an explicit scheme used in a sequential non iterative approach. The resulting nonlinear system is solved at each time step with a fixed-point method. Thus chemistry can also be separated from transport ; for example, SIA is implemented in HYDROGEOCHEM [40], HYTEC using the geochemistry model CHESS [37]. In a global approach, an implicit Euler scheme is also used in general, still without stability restrictions, but non-linear equations are solved at each time step with a Newton method. The model can be based on a reduction scheme [23] or on total analytical concentrations [13]. Compared with a sequential approach, the main drawback of a global approach is that chemistry functions cannot be derived from a black-box software. However, it should be pointed out that chemistry and transport modules can be well separated. Another drawback is the size of the global system, whereas independent systems are solved at each mesh point in sequential approaches. But a Newton method converges faster than a fixed-point method [14], [21]. Moreover, it seems that it can take larger time steps than a sequential approach. Among the software currently built up on this approach are CRUNCHFLOW [36], RETRASO [34], TOUGHREACT [38], MIN3P [26], and GRT3D [35].

The benchmark Momas was designed as a set of academic examples, in order to run experiments with several methods and software [7], [5]. Several authors participated in the exercise [27], [19], [24], [1], [12]. A synthetic comparison of their results indicate that, for this benchmark, the fastest results were obtained with global approaches [6].

A global approach can be designed in different ways. Here we use an approach based on a distinction between components and secondary species and on the introduction of total analytical concentrations. Once the scheme for time discretization is chosen, a so-called substitution technique eliminates the total analytical concentrations, in order to keep only the concentrations of species. Classically, a global approach uses an implicit Euler scheme and must design a control of the time step. However, using a DAE solver provides time discretization with a variable order, an adaptive control of time step and of Newton convergence [13]. With this technique, the total analytical concentrations are kept in the system. In this paper, we show that it is still possible to use a substitution technique with a DAE framework.

Since concentrations of species are positive and because mass action laws in the chemistry model involve products and powers, it seems natural to use logarithms of concentrations (assumed strictly positive) as unknowns. In this paper, we compare two chemistry models, one with logarithms and the other one without logarithms. We observe experimentally that the Jacobian in the Newton iterations is better conditioned without logarithms and that CPU time is drastically reduced.

The paper is organized as follows. In section 2, we define the chemistry model. In section 3, we define the coupled reactive transport model and show how substitution can be done in the numerical model using a DAE solver. The software developed to implement the numerical model is described in section 4, and numerical experiments are discussed in section 5. Concluding remarks are in section 6.

2 Chemistry model

We consider a geochemical system composed of aqueous, sorbed and precipitated chemical species and we assume that all chemical processes are in thermodynamical equilibrium. We use the model defined in [11], [13], [12], except that we do not introduce logarithms.

2.1 Mass action laws

Following the method proposed in [30, 31], we split the species into components (primary species) and secondary species. Moreover, we define separately aqueous and fixed species.

We introduce the following notations :
- N_c is the number of aqueous components,
- N_s is the number of sorbed components,
- N_x is the number of secondary aqueous species,
- N_y is the number of secondary sorbed species,
- N_p is the number of minerals,
- $c \in \mathbf{R}^{N_c}$ is the vector of concentrations of the aqueous components,
- $s \in \mathbf{R}^{N_s}$ is the vector of concentrations of the sorbed components,
- $x \in \mathbf{R}^{N_x}$ is the vector of concentrations of the aqueous secondary species,
- $y \in \mathbf{R}^{N_y}$ is the vector of concentrations of the sorbed secondary species,
- $p \in \mathbf{R}^{N_p}$ is the vector of the number of moles of the precipitated species per unit of volume.

The chemistry model has thus $(N_c + N_s + N_p)$ unknowns $X^T = (c, s, p)$.

The chemical reactions between aqueous and sorbed species are described by the mass action laws, where we use the same notation for a chemical species and its concentrations and take the activity coefficients equal to one ; the mass action laws are written

$$\begin{cases} x_i(c) = K_{ci} \prod_{j=1}^{N_c} c_j^{S_{ij}}, \quad i = 1, \dots N_x, \\ y_i(c,s) = K_{si} \prod_{j=1}^{N_c} c_j^{A_{ij}} \prod_{j=1}^{N_s} s_j^{B_{ij}}, \quad i = 1, \dots N_y, \\ c_i \geq 0, \quad i = 1, \dots N_c, \\ s_i \geq 0, \quad i = 1, \dots N_s. \end{cases} \tag{1}$$

where :
- $K_c \in \mathbf{R}^{N_x}$ and $K_s \in \mathbf{R}^{N_y}$ are the vectors of equilibrium constants,
- $S \in \mathbf{R}^{N_x \times N_c}, A \in \mathbf{R}^{N_y \times N_c}, B \in \mathbf{R}^{N_y \times N_s}$ are the stoichiometric coefficients.

