

## **ACCRETE - An explicit algorithm to solve kinetically constrained CO<sub>2</sub>-water-rock interactions**

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### *Abstract:*

Increasing atmospheric concentrations of CO<sub>2</sub> are suspected to have caused a gradual warming of the Earth's surface. Underground storage of CO<sub>2</sub> in porous rocks or sediments is one feasible option for reducing emissions. As CO<sub>2</sub> is injected into the pore space, it dissolves in the reservoir pore waters causing an acid corrosive environment. This leads to dissolution of the rock or sediment framework and precipitation of new mineral phases. The resultant carbonate minerals are believed to be a safe storage host over geological timescales.

To understand the magnitude of these reactions at long time scales we need to perform numerical simulations. 3D reactive transport simulations are most appropriate given the dynamics and scales of injection. This involves solving a reaction term that commonly consists of a stiff system of ordinary differential equations (ODE). Such systems can be solved with implicit schemes like a backward differential formulation (BDF).

This paper reports an alternative explicit algorithm to solve kinetically constrained mineral reactions in CO<sub>2</sub>-water-rock systems. The algorithm is used on a comprehensive mineral system that is representative for a Utsira-like reservoir. Simulations suggest that aluminium at low concentrations causes numerical instabilities. By integrating the mineral reactions over short time steps we are able to find an independent function or constant for aluminium that facilitates the calculations and still produces reliable results. Using this method, a 1000 years single-grid simulation can be completed in a few seconds or less. This demonstrates that it is possible to solve the stiff ODE systems involved in the reactive transport equation using a simple explicit algorithm.

*Key-words:* CO<sub>2</sub> storage, Utsira reservoir, Sleipner injection site, mineral kinetics, ACCRETE, stiffness, ODE

## 1 Introduction

Measurements of atmospheric CO<sub>2</sub> concentration during the last decades have revealed a rapid increase, and different strategies have been suggested of how to reduce such emissions. Examples are storage in saline aquifers, storage in abandoned oil- and gas fields, storage in deep unminable coal seams, and storage combined with enhanced recovery of hydrocarbon from active oil and gas fields [1]. The probability of leakage from a storage site is dependent on several factors like hydrodynamic conditions, numbers of wells penetrating the reservoir, storage depth, and reservoir integrity [2]. The probability is also time dependent in the sense that CO<sub>2</sub> is immobilized with time by dissolution into formation waters and by reactions with the solid rock or sediment framework.

Information on the reactivity of CO<sub>2</sub> with formation water and minerals, and the way this affects mobility may be solved by reactive transport simulations (e.g., [3]). A general reactive transport equation for aqueous component  $u$  can be written as:

$$u_t + \nabla \cdot (vu - D\nabla u) = R(\vec{u}), \quad (1)$$

where  $v$  is a velocity field,  $D$  is the diffusion tensor, and  $R$  is a reaction term dependent on the aqueous chemistry  $\vec{u}$ . The reaction term on the right-hand side of equation (1) is intimately connected to the transport operators on the left-hand side. To ease the calculations a time-split to separate the transport from the source term is usually performed. In this way the transport operators are discretized in space and solved separately from the geochemical reactions, and the source term becomes a set of ordinary differential equations (ODEs) of the form:

$$\frac{du_i}{dt} = R_i(\vec{u}). \quad (2)$$

Reaction (2) covers both equilibrium reactions between aqueous components and between the CO<sub>2</sub> gas or liquid phase and the aqueous phase, as well as mineral reactions constrained by their reaction rates.

Equation (2) must be solved for each grid point in the spatial mesh. For large 3D reactive transport simulations the number of grid points may exceed hundreds of thousands. Since equation (2) usually is attributed to some degree of stiffness, the equation represents a bottleneck in solving the reactive transport equation, and effective algorithms, for solving equation (2) is strictly necessary. A common approach for such equations is backward differential formulations (BDF) which have proven to be very robust.

