

TWO MODEST IMPROVEMENTS FOR SEQUENTIAL ITERATIVE APPROACHES IN REACTIVE TRANSPORT

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Summary. We present here two different improvements for the SIA approach in reactive transport.

1. The SIA approach is very well-suited to reactive transport when the chemistry is at thermodynamic equilibrium. It allows to solve the non-linear chemical system locally instead of globally. However, when the chemistry is - if only partially - kinetically-controlled, this approach leads to treating kinetics as a displacement of equilibrium, which may cause convergence or precision problems, directly linked to the characteristic times of the kinetic laws.

For kinetically-controlled species, usually minerals, the chemical source terms of their equation of evolution may be explicitly written according to the associated kinetic laws. By separating the solving of the chemistry between the chemistry at equilibrium and the kinetically-controlled chemistry, we propose a modified operator-splitting approach, applied to a fixed-point algorithm. This methodology allows us to address and solve locally problems of convergence. Tested in the mainframe of the ALLIANCES code, this method has proven to be more precise and more robust in a series of test-cases. These test-cases were chosen close to real reactive transport cases in the context of nuclear waste storage simulations.

2. The fact that chemical concentrations come as a result of a local equilibrium makes impossible to write explicitly the chemical source term in the reactive-transport equation. It is fairly common to use an operator-splitting technique for sequential approaches and the direct substitution for a global approach. In both cases the jacobian is very often evaluated through a numerical approximation.

We propose here to evaluate the jacobian through an analytic calculation, using the mathematical properties of the chemical system (action mass laws), in the mainframe the Non Linear Conjugate Gradient method. This analytical calculation is possible although the analytical expression of the function whose jacobian is calculated is unavailable. Comparing it to the use of a numerical jacobian on a few test-cases, we see that the use of an exact jacobian improves the robustness of the algorithm and reduces the number of iterations to convergence.

1 INTRODUCTION

The work we present here deals with reactive transport in a saturated porous media. The classical modelling of this physical phenomena leads to a complex nonlinear coupled system of PDE describing the evolution of the concentrations of the chemical species. Since chemical systems contain very often large numbers of species, the number of variables grow easily around hundreds, which adds to the numerical difficulty of solving such systems.

This field of investigation in numerical simulation has many applications, ranging from CO₂ sequestration to nuclear waste disposal. Various numerical methods have been used, which we can split into two main groups: the global iterative approach (GIA), solving directly the global system, and the sequential iterative approach (SIA) which splits the transport operator and the chemistry operator, leading to the separate solving of a global linear system and many local nonlinear chemical systems.

We propose here two modest improvements of the latter approach, one for addressing specific problems raised by the use of kinetic laws in the chemistry, the other for using an analytical jacobian with a NonLinear Conjugate Gradient method instead of a numerical one, using the mathematical properties of the chemical system. Although unconnected, both these studies are in the same mainframe, which is why we chose to present them together.

2 A venerable technique: Sequential Iterative Approach with operator-splitting for reactive transport systems with chemistry at equilibrium

Let us introduce a few notations first:

V_T	volume of a elementary representative cell
$a_i(m)$	concentration of the aqueous specie i in moles per liter of aqueous volume in the cell m
$f_j(m)$	concentration of the fixed specie j in moles per liter of aqueous volume in the cell m
N_r	number of chemical reactions
N_e	number of chemical reactions at thermodynamical equilibrium
N_a	number of aqueous species of variable activity (i.e. all except water)
N_f	number of mineral species (all of them of constant activity)
N_i	number of chemical invariants
$\mathcal{R}_{i,j}$	chemical source term of the chemical specie i or j
I_r	evolution term of the reaction r
\mathbf{R}	N_r -vector of the I_r/V_T
ω	porosity
\mathbf{M}	number of cells
\mathbf{L}	common transport $\mathbf{M} \times \mathbf{M}$ matrix for every mobile specie
$\nu_{i,j}^r$	stoichiometric coefficient of the specie i or j in reaction r
S_a	stoichiometric matrix $N_r \times N_a$ for aqueous species
S	stoichiometric matrix $N_r \times (N_a + N_f)$ for all species
$\vec{\log K}$	N_r -vector of the log of chemical equilibrium constants
$\vec{\log \Gamma}(m)$	N_a -vector of the log of chemical activities in cell m