At equilibrium, reactions of precipitation and dissolution are governed by a saturation threshold $\Pi \in \mathbf{R}^{N_p}$ defined by

$$\Pi_i(c) = K_{pi} \prod_{j=1}^{N_c} c_j^{E_{ij}}, \quad i = 1, \dots N_p, \tag{2}$$

where
- $K_p \in \mathbf{R}^{N_p}$ is a vector of constants,
- $E \in \mathbf{R}^{N_p \times N_c}$ is a matrix of coefficients.

Below a threshold value, the mineral is dissolved and above, it precipitates.

This model can be written as a linear complementary problem [9] :

$$\begin{cases} p_i(1 - \Pi_i(c)) = 0, \\ p_i \geq 0, \\ \Pi_i \leq 1. \end{cases}$$

Semi-smooth Newton methods can be used to solve this difficult problem [4]. From now on, we assume that each mineral is either always totally dissolved ($p_i = 0$) or never totally dissolved ($p_i > 0$) ; with this assumption, the number N_p of precipitated species where the threshold is attained is known and fixed, so that the equations above can be rewritten as

$$\begin{cases} \Pi(c) - 1 = 0, \\ p > 0, \end{cases} \tag{3}$$

where Π is defined by equations (2). A classical Newton method can be used to solve this nonlinear problem.

2.2 Mass conservation laws

Mass action laws are completed by a mass conservation relation for each component. Let T and W be the total analytical concentrations for mobile and fixed components [25], [22]. In the context of a closed chemical system, T and W are given. For an open system, W and T are obtained by coupling the chemistry model with another model.

These total concentrations are expressed with the concentrations c, s, x, y, p. Let

$$\Phi(X) = \begin{pmatrix} c + S^T x(c) + A^T y(c,s) + E^T p \\ s + B^T y(c,s) \\ \Pi(c) \end{pmatrix} \tag{4}$$

where $x(c)$ and $y(c,s)$ are given by equations (1) and $\Pi(c)$ is given by (2). The chemistry model is then written

$$\begin{cases} \Phi(X) = \begin{pmatrix} T \\ W \\ 1 \end{pmatrix}, \\ c \geq 0, \\ s \geq 0, \\ p > 0. \end{cases} \tag{5}$$

When T and W are given, it is a nonlinear system of $(N_c+N_s+N_p)$ unknowns with $(N_c+N_s+N_p)$ equations and inequality constraints.

We assume that the system has a unique solution, that the functions are differentiable and that the Jacobian of the system is non singular.

The Jacobian of this system is given by

$$\Psi(X) = \begin{pmatrix} I + S^T \frac{dx}{dc} + A^T \frac{\partial y}{\partial c} & A^T \frac{\partial y}{\partial s} & E^T \\ B^T \frac{\partial y}{\partial c} & I + B^T \frac{\partial y}{\partial s} & 0 \\ \frac{d\Pi}{dc} & 0 & 0 \end{pmatrix},$$

where the derivatives are computed from (1) and (2).

2.3 Model with logarithms

In some models, it is further assumed that $c > 0$ and $s > 0$ so that these unknowns can be defined by their logarithms [11], [13], [12]. In other words, the vector X is replaced by the vector $\hat{X}^T = (\hat{c}, \hat{s}, p)$, with $\hat{c} = \log c$, $\hat{s} = \log s$ (log means the natural logarithm here). The nonlinear function $\Phi(X)$ is replaced by $\hat{\Phi}(\hat{X})$ and the Jacobian is replaced by $\hat{\Psi}(\hat{X})$. The positivity constraints are of course satisfied. Moreover, the derivatives are quite easy to compute. Indeed, we get

$$\begin{cases} x = \exp\left(\log K_c + S\,\hat{c}\right), \\ y = \exp\left(\log K_s + A\,\hat{c} + B\,\hat{s}\right), \end{cases}$$

and the Jacobian is written

$$\hat{\Psi}(\hat{X}) = \begin{pmatrix} \mathbf{diag}(\exp(\hat{c})) + S^T \mathbf{diag}(x)\, S + A^T \mathbf{diag}(y)\, A & A^T \mathbf{diag}(y)\, B & E^T \\ B^T\,\mathbf{diag}(y)\, A & \mathbf{diag}(\exp(\hat{s})) + B^T \mathbf{diag}(y)\, B & 0 \\ E & 0 & 0 \end{pmatrix},$$

where $\mathbf{diag}(y)$ is a diagonal matrix with the vector y along the diagonal.