This paper presents the simple explicit scheme used in the ACCRETE geochemistry code to solve CO<sub>2</sub>-water-rock interactions. A 1000 years batch simulation illustrates the use of the code on a typical CO<sub>2</sub> storage setting. The initial mineral composition, aqueous chemistry, and physical condition resemble those found in the Utsira Reservoir at the Sleipner West injection site in the North Sea [4]. For this kind of problems involving aluminosilicate stability coupled via aqueous aluminium and silica, and also carbonate stability coupled via dissolved carbonate, only aqueous aluminium is shown to cause instability in the ODE solver for proper step sizes. A solution to this specific instability problem is here suggested.

## 2 The ACCRETE algorithm

ACCRETE is an acronym for Athena Carbon Capture and stoRage geochemisTry module. The development of the code was initiated as the Athena multiphase 3D flow research code, developed at the University of Bergen, was expanded to cover reactive transport simulations of geological storage of CO<sub>2</sub> [5, 6]. ACCRETE is executed as an external module for each Athena time step and updates the geochemistry according to directives given by Athena. ACCRETE can also be run as a stand-alone batch geochemistry solver as in the case of this report. The present ACCRETE version simulates interactions between 16 mineral phases, 14 aqueous solutes, H<sub>2</sub>O as a solvent, and CO<sub>2</sub> as a separate gaseous or supercritical phase.

The CO<sub>2</sub>-water-rock solver is divided into two main solvers: (1) the aqueous phase speciation solver; and (2) the mineral solver. The two solvers are presented in the following sections.

### 2.1 Thermodynamics

The standard state adopted in this study is that of unit activity for pure minerals and H<sub>2</sub>O at any temperature and pressure. For aqueous species other than H<sub>2</sub>O, the standard state is unit activity of species in a hypothetical 1 molal solution referenced to infinite dilution at any temperature and pressure. For gases, the standard state is for unit fugacity of a hypothetical ideal gas at 1 bar pressure. Thermodynamic data are extrapolated from data calculated with the SUPCRT92 program [7] using the dprons96.dat database.

### 2.2 Solving the aqueous speciation

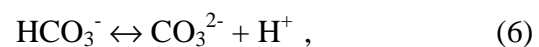
Aqueous speciation is constrained by five equilibrium reactions, and the demand for a mass- and charge balanced system. The first equilibrium that needs to be satisfied is the dissolution of gaseous or supercritical CO<sub>2</sub> into the aqueous phase



This equilibrium is constrained by the bubblepoint of CO<sub>2</sub> calculated from

$$x_{\text{CO}_2}^b = \frac{Py\phi}{K_H} \exp\left\{-\frac{\bar{v}^\infty}{RT}(P-1)\right\}, \quad (4)$$

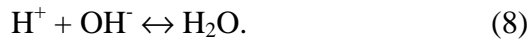
where  $P$  is pressure,  $y$  is fraction CO<sub>2</sub> in the gas phase,  $\phi$  is the fugacity coefficient,  $K_H$  is the Henrys law coefficient for CO<sub>2</sub>,  $\bar{v}^\infty$  is the average partial molar volume of CO<sub>2</sub> in water at infinite dilution, and  $T$  is temperature. With polynomials for both  $\phi(T,P)$  and  $K_H(T, \text{salinity})$ , expression (4) provides good estimates of CO<sub>2</sub> solubility using a fast non-iterative procedure [8]. The next four equilibria provides the speciation of aqueous carbon



and



The two first (5,6) represents the dissociation of carbonic acid to bicarbonate and carbonate, whereas (7) is needed to reduce the activity of bicarbonate and achieve a more accurate pH. The last equilibrium reaction (8) is dissociation of water into H<sup>+</sup> and OH<sup>-</sup>