We start from a classical reactive transport system in a saturated porous media with a variable porosity:

$$\left\{ \begin{array}{l} \partial_t(\omega a_k) = -\text{div}(a_k \vec{U}_l - \vec{D}_k^a (\vec{U}_l) \vec{\nabla} a_k) + \mathcal{R}_k \quad \forall i \in [1, N_a] \\ \partial_t(\omega f_j) = \mathcal{R}_j \quad \forall j \in [1, N_f] \\ \omega = \omega^0 \frac{1 + f_{mv}^0}{1 + f_{mv}} \quad \text{with } f_{mv} = \sum_j \nu_j^{\text{mol}} f_j \\ \mathcal{R}_{k,j} = \frac{1}{V_T} \sum_{r=1}^{N_r} \nu_{k,j}^r I_r \quad \forall i \in [1, N_a] \quad \forall j \in [1, N_f] \end{array} \right.$$

Source terms \mathcal{R} are unavailable for chemical reactions at thermodynamic equilibrium, since they have the necessary value so that at each time iteration the chemical system is at equilibrium.

The global system can be rewritten as follows:

$$\begin{cases} \partial_t \vec{c} &= \underbrace{\vec{\mathcal{L}}}_{\text{transport}} + \underbrace{S^T}_{\text{stoichiometric}} \vec{r} \\ \omega &= \omega^0 \frac{1 + S_r^0 f_{mv}^0}{1 + S_r f_{mv}} \\ \vec{r} &= \Phi_\chi(\omega, \vec{c}) \end{cases}$$

We know, through the rank-nullity theorem that there exists a matrix U such as US^T is equal to the null matrix. Therefore if $\vec{u} = U\vec{c}$ we get $\partial_t \vec{u} = U\partial_t \vec{c} = U\vec{\mathcal{L}} + US^T \vec{r} = U\vec{\mathcal{L}}$ \vec{u} is usually called the **components** vector, i.e. the vectors of chemical invariants obtained from linear combinations of the chemical species concentrations. \vec{u} is by definition invariant in respect to the local chemistry.

We use then this property to split chemical and transport terms:

1. Transport step: we solve the **linear and global** system:

$$\partial_t \vec{u} = U\vec{\mathcal{L}} \quad \vec{u} = (\vec{A}, \vec{F}) \quad (1)$$

2. Chemical step: we use the new values of \vec{u} to calculate \vec{c} through a set of **nonlinear and local** chemical systems:

$$\begin{cases} U\vec{c} &= \vec{u} \\ S_a \log \gamma &= \log K \\ f_j &= 0 \text{ or saturation product} = \log K_j \\ \omega &= \omega^0 \frac{1 + S_r^0 f_{mv}^0}{1 + S_r f_{mv}} \end{cases}$$

We can solve this system via various algorithms, such as Fixed-Point (or Picard) algorithm, Non Linear Conjugate Gradient, Newton, Newton-Krylov...

3 Adaptation of this approach with a kinetically-controlled chemistry

3.1 What happens with a (even partially) kinetically-controlled chemistry?

Usually kinetics are treated as a displacement of the equilibrium. For example, if the aqueous speciation is at equilibrium and the precipitation-dissolution kinetic (wich is a fairly common case in the context of reactive transport), the global system writes:

$$\begin{cases} U\vec{c} &= \vec{u} \\ S_a \log \gamma &= \log K \\ \vec{f} - \vec{f}(t=0) &= \int_0^t S_f^T \vec{r}_k dt \\ \omega &= \omega^0 \frac{1 + S_r^0 f_{mv}^0}{1 + S_r f_{mv}} \end{cases}$$

Usually the kinetic law is then explicitly integrated for the global non-linear solving method, and solved within the chemical step, which is equivalent as considering kinetics as a simple displacement of the equilibrium. The point of the operator-splitting approach is to avoid the evaluation of the chemical source terms, since their analytical form is unavailable, whereas, in the case of kinetics, the analytical form of chemical source terms is known, since it is precisely a linear combination of the kinetic laws of the reactions associated to the considered specie. Here we propose to use this property in the so-called "free kinetics" approach, by "freeing" the kinetically-controlled chemistry from the splitting of the operators.

3.2 "Free Kinetics" approach

We make a few hypotheses:

1. The aqueous speciation is at equilibrium (very common for nuclear waste storage).
2. To each fixed species we associate one and only one reaction (sorption or precipitation).
3. The kinetics laws are fully determined by the aqueous speciation and/or the time.