However, this formulation with logarithms has several drawbacks. Since the concentrations are strictly positive, all the components must be present. In practice, a null concentration is replaced by a very small value.

Let us consider the impact on the Jacobian : the upper left identity block is replaced by $\mathbf{diag}(\exp(\hat{c}))$. When the concentration c_i of a component i is very small, the corresponding line in the block is close to zero. The same remark can be done with s.

Now, consider the case of a spectator ion, which is an inert component. The corresponding stoichiometric coefficients are thus zero. Then the corresponding line in the Jacobian is close to zero and the Jacobian is close to singularity. This is not a real problem since this component can be removed from the model. But in our experiments, we observed that the Jacobian becomes also close to singularity when an active component becomes very small.

On the other hand, when dealing directly with c and s, we observed that the Jacobian is well conditioned, thanks to the identity blocks. Moreover, the concentrations of some components can be zero.

2.4 Chemistry solvers

In reactive transport models, it is useful to define the total mobile concentrations

$$C(X) = c + S^T x(c). \tag{6}$$

Most chemistry solvers get T and W as input and compute X and $C(X)$ as output. Some solvers use the logarithms and some others not, but it is not always clearly stated. The solver is in general based on a modified Newton method, with global convergence. The software implementing a chemistry solver is in general a black box, in the sense that there is no function returning the nonlinear equations or their derivatives. In particular, there is no software module providing the function $\Phi(X)$ or the Jacobian $\Psi(X)$.

3 Model of reactive transport

3.1 Transport equations

We consider a porous medium in the subsurface and make some classical assumptions :
- the flow is stationary and the porous medium is saturated ;
- the fluid velocity v is computed beforehand by a flow simulation ;
- the porosity is constant ;
- the transport by advection and dispersion affects only aqueous species (by definition) ;
- the dispersion coefficients do not depend on the species.

The dispersion tensor is defined by

$$D = d_m I + \alpha_T \|v\| I + (\alpha_L - \alpha_T) \frac{vv^T}{\|v\|},$$

where d_m is the molecular diffusion coefficient, α_L (resp. α_T) is the longitudinal (resp. transverse) dispersion coefficient.

Under these assumptions, transport can be written

$$\mathcal{L}(u) = \nabla \cdot (vu - D\nabla u) \, .$$

Both v and D may depend on space but do not depend on u so that $\mathcal{L}$ is linear.

Transport equations are defined for each species, with a given source term and a chemistry reaction term. Of course, in the equilibrium case, these reaction terms are not known but it is possible to eliminate them by different ways. A solution is to reduce the number of transport equations and to decouple some of them [23], [33], [28].

Here, we use the components and secondary species introduced above, as well as the total analytical concentrations T_i and the total mobile concentrations C_i [39], [3]. With this strategy, it is possible to write a set of independent transport equations for each aqueous component

$$\omega \frac{\partial T_i}{\partial t} + \mathcal{L}(C_i) = Q_i, \quad i = 1, \ldots, N_c, \tag{7}$$

where ω is the given porosity and Q_i is a given source term of the i aqueous component.

These partial differential equations are written in a domain Ω of $\mathbf{R}^3$, completed by boundary conditions. For example, Dirichlet conditions prescribe T for inflow and Neumann conditions prescribe the flux for outflow. Fluxes of fixed species are zero thus fluxes of T and C are equal, so that Neumann boundary conditions can be applied directly to C. Moreover, an initial condition prescribes T at the initial time.

Transport equations (7) (with boundary and initial conditions) are coupled with the chemistry equations (5) to get the reactive transport model. We assume that the total concentrations W of fixed components, written at each point of Ω, are constant in space and time.

3.2 Space discretization

We choose to discretize the equations by the method of lines [20]. For example, we do not consider a splitting of the transport operator into an advection part and a dispersion part.