In addition to the equilibrium reactions, the aqueous solution must be charge balanced

$$-\sum_{i \neq \text{H}} n_i z_i - n_{\text{H}} = 0, \quad (9)$$

where  $n$  and  $z$  are moles and charge of aqueous species  $i$ . The final requirement is that the aqueous carbon mass balance is satisfied

$$C - (n_{\text{CO}_2, \text{aq}} + n_{\text{HCO}_3} + n_{\text{CO}_3} + n_{\text{NaHCO}_3}) = 0, \quad (10)$$

where  $C$  is total dissolved carbon. The aqueous speciation is solved iteratively by the requirement that the difference between  $n_{\text{H}}$  given by expressions (9) and  $n_{\text{H}}$  estimated from reaction (5)

$$n_{\text{H}} = \frac{K_1 a_{\text{CO}_2, \text{aq}} a_{\text{H}_2\text{O}}}{a_{\text{HCO}_3} \gamma_{\text{H}}}, \quad (11)$$

is less than a predefined limit

$$\sqrt{(n_{\text{H}}^{(9)} - n_{\text{H}}^{(11)})^2} < \alpha V_{\text{aq}}, \quad (12)$$

where  $V_{\text{aq}}$  is volume aqueous phase and  $\alpha$  is  $10^{-6} - 10^{-8}$ .

### 2.3 Solving mineral reactions

The extent  $\xi$  of a mineral reaction over one time step can be calculated from

$$\xi_i^t = k_i S_i (\Omega_i - 1) \cdot \Delta t, \quad (13)$$

where  $k$  and  $S$  are the kinetic constant and reactive surface area of the reaction respectively,  $\Delta t$  is the step size, and the  $\Omega$ -1 term is the affinity of the reaction and

provides the reaction direction. The affinity is given by:

$$\Omega_i = \frac{Q_i}{K_i}, \quad (14)$$

where  $K$  is the equilibrium constant and  $Q$  is the activity product of the reaction given by

$$Q = \frac{\prod_p a_p^{v_p}}{\prod_r a_r^{v_r}}. \quad (15)$$

The contribution of the mineral reactions to the aqueous components can be expressed as:

$$n_k^{t1} = n_k^{t0} + \sum_i \xi_i \nu_{i,k}, \quad (16)$$

where  $\nu$  is the stoichiometric coefficient for aqueous component  $k$  in mineral reaction  $i$ . Superscripts  $t0$  and  $t1$  indicates the integration timestep  $\Delta t = t1 - t0$ . The integration is accepted if all  $k$  aqueous components at time  $t1$  have concentrations  $n_k^{t1} \geq 0$ . If this is not the case, the integration time step is reduced and equation (16) is solved again. Because one or more of the equations in the aqueous phase speciation is always affected by the mineral reactions, the speciation algorithm must be called for each integrated time step in the mineral solver. The system is solved when the sum of all integration time steps equals the predefined simulation time.

## 3 Results and discussion

To show how the ACCRETE algorithms solve  $\text{CO}_2$ -water-rock interactions, the

mineralogy, chemistry and physical conditions from the Sleipner West injection site were chosen (See Table 1 and 2). Three simulations are presented here and include: (1) simulation where the mineral reactions are integrated over short time steps to avoid instabilities; (2) simulation with larger time steps to illustrate where the instability occur and how it affect the simulated results; and (3) simulation with large time steps with a problem-specific solution to the instability problem. The simulations are all one-grid single-phase batch problems with an aqueous phase in contact with an infinite CO<sub>2</sub> reservoir. The simulations cover 1000 years of CO<sub>2</sub>-water-rock interactions.

Table 1

Initial mineral volume fractions and kinetic data for Utsira sand. Mineral information is based on data reported by [4], whereas the kinetic data (k and S) is from [5] and [6]. Note that kinetic constant for 298.15K is listed here. This value is recalculated to the ambient temperature using an Arrhenius relationship.