We now identify a chemical sub-system with only the species controlled by reaction at thermodynamic equilibrium and split the chemical invariants in a kinetic and equilibrium part: $\vec{u} = \vec{u}_{eq} + \vec{u}_\kappa$. Then we take advantage of the explicit nature of the kinetic source terms. We modify the classical SIA in this fashion:

1. Transport and "free kinetics" (as in free from the chemical module) step:

$$\partial_t \vec{u}_{eq} = U \vec{\mathcal{L}} - \partial_t \vec{u}_\kappa = U \vec{\mathcal{L}} - \Phi_\kappa \quad (2)$$

where Φ_κ is explicitly known through the kinetic laws.

2. Equilibrium chemical step : solving of the equilibrium sub-system using

$$\begin{cases} U_{eq} \vec{c} & = \vec{u}_{eq} \\ \chi^e(\vec{c}) & = 0 \end{cases}$$

where χ^e stands for the chemical mass action laws associated to the sub-system containing the reactions at equilibrium, as if the kinetically-controlled minerals were not taken into account. It's a nonlinear system of N_a unknowns with N_e chemical equilibria et N_i pseudo-invariants. Thanks to the hypothesis made for the minerals we know that $N_r = N_e + N_f$ and that we have $N_a = N_i + N_r - N_f = N_i + N_e$. Therefore the chemical sub-system is closed.

In the end we solve rigorously the same mathematical system. We can use this approach in the context of a Fixed Point resolution. We use the following decomposition for every chemical invariant:

$$u = A(\text{aqueous}) + F(\text{fixed : kinetics}) + E(\text{fixed : equilibrium})$$

The Fixed Point algorithm can be classically written as follows (σ^n stands here for the sum of explicit terms):

1. Transport step : $(\frac{\omega}{\Delta t} Id + \mathcal{L})A^{n+1,l+1} = -\frac{\omega}{\Delta t}E^{n+1,l} - \frac{\omega}{\Delta t}F^{n+1,l} + \sigma^n$
2. Equilibrium chemistry step : $(\vec{a}^{n+1,l+1}, \vec{g}^{n+1,l+1}) = \Phi_e(A^{n+1,l+1} + E^{n+1,l})$
3. Kinetically-controlled chemistry step : $F^{n+1,l+1} = F^n + \Delta t \Phi_\kappa(\vec{a}^{n+1,l+1})$

This "free kinetics" variant of the Fixed Point algorithm and its classical version are rigorously equivalent after convergence. However we observe a substantial improvement of the results in numerical tests, in terms of precision and stability, as we illustrate in the following section via a few examples.

3.3 Test-cases with ALLIANCES code

First we consider an analytic test-case : 1D Diffusion of a single aqueous specie precipitating into a kinetically-controlled mineral, whose analytic solution writes:

$$\partial_t C = D \partial_{x^2} C - k S \left(\frac{C}{K_s} - 1 \right),$$

where C is the concentration of the aqueous specie, D the diffusion term, K_s the saturation constant of the precipitate, k the kinetic constant and S the constant reactive surface associated to the kinetic law. After having reached time and space convergence :

- With the classical approach : a L^∞ relative error of 12% (huge!)
- With the "free kinetics" approach : a L^∞ relative error of 0.17% (order of the precision of the coupling algorithm)

Using the same tools and the same mathematical system we gained 2 orders of magnitude just by changing the approach.

Then we consider a relatively simple 1D reactive transport system with only 9 minerals (calcite, pyrite, gypsum, goethite, sphalerite, smithsonite, $\text{Fe}(\text{OH})_3$, hydrozincite, zinc hydroxide) : this test-case emulates many difficulties of a study of the evolution of high activity and long-term nuclear waste in a glass matrix (french concept) in contact with a clayish environment

- General form of the kinetic laws: $\omega \partial_t f_j = k S (\Omega_j^{p_j} - 1)^{p_2} \prod_{i \in I_\kappa} a_i^{p_i^\kappa}$ with $\Omega_j = \frac{\prod_{i=1}^{N_a} a_i^{\mu_i^r}}{K_s}$

- A stiff system with very different characteristic times: $k_{sphalerite} = 10^{-5} mol.m^{-2}.s^{-1} \rightarrow k_{goethite} = 10^{-14} mol.m^{-2}.s^{-1}$
- different catalyts: $[H+]^{0.7}$ for calcite, $[O_2(aq)]^{0.5}$ for pyrite
- different laws for precipitation and dissolution (values of p_1 and p_2)

This test-case fails to converge with the classical approach but converges with the "free kinetics" approach. This behaviour was verified on many similar cases

4 Using an exact Jacobian for the Nonlinear Conjugate Gradient method

Using a Nonlinear conjugate gradient method^{2,3,4} in reactive transport is a competitive alternative to the classical Fixed Point algorithm in this mainframe.