The method of lines first applies a spatial discretization to the transport operator $\mathcal{L}$, where the Partial Differential Equations (7) are replaced by a system of Differential Equations of finite dimension. This discretization can be achieved for example by a Finite Difference or a Finite Element Method, using a mesh of the computational domain. We do not discuss here the choice of the scheme, but it should avoid numerical artefacts such as oscillations or artificial diffusion [20].

Let N_m be the number of unknowns in the mesh, called points in the following. The linear transport operator $\mathcal{L}(u)$ is discretized by $LU - G$, with $L \in \mathbf{R}^{N_m \times N_m}$, where U represents the discretization of u, $G \in \mathbf{R}^{N_m}$ represents the contributions of the boundary conditions.

The discretized transport model is coupled with the chemistry model, which is written for each point of the mesh, in order to get N_m chemistry equations.

In order to get well-defined notations, we introduce a matrix storage of the data. The matrix $T \in \mathbf{R}^{N_c \times N_m}$ is written $T = (T_1, \ldots, T_{N_m})$. Each column of T, denoted by $T_j, j = 1, \ldots, N_m$, represents all the components at one point of the mesh and each row of T, noted $T_i, i = 1, \ldots, N_c$, represents one component at all points of the mesh. Other variables and data C, Q, G follow the same storage with the same size.

The matrix $X \in \mathbf{R}^{(N_c+N_s+N_p) \times N_m}$ is also defined as $X = (X_1, \ldots, X_{N_m})$. We introduce the matrix $F = (F_1, \ldots, F_{N_m}) \in \mathbf{R}^{(N_c+N_s+N_p) \times N_m}$, with $F_j = (0, W_j, 1)$, where W_j is given and constant.

We also define the matrix $N = \begin{pmatrix} I \\ 0 \\ 0 \end{pmatrix} \in \mathbf{R}^{(N_c+N_s+N_p) \times N_c}$.

With these notations, the semi-discretized reactive transport model is written

$$\left\{ \begin{array}{l} \omega \frac{dT_i}{dt} + LC_i(X) = Q_i + G_i, \quad i = 1, \ldots, N_c, \\ \Phi(X_j) = NT_j + F_j, \quad j = 1, \ldots, N_m, \\ \text{initial condition for } T, \end{array} \right. \tag{8}$$

where $C(X)$ is defined by (6) and $\Phi(X)$ is defined by (4).

This semi-discrete reactive transport numerical model is a system of Differential Algebraic Equations of index one (DAE) [17]. Indeed, if we differentiate only once the algebraic chemistry equations, we get a system of Ordinary Differential Equations (ODE). This implies that the differentiation index is equal to one.

3.3 Time discretization

We can use the framework of DAE solvers to define the time discretization [13]. We introduce the $\mathbf{vec}$ operator, which rearranges matrices into vectors and we use the Kronecker product $(L \otimes I)$. We also define the variable $Y^T = \begin{pmatrix} \mathbf{vec}\, T, \mathbf{vec}\, X \end{pmatrix}$ of size $N_m(2N_c + N_s + N_p)$.

System (8) can be written

$$M \frac{dY}{dt} + f(Y) = 0, \tag{9}$$

where $M = \begin{pmatrix} \omega I & 0 \\ 0 & 0 \end{pmatrix}$, $f(Y) = \begin{pmatrix} (L \otimes I)\mathbf{vec}\, C(X) - \mathbf{vec}\, Q - \mathbf{vec}\, G \\ \mathbf{vec}\, \Phi(X) - (I \otimes N)\mathbf{vec}\, T - \mathbf{vec}\, F \end{pmatrix}$.

The Jacobian J of f is

$$J(Y) = \begin{pmatrix} 0 & (L \otimes I)\mathbf{diag}(\frac{dC}{dX}(X_j)) \\ -I \otimes N & \mathbf{diag}(\Psi(X_j)) \end{pmatrix}.$$

Here $\mathbf{diag}(\Psi(X_j))$ is the block-diagonal matrix composed of the blocks $\Psi(X_j)$ which are the chemistry Jacobian matrices defined at each point j of the mesh.

When dealing with logarithms of concentrations, the variable X is replaced by $\hat{X}$.