Mineral	$X^{Utsira}$	$k_{298}$ (mol/m <sup>2</sup> s)	S (cm <sup>2</sup> /cm <sup>3</sup> )
Calcite	0.0285	$1.00 \times 10^{-7}$	$1.00 \times 10^2$
Magnesite	0	$1.00 \times 10^{-9}$	$1.00 \times 10^2$
Siderite	0	$1.00 \times 10^{-9}$	$1.00 \times 10^2$
Dawsonite	0	$3.06 \times 10^{-11}$	$2.44 \times 10^4$
Albite	0.03	$1.00 \times 10^{-12}$	$8.75 \times 10^2$
Microcline	0.038	$1.78 \times 10^{-13}$	$1.11 \times 10^3$
Quartz	0.496	$1.04 \times 10^{-14}$	$5.74 \times 10^2$
Chalcedony	0	$3.45 \times 10^{-13}$	$1.25 \times 10^4$
Kaolinite	0	$4.00 \times 10^{-13}$	$1.25 \times 10^4$
Clinochlore-14A	0.003	$3.00 \times 10^{-13}$	$1.25 \times 10^4$
Daphnite-14A	0	$3.00 \times 10^{-13}$	$1.25 \times 10^4$
Muscovite	0.04025	$1.00 \times 10^{-13}$	$1.25 \times 10^4$
Phlogopite	0.01425	$4.00 \times 10^{-13}$	$1.25 \times 10^4$
Annite	0	$4.00 \times 10^{-13}$	$1.25 \times 10^4$
Labradorite	0	$2.04 \times 10^{-10}$	$8.06 \times 10^2$
Gibbsite	0	$3.16 \times 10^{-12}$	$8.66 \times 10^3$
Porosity	0.35		

### 3.1 Simulated CO<sub>2</sub> storage system

The simulated system comprises chemistry, mineralogy and physical properties ( $T$ ,  $P$ ) that correspond to information published from the Sleipner CO<sub>2</sub> injection site, Norwegian North Sea (see [4]). The mineralogy is listed in Table 1 together with data used in the kinetic expression (13). Some minerals are proxies for similar minerals observed in the sediments. The aqueous chemistry is based on data from the Sleipner injection site presented in [3]. Original data in [3] is slightly modified to provide a charge balanced solution at the starting pH of 7.1 shown in Table 2.

Table 2

Initial aqueous chemistry (molefractions).

Component	$X_i$ (mol/mol)
H <sup>+</sup> /pH	$1.963 \times 10^{-9} / 7.1$
Ca <sup>2+</sup>	0.0001345904
CO <sub>2, aq</sub>	$3.1454 \times 10^{-6}$
HCO <sub>3</sub> <sup>-</sup>	$2.91976 \times 10^{-5}$
Na <sup>+</sup>	0.008462067
Cl <sup>-</sup>	0.0094557953
Al <sup>3+</sup>	$2.358 \times 10^{-10}$
CO <sub>3</sub> <sup>2-</sup>	$5.3387 \times 10^{-8}$
Mg <sup>2+</sup>	0.0003288578
SiO <sub>2, aq</sub>	$3.514 \times 10^{-9}$
K <sup>+</sup>	$3.01831 \times 10^{-6}$
Fe <sup>2+</sup>	$9.613604 \times 10^{-5}$
NaHCO <sub>3</sub>	0.0

### 3.2 Temporal evolution of mineral carbonates and aqueous components

The first simulation integrates the mineral reactions over short time steps to avoid instabilities in the stiff mineral solver. This simulation is slow, but provides reliable estimates of the reactivity of the system. Selected mineral data and aqueous chemistry of the simulation are presented in Fig. 1.

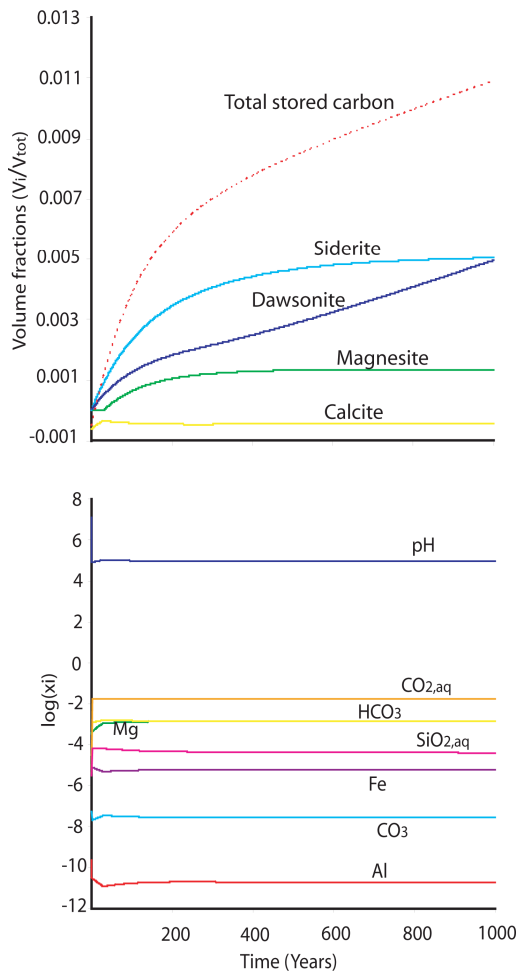
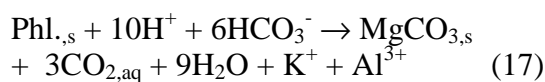