When chemical reactions are taken at thermodynamic equilibrium, it is impossible to write explicitly the chemical source terms in the reactive species' equations of evolution. Thus it is fairly common to use an operator-splitting technique for sequential approaches and the direct substitution for a global approach. In both cases the **Jacobian**, when needed, is very often evaluated through a **numerical approximation**, which requires solving an extra chemistry system at each step.

We aim here to evaluate the jacobian through an **analytical calculation**, using the mathematical properties of the chemical system (action mass laws), in the mainframe of a global approach, but without direct substitution. This analytical calculation is possible although the analytical expression of the function whose jacobian is calculated is unavailable. It has been used in the context of a Newton-Krylov method¹.

4.1 Outline of the method

Let us begin with a short reminder of the Nonlinear Conjugate Gradient method in general for solving $f(x) = 0$:

- Compute the step-length: $\alpha_k = -f(x_k)^T d_k / d_k^T \nabla f(x_k) d_k$
- Update the solution: $x_{k+1} = x_k + \alpha_k d_k$
- Compute the residual: $r_{k+1} = f(x_{k+1})$
- Compute the new search direction, e.g. with Polak-Ribière formula $d_{k+1} = -r_{k+1} + \beta_{k+1} d_k$ where $\beta_{k+1} = \max(0, r_{k+1}^T (r_{k+1} - r_k) / r_k^T r_k)$

The evaluation of $\nabla f(x)d$ can be made via two different approaches:

$$\nabla f(x) \cdot d \approx \frac{f(x + \epsilon d) - f(x)}{\epsilon}$$

1. Numerical approximation: $\nabla f(x) \cdot d \approx \frac{f(x + \epsilon d) - f(x)}{\epsilon}$
2. Analytical calculation: $f(T) = \text{diag}(\bar{\omega})T + \Delta t \cdot \text{diag}(L) \cdot \Psi(T) = 0$
 $\nabla f = \text{diag}(\text{diag}(\bar{\omega})) + \Delta t \cdot \text{diag}(L) \cdot \frac{\partial \Psi}{\partial T} \rightarrow$ Calculation of $\frac{\partial \Psi}{\partial T}$ in each cell

The main drawback of the numerical approximation is that it implies to solve the chemistry a second time, which is very time-consuming, and of course that its precision is lower. We propose here to use the analytical calculation.

We use the following variable:

$$W = \begin{bmatrix} c(1) \\ \vdots \\ c(m) \\ \vdots \\ c(M) \end{bmatrix} \quad \text{where } c(m) = \begin{bmatrix} a_i(m) \\ f_j(m) \end{bmatrix} \text{ } (N_a + N_f)M \text{ vector}$$

$u(m)$ is the vector of the N_i chemical invariants in cell m . The chemical invariants are linear combinations of the concentrations, chosen so that their value is independent of chemical reactions.

Referring to the notations introduced in the previous paragraphs we have $\forall m \ u(m) = Uc(m)$. Let us write now:

$$Y = \begin{bmatrix} u(1) \\ \vdots \\ u(m) \\ \vdots \\ u(M) \end{bmatrix} \quad \text{vecteur } (N_i)M \text{ composantes}$$

We have of course: $(Id_M \times U)W = Y$.

We get the following system:

$$\begin{cases} \partial_t Y & = (Id_M \times U)(L \times J)W \\ (Id_M \times U)W & = Y \\ S_a \log \Gamma(m) & = \log K \end{cases} \quad \forall m \quad (3)$$

with $J = \begin{pmatrix} Id_{N_a} & 0 \\ 0 & 0 \end{pmatrix}$ matrice $(N_a + N_f) \times (N_a + N_f)$.