An efficient way to solve the DAE equations is to use a DAE solver with an implicit time discretization [13], [12]. This method is a generalization of a global approach, where an implicit Euler scheme with a fixed time step is classically used [6]. A big advantage of DAE solvers is their control of accuracy and robustness, with a variable order scheme, a variable time step and a control of Jacobian updates, ensuring convergence of Newton iterations. It is in principle possible to implement these controls but they are rather sophisticated in DAE solvers and not so easy to reproduce.

3.4 Size reduction with substitution

On the other hand, an apparent drawback of the DAE solver is the size of the nonlinear systems at each timestep, with the unknown $Y^T = (T, X)$ [6]. In a global approach with substitution, only X is unknown in the nonlinear systems. Here, we show that it is easy to eliminate T in the nonlinear equations, in order to get a nonlinear system with only X as unknown.

Using for example a BDF scheme, the derivative is approximated by

$$\frac{dY}{dt} \simeq \frac{a}{\Delta t} Y + \frac{1}{\Delta t} Z,$$

where a is a real and Z is a linear combination of values of Y at previous times. Then, at each time step, the implicit scheme requires solving the nonlinear system

$$M(\frac{a}{\Delta t} Y + \frac{1}{\Delta t} Z) + f(Y) = 0,$$

which is written here :

$$\begin{cases} \frac{a\omega}{\Delta t}\mathbf{vec}\, T + (L \otimes I)\mathbf{vec}\, C(X) - ... = 0, \\ -(I \otimes N)\mathbf{vec}\, T + \mathbf{vec}\, \Phi(X) - ... = 0, \end{cases}$$

where ... means a known quantity. It is easy to eliminate T from this system, yielding the nonlinear system $R(X) = 0$, with

$$R(X) = \frac{\Delta t}{a\omega}(L \otimes N)\, \mathbf{vec}\, C(X) + \mathbf{vec}\, \Phi(X) - ... = 0.$$

The Jacobian of R is

$$J_R(X) = \frac{\Delta t}{a\omega}(L \otimes N)\, \mathbf{diag}\, (\frac{dC}{dX}(X_j)) + \mathbf{diag}(\Psi(X_j)).$$

This elimination can also be done at the linear level.

Thus using a DAE solver is as efficient as a global approach with substitution and provides efficient controls of convergence and accuracy.

4 Software GRT3D

We have developed a scientific software, called GRT3D, implementing the numerical model described above [35]. We used a modular approach, where transport and chemistry modules are well defined and isolated.

- The transport modules define the discretized operator L, the source term Q and the boundary conditions G. They use a flow module which computes the velocity v. In our experiments, we use MODFLOW and MT3D libraries [41], but any library could be interfaced.
- The chemistry modules define the functions $\Phi(X)$ and $C(X)$ with their derivatives $\Psi(X)$ and $\frac{dC}{dX}(X)$. Since we did not find any library providing these functions, we implemented these modules.

Using the transport and chemistry modules, it is easy to implement the functions $f(Y)$, $R(X)$ and the derivatives $J(Y)$, $J_R(X)$. We apply a DAE solver (in our experiments, the IDA module, from the SUNDIALS package [18]), to which we provide the mass matrix M, the functions, the Jacobians and consistent initial conditions.

The DAE solver implements an implicit time discretization based on a BDF scheme ; at each time step, it solves a nonlinear system of equations with the Newton-LU method, meaning that the linearized equations are solved with a direct method based on a LU factorization. The DAE solver uses a modified Newton method, where the Jacobian and its factorization are freezed during several iterations. The solver controls accuracy and convergence and updates the Jacobian only when necessary. The Jacobian is stored in a sparse matrix and we use a sparse direct solver interfaced with the DAE solver (in our experiments, UMFPACK [10]).

We designed three versions of our software GRT3D :

- the first version implements a model with logarithms and with T, X, C as unknowns. It does not eliminate them in the system [11], [35].
- the reduced version still uses logarithms but eliminates T and C, keeping only X. For practical reasons, substitution is done in the linearized equations.
- the optimized version does not use logarithms and keeps only X in the linearized equations.

5 Numerical experiments

We run numerical simulations for a test case provided by ANDRA (French national agency for nuclear waste storage). More precisely, we use the second test case of the qualification plan of Alliances project (Alliances 6.2) [29], [11], [35]. It simulates the injection of alcaline water (Na OH) in a 2D porous medium containing quartz grains (SiO_2).