Fig. 1. Temporal evolution of carbonate minerals (upper) and dissolved aqueous species (lower) for short time steps in the integration of mineral reactions.

One of the main issues concerned with safe long-term storage of  $\text{CO}_2$  is to quantify the amount of stable solid carbonates that form. The minerals presented in Fig. 1 are those carbonates included in the present simulations and the total amount of carbon formed. Carbonates form as a consequence of a lowering of pH as  $\text{CO}_2$  is injected, which in turn triggers dissolution of primary minerals present in the sediment. This is illustrated in equation (17) for the dissolution of phlogopite and formation of magnesite ( $\text{MgCO}_3$ ).



Reaction (17) is one of several that leads to formation of Fe-, Mg-, and NaAl(OH)-carbonates. The second part of Fig. 1 shows the temporal evolution of aqueous components. As expected, pH falls to a steady value around 5.0, and the system reach a steady non-equilibrium state after a few tens of years.

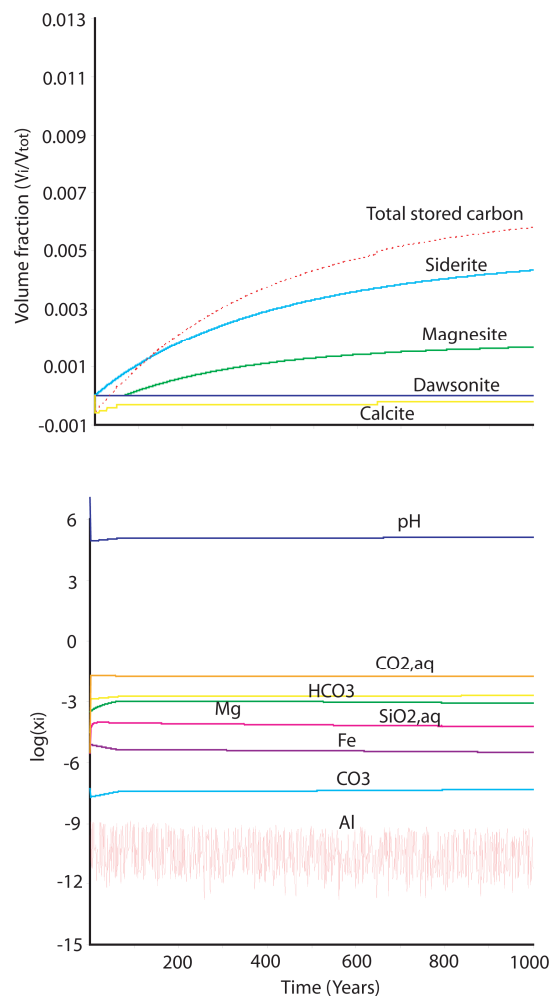


Fig. 2. Temporal evolution of carbonate minerals (upper) and dissolved aqueous species (lower) for large time steps in the integration of mineral reactions.

### 3.3 Stiffness problems caused by Al-fluctuations

The second simulation illustrates stiffness problems in the algorithm caused by integrating mineral reactions over large time steps. This simulation is fast but data produced are less reliable. Results are presented in Fig. 2 that shows carbonate formation and aqueous chemistry with time. The main difference between the former simulation and this one is that significantly less solid carbonate forms. The explanation is found in the aqueous chemistry. Whereas most aqueous components show a temporal evolution similar to the first case, aqueous aluminium fluctuates. The reason for this can be found by comparing the concentration of aluminium with the extent of aluminium-containing reactions