The system (3) is temporally discretized in the following fashion:

$$\left\{ \begin{array}{l} Y^{n+1} \\ S_a \vec{\log} \Gamma(m) \\ (Id_M \times U)W^{n+1} \\ (Id_M \times U)W^n \end{array} \right. = \begin{array}{l} Y^n + \theta \Delta t (Id_M \times U)(L \times J)W^{n+1} + (1 - \theta) \Delta t (Id_M \times U)(L \times J)W^n \\ \vec{\log} K \\ Y^{n+1} \\ Y^n \end{array} \quad \forall m \quad (4)$$

Let S^n be the explicit terms at time t_n . By writing $\Psi_L(W) = \theta \Delta t (Id_M \times U)(L \times J)W$, we get $Y^{n+1} = S^n + \Psi_L(W^{n+1})$. Ψ_L is a multilinear function of W , independant with time.

Let $\Psi_\chi(Y)$ be the function (similar to Φ_χ) giving the solution of the chemical equilibrium system in function of the chemical invariants Y . The remaining term can be then written as follows:

$$\mathcal{R}(W) = W - \Psi_\chi \circ \Psi_L(W) = W - \Psi(W) \quad (5)$$

Ψ cannot be evaluated analytically, but its jacobian can be. We have:

$$\Psi' = \left(\frac{\partial \Psi_l}{\partial W_p} \right)_{l,p \in [1, (N_a + N_f)M]} \quad (6)$$

We know that: $\frac{\partial \Psi_l}{\partial W_p} = \sum_{q \in N_i M} \frac{\partial \Psi_l}{\partial Y_q} \frac{\partial Y_q}{\partial W_p}$.

1. The $\frac{\partial Y_q}{\partial W_p}$ can be evaluated at the beginning of the simulation since we have explicitly:

$$Y(W) = S^n + \Psi_L(W) = S^n + \theta \Delta t (Id_M \times U)(L \times J)W$$

The transport terms being independant of W the $\frac{\partial Y_q}{\partial W_p}$ are given by the matrix $(NiM \times (N_a + N_f)M) : \theta \Delta t (Id_M \times U)(L \times J)$.

2. The $\frac{\partial \Psi_l}{\partial Y_q}$ can also be evaluated at the beginning of the simulation. We write:

$$\Psi = \begin{pmatrix} \psi(1) \\ \vdots \\ \psi(m) \\ \vdots \\ \psi(M) \end{pmatrix},$$

we get then $\frac{\partial \Psi_t}{\partial Y_q} = \frac{\partial \psi(m)_s}{\partial u(m')_t} = 0$ if $m \neq m'$, with $m, m' \in [1, M]$, $s \in [1, N_a + N_f]$ et $t \in [1, N_i]$. We still have to evaluate the $MN_i(N_a + N_f)$ following terms: $\frac{\partial \psi(m)_s}{\partial u(m)_t}$. We get them by solving locally a linear system. The solution will be valid for every cell with the same chemical system. We have $\forall m \in [1, M]$ a set of N_r linear equations:

$$S_a \vec{\log} \Gamma = \vec{\log} K \implies S_a \vec{\log} \gamma \psi = \vec{\log} K \quad (7)$$

And we have:

$$\frac{\partial \log(\gamma(m)_s \psi(m)_s)}{\partial u(m)_t} = \frac{1}{\gamma(m)_s \psi(m)_s \ln(10)} \frac{\partial (\gamma(m)_s \psi(m)_s)}{\partial u(m)_t}$$

The activity coefficient γ are supposed independant of the chemical concentrations, so we get:

$$\frac{\partial \log(\gamma(m)_s \psi(m)_s)}{\partial u(m)_t} = \frac{1}{\psi(m)_s \ln(10)} \frac{\partial \psi(m)_s}{\partial u(m)_t} \quad (8)$$

m et t being chosen, every set of N_r equations (7) can be derivated by $\frac{\partial}{\partial u(m)_t}$ to get (using (8)) N_r linear equations for the $N_a + N_f \frac{\partial \psi(m)_s}{\partial u(m)_t}$ terms.

For the N_i necessary remaining equations, we can apply the same operation for the N_i following equations : $U\psi(m) = u(m)$. In the end we have a linear system of $N_a + N_f$ equations for $N_a + N_f$ unknowns $\frac{\partial \psi(m)_s}{\partial u(m)_t}$.

So we get an exact evaluation of the jacobian, wich can be used in the course of a Newton or non-linear conjugate gradien method for solving $W - \Psi(W) = 0$.

We compare both approaches on two test-cases: one analytical and one taken from the MOMAS Reactive Transport Benchmark⁵.