5.1 Chemistry model

The reactions involved here are :

$$\begin{array}{llll} H_2O & \leftrightarrow & H^+ + \mathrm{OH}^- & K_1 = 10^{-14} \\ H_4\mathrm{SiO}_4 & \leftrightarrow & H_3\mathrm{SiO}_4^- + H^+ & K_2 = 10^{-9.8} \\ H_4\mathrm{SiO}_4 & \leftrightarrow & \mathrm{SiO}_2(s) + 2H_2\mathrm{O} & K_3 = 10^{3.6} \end{array} \tag{10}$$

The chemical system is thus composed of :

- three aqueous components Na^+, OH^- and $H_4\mathrm{SiO}_4$,
- one precipitated species $\mathrm{SiO}_2(s)$,
- two aqueous secondary species H^+ and $H_3\mathrm{SiO}_4^-$.

It should be noted that Na^+ is a spectator ion here, since it does not participate in the chemical reactions. As the medium is composed of quartz grains, the number of moles of $\mathrm{SiO}_2(s)$ remains strictly positive during the whole simulation.

For this test case, we can write in detail all the chemical equations and we get

$$\begin{aligned}
c_{H_4SiO_4} &= \frac{1}{K_3}, x_{H^+} = \frac{K_1}{c_{OH^-}}, x_{H_3SiO_4^-} = \frac{K_2}{K_1} c_{H_4SiO_4} c_{OH^-},\\
C_{Na^+} &= c_{Na^+}, C_{OH^-} = c_{OH^-} - x_{H^+} + x_{H_3SiO_4^-}, C_{_{H_4SiO_4}} = c_{H_4SiO_4} + x_{H_3SiO_4^-},\\
T_{Na^+} &= C_{Na^+}, T_{OH^-} = C_{OH^-}, T_{_{H_4SiO_4}} = C_{_{H_4SiO_4}} + p_{SiO_2}.
\end{aligned}$$

Here, we could eliminate the unknown $c_{H_4SiO_4}$ which is constant, but we keep it and use it for validation.

Moreover, we can write the law of electric neutrality :

$$T_{Na^+} = C_{Na^+} = T_{OH^-} = C_{OH^-},$$

which is equivalent to

$$c_{Na^+} - c_{OH^-} + x_{H^+} - x_{H_3SiO_4^-} = 0.$$

Still for validation, we do not use this invariant for reducing the size of the system.

When C_{OH^-} is known, it is easy to compute the pH (equal to $-\log_{10} x_{H^+}$) in the porous medium. Indeed, the concentration x_{H^+} is solution of the quadratic equation

$$x_{H^+}^2 + (C_{OH^-})x_{H^+} - (K_1 + \frac{K_2}{K_3}) = 0. \tag{11}$$

5.2 Initial conditions

The 2D domain is a rectangular of length 5 m and width 3.5 m. Initially, the porous medium contains everywhere 10 moles of quartz by volume of one liter and does not contain any sodium. Alcaline water is injected at the point M of coordinates $(1, 1.75)$. These initial conditions, which respect the law of electric neutrality, are given in Table 1.

condition	Na^+	OH^-	H_4SiO_4
Initial T except M	0	0	10.
Initial T at M	10^{-2}	10^{-2}	10.

TABLE 1 – Initial chemical composition (unit : $mol.l^{-1}$).

We can compute the pH outside the injection point. Here, $C_{OH^-} = 0$ thus the solution of equation (11) is

$$x_{H^+} = (K_1 + \frac{K_2}{K_3})^{1/2},$$

showing that the initial pH in the porous medium is close to 7.

At the injection point, $C_{OH^-} = 10^{-2}$, thus, by solving equation (11), we get an initial pH close to 12.

5.3 Transport data

The porosity is taken equal to 1 in the whole domain. We consider a transport by advection and dispersion, with a constant flow velocity and constant dispersion coefficients, given in Table 2. The duration of simulation is 30 days. No flux boundary conditions (homogeneous Neumann conditions) are imposed everywhere at the border.

Data	Value
porosity ω	1.
longitudinal flow velocity v_1	$5.7\,10^{-7}\,\mathrm{m.s}^{-1}$
transverse flow velocity v_2	$0\,\mathrm{m.s}^{-1}$
molecular diffusion coefficient d_m	0
longitudinal dispersion coefficient α_L	$0.2\,\mathrm{m}$
transverse dispersion coefficient α_T	$0.05\,\mathrm{m}$
time duration	$2.592\,10^6$ s (30 days)
boundary conditions	no flux

TABLE 2 – Transport conditions.

Since we have $T_{Na^+} = T_{OH^-} = C_{Na^+} = C_{OH^-}$, we get the same transport equation for both C_{Na^+} and C_{OH^-}, which is

$$\frac{\partial C}{\partial t} = -v_1 \frac{\partial C}{\partial x} + \alpha_L v_1 \frac{\partial^2 C}{\partial^2 x} + \alpha_T v_1 \frac{\partial^2 C}{\partial^2 y}. \tag{12}$$

In an infinite domain, we can compute an analytical solution of this transport equation and use this solution for validating the numerical simulation [11].

Once C_{OH^-} is computed, we can solve equation (11) everywhere to compute the pH. We can also compute all the concentrations of the chemical species. This method is used for validating the software GRT3D.

5.4 Simulation data

The discrete transport operator is computed with the software MT3D, using a finite difference method. The DAE system is solved with the software SUNDIALS, and the linearized equations are solved with the software UMFPACK. Computations are done on a machine composed of two six-core Intel Xeon processors X5690, with a frequence of 3.46 GHz and 4GB of RAM per core.

The rectangular domain is meshed with a regular grid of $n_1 \times n_2$ cells. We use six different mesh sizes, ranging from a coarse mesh of 21×42 cells to a fine mesh of 322×224 cells.

In order to analyze the impact of substitution in the linearized equations and the impact of the logarithms in the chemistry model, we compare the three versions of GRT3D. We run these three models, where we remove the inspector ion Na^+. We compute the concentration of Na^+ simply by solving the decoupled transport equation. For the versions with logarithms, the initial data of T_{Na^+} and T_{OH^-} are set to 10^{-20} instead of 0. We do not use equation (11) in GRT3D.

5.5 Simulation results

Now, we show results with the finest mesh of 322×224 cells and with the optimized version. In Figure 1, we plot the concentration c_{Na^+} at time $t_1 = 10s$ and $t_2 = 190s$. We can observe the effect of advection and dispersion on this inert component. In Figure 2, we plot the concentration x_H^+ (from which it is easy to compute the pH) at the same times. We can observe the effect of the coupling between transport and chemical reactions. Groundwater in the porous medium becomes basic, due to the plume of ions OH^-.

5.6 Accuracy

The comparison with the analytical solution shows a good agreement [11]. It is easy to compare the computed value of c_{H4SiO4} with the exact value $\frac{1}{K_3}$. For the three versions and all the mesh sizes, we get an error of about 10^{-15}.

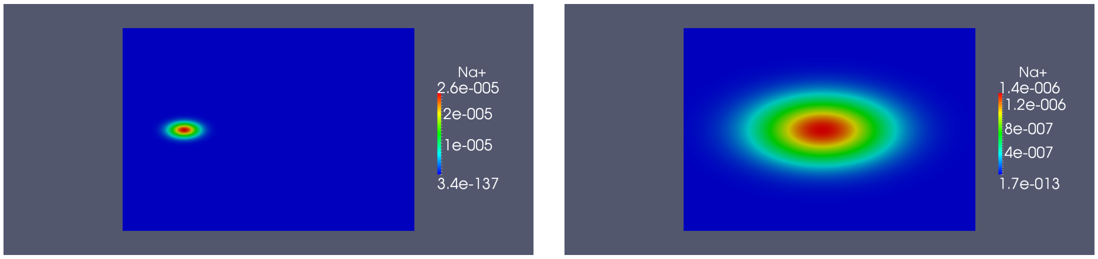

FIGURE 1 – Computed concentration of sodium at times $t_1 = 10s$ and $t_2 = 190s$.

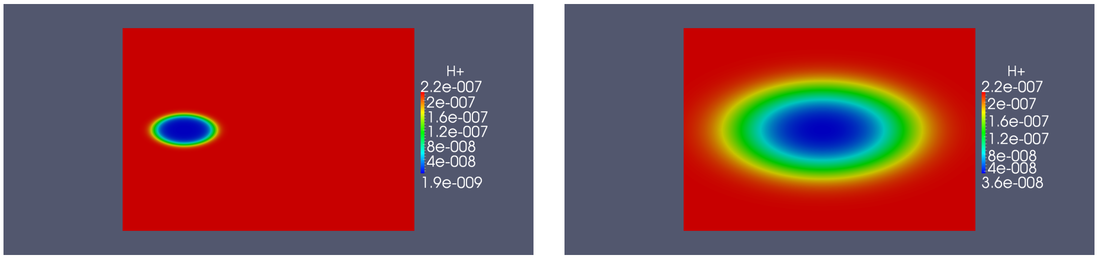

FIGURE 2 – Computed pH at times $t_1 = 10s$ and $t_2 = 190s$.