4.2 1D Numerical Tests

These two numerical mono-dimensional test-cases lead to the same conclusion: for the same precision of the results, the Exact jacobian approach takes less iterations to converge than the Numerical jacobian approach, in terms of iterations at each time step, and the Exact jacobian approach requires less CPU time than the Numerical jacobian approach. Moreover, this difference increases when the CFL (Courant-Friedrichs-Levy) parameter increases.

4.2.1 Analytical test-case

We consider five chemical species, convection-diffusion, aqueous chemistry and sorption. The chemical species are conventionally noted X_1 , X_2 and C for the aqueous species, S for the sorbing specie and CS for the sorbed specie. The stoichiometric coefficients and equilibrium constants are given as:

	X_1	X_2	S	K
C	-1	0	0	1
CS	0	1	1	1

The hydraulic transport parameters are:

- porosity: $\omega = 1$
- pore velocity: 10^{-3}
- diffusion: 10^{-3}

We use the following initial and boundary conditions:

T_1	T_2	TS
Initial values of the total concentrations $m \cdot L^{-3}$		
$(x - 2)^2 + 1$	1	5
Imposed total concentrations at inflow boundary		
$4\cos^2t + 1$	$4\sin^2t + 1$	
Zero total concentrations gradient at outflow boundary		

The analytical solution for the total concentrations gives:

$$T_1(x, t) = (x - 2)^2 \cos^2 t + 1 ; T_2(x, t) = (x - 2)^2 \sin^2 t + 1$$

The following table proposes the comparison of the CPU time for the Exact and Numerical Jacobian:

Jacobian	cells	$CFL = 10^{-4}$	$2.5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	10^{-3}
Numerical	50	12	6	3	2
	100	46	27	15	11
	200	207	101	73	60
	400	963	512	405	363
Exact	50	10	4	2	1
	100	31.4	13	8	4.6
	200	103	55	31.5	20
	400	491	240	151	99

4.2.2 MOMAS Benchmark easy 1D test-case

We consider now 12 chemical species, convection-dispersion, aqueous chemistry and sorption and two different media. The species are conventionnaly noted $X_{1 \rightarrow 4}$ and $C_{1 \rightarrow 5}$ and S for the aqueous species, S for the sorbing specie and CS_1 and CS_2 for the sorbed species. The stoichiometric coefficients and equilibrium constants are given as:

	X_1	X_2	X_3	X_4	S	K
C_1	0	-1	0	0	0	10^{-2}
C_2	0	1	1	0	0	1
C_3	0	-1	0	1	0	1
C_4	0	-4	1	3	0	0.1
C_5	0	4	3	1	0	10^3
CS_1	0	3	1	0	1	10^3
CS_2	0	-3	0	1	2	10^{-1}

Here in the absence of an analytical solution, we use the solution given by the classical Fixed Point algorithm as a reference for the evaluation of the precision of the solution. The hydraulic transport parameters are:

- porosity: $\omega_A = 0.25$ $\omega_B = 0.5$
- pore velocity: $u_A = 2.2 \cdot 10^{-2}$ $u_B = 1.1 \cdot 10^{-2}$
- dispersion: $D_A = 2.2 \cdot 10^{-4}$ $D_B = 6.6 \cdot 10^{-4}$

We use the following initial and boundary conditions:

	T_1	T_2	T_3	T_4	TS
Initial values of the total concentration $m \cdot L^{-3}$					
Medium A	0	-2	0	2	1
Medium B	0	-2	0	2	10
Imposed total concentrations at inflow boundary					
	0.3	0.3	0.3	0	
Zero total concentrations gradient at outflow boundary					

Here in the absence of an analytical solution, we use the solution given by the classical Fixed Point algorithm as a reference for the evaluation of the precision of the solution. The following table proposes the comparison of the CPU time for the Exact and Numerical Jacobian:

Jacobian	cells	$2.2.10^{-3}$	$5.5.10^{-3}$	$1.1.10^{-2}$	$2.2.10^{-2}$
Numerical	100	46	22	15	9
	200	164	97	57	38
	400	730	417	279	204
	800	3877	2484	1673	DNC
Exact	100	35.5	16	10	5.5
	200	117	60	34.8	21
	400	471	260	152	91
	800	3484	1897	803	587

5 CONCLUSION

Both methods described here can be used to improve the quality of reactive transport calculation using the sequential iterative approach. In both cases we still lack theoretical proof of the advantage of using these techniques instead of the more classical options.

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