We also compare the results of the different versions. The main difference between the first and the reduced version is the linearized matrix. On the other hand, the optimized version is quite different, since it does not use exactly the same initial conditions and it does not use logarithms. For each simulation, we use an external time step for the outputs and get N_t results.

We denote by $x_{H^+}(m_j, t_n)$ the concentrations of H^+ computed with GRT3D, at the various points $m_j, j = 1, \dots, N_m$ and at various times $t_n, n = 1, \dots, N_t$. We also use the concentration of Na^+, computed with the transport equation (using MT3D), to solve the quadratic equation (11) and to get a semi-analytical solution, noted $\tilde{x}_{H^+}$. Then we compare the two results, by using the following criterium :

$$E_{H^+} = \|\tilde{x}_{H^+} - x_{H^+}\|$$

where $\|x\| = (\frac{1}{N_m N_t} \sum_{n,j} x(m_j, t_n)^2)^{1/2}$

In Table 3, we give the values of this criterium for the three versions and for the different mesh sizes. With the finest mesh, the chemistry equations cannot be solved with the first model. Indeed, the Jacobian is too ill conditioned, whereas it is better conditioned for the reduced version. The three versions give results with roughly the same accuracy, for any mesh size.

Mesh	first GRT3D	reduced GRT3D	optimized GRT3D
21x14	1.333005E-11	1.591450E-11	8.040057E-11
41x28	2.489791E-09	2.489787E-09	8.113751E-11
81x56	7.640456E-09	7.640825E-09	3.055914E-10
71x101	7.747011E-09	7.746415E-09	4.161827E-10
161x112	7.9736E-09	7.9738E-09	2.6672E-10
322x224	-	3.0871E-09	4.3067E-10

TABLE 3 – Comparison of computed pH for the three versions of GRT3D and for different mesh sizes.

5.7 Computing times

In Table 4, we give the CPU times for the three versions and for various numbers of cells. The substitution technique (elimination of T and C in the linearized equations) clearly reduces the memory usage and the CPU time. We observe that the Jacobian is better conditioned with the reduced model and that Newton iterations converge faster.

The model without logarithms is much more efficient than the model with logarithms, with a gain increasing when refining the mesh. We observe that the Jacobian is well conditioned without logarithms and that Newton iterations converge much faster for most time steps.

Mesh	first GRT3D		reduced GRT3D		optimized GRT3D
	system size	CPU time	system size	CPU time	CPU time
21x14	2058	18 s	882	4 s	2 s
48x28	9408	1 min 36 s	4032	21 s	8s
81x56	31752	6 min 33 s	13608	1 min 53 s	50 s
71x101	50197	11 min 55 s	21513	3 min 28 s	1 min 21 s
161x112	126224	32 min 43 s	54096	16 min 30 s	4 min 32 s
322x224	504896	-	216384	1 h 52 min	37 min 38 s

TABLE 4 – CPU times of the three versions of GRT3D for different mesh sizes.

6 Conclusion

In this paper, we studied a global approach for reactive transport models, where transport of contaminant is coupled with chemical reactions. We show how a DAE solver can be used efficiently, by reducing the number of unknowns at each time step, in a way similar to a direct substitution approach. Our numerical experiments show a significant reduction of computational time with the reduced model. We also investigate the difference between two chemistry models, using either the concentrations of the species or their logarithms. It appears in our experiments that the version without logarithms is much faster than the version with logarithms. It seems that the gain in CPU is mostly related to the condition number of the Jacobian matrices. We plan to further analyze this result, from a mathematical point of view.

We also plan to design a parallel version of our software GRT3D. A first step is to use a parallel sparse direct solver, since solving the linearized systems represents a high percentage of CPU time. Another step is to use the specific structure of the reduced Jacobian and to tune a linear solver.

We intend to implement a semi-smooth Newton method to deal with precipitation-dissolution reactions, where the mineral can appear or disappear at various points of the domain during the simulation. One technical difficulty is to interface the DAE solver. Finally, we will also introduce kinetic reactions in our model.

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