$$\eta = \frac{\sum_i \xi_i \nu_{i,Al}}{n_{Al}^{t0}} \quad (18)$$

The concentration of aluminium as a function of  $\eta$  is presented in Fig. 3. This figure shows that as  $\eta$  approach the limit  $-1$  from right, the aluminium at time  $t1$  may shift by orders of magnitude. Since 11 of the 16 included reactions that represent a typical  $\text{CO}_2$ -water-rock simulation, are dependent on the aluminium concentration, both with respect to reaction rate and direction, a rapid change may induce instability. In this case, several fast reacting minerals that are close to equilibrium, like dawsonite, oscillate between saturation states because of the rapidly changing aqueous aluminium. These rapid changes in saturation states move the system in the right direction with respect to the global thermodynamic driving force, but at a slower rate than in a stable system. The reactivity of individual

mineral reactions, like the formation of dawsonite, are in addition wrongly estimated. Values of  $\eta$  for other aqueous species are never close to  $-1$ , and aluminium is hence the only cause of instability in the system.

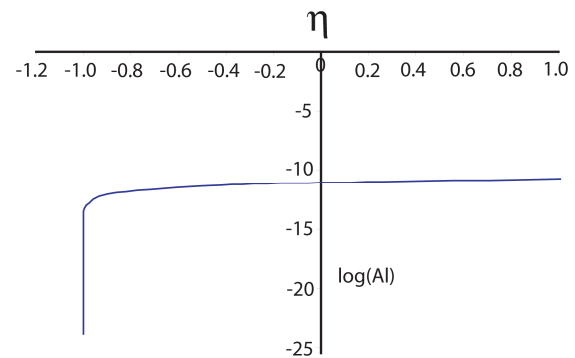


Fig. 3. As  $\eta$  is approached from the right hand side the concentration of aluminium at time  $t1$  drops rapidly.

### 3.4 A solution to the present stiffness problem

For the present system, which is representative for a  $\text{CO}_2$ -water-rock system with a few proxies replacing the natural reservoir minerals, aluminium is identified as the cause of a major stiffness problem. If we go back to the first simulation we notice that aluminium shows some variation during the first 50 to 100 years, and gradually converge towards a steady value. Using this information, we can attempt to remove the aluminium as a variable in the system and replace its temporal evolution with an independent function. Since most of the 1000 years simulated shows constant aluminium concentration, the first attempt is to simulate the system using a constant concentration. From the first simulation we notice that aluminium reach a steady mole fraction of approximately  $2.0 \times 10^{-11}$ . An attempt using this value as a constant and integrating the mineral reactions over

the same large time steps as used in the second simulation is presented in Fig. 4 and compared to the first simulation. The upper part of the figure shows a direct comparison to the first simulation, whereas the lower part plots the difference between simulated values. It is evident that it is a very close agreement with the two simulations. The first 100 years dawsonite formation is overestimated, and also the total carbon formed. This corresponds to first period of the first simulation where aluminium shows most variation. During the last 900 years the two simulations converges to values that are indistinguishable for all minerals. An even closer fit would be obtained if a proper function is constructed for the first 100 years. This would be trivial, but is not necessary if the focus is a long-term reactive system.

### 3.5 Are large reactive transport simulations possible with the present algorithm?

Without a solution to the stiffness caused by aqueous aluminium, a single grid simulations that covers 1000 years of CO<sub>2</sub>-water-rock interactions, like the first simulation in the present report, requires two or three days of simulation time. A 1000 years large-scale reactive transport simulation is therefore not achievable. On the other hand, by replacing the aluminium variable with a proper independent function, the runtime may decrease to a few seconds. For example, the execution time for the third simulation on a standard 32 Bit Linux architecture, including extensive formatted reporting, is approximately 50 seconds. By restricting the amount of reporting, using a non-formatted output, and increasing the integration step size further, execution

times can probably be decreased further down to sub-seconds. The burden of solving the reaction term in a large 3D system would then be feasible. For example, the penalty for including the reaction term in the 1944 grids 3D system simulated in [5] and [6] could be less than 30 minutes. We still have to keep in mind however that a multi-grid dynamic system is different than the batch simulations presented here. For example to find one function appropriate for all grids at all times may be impossible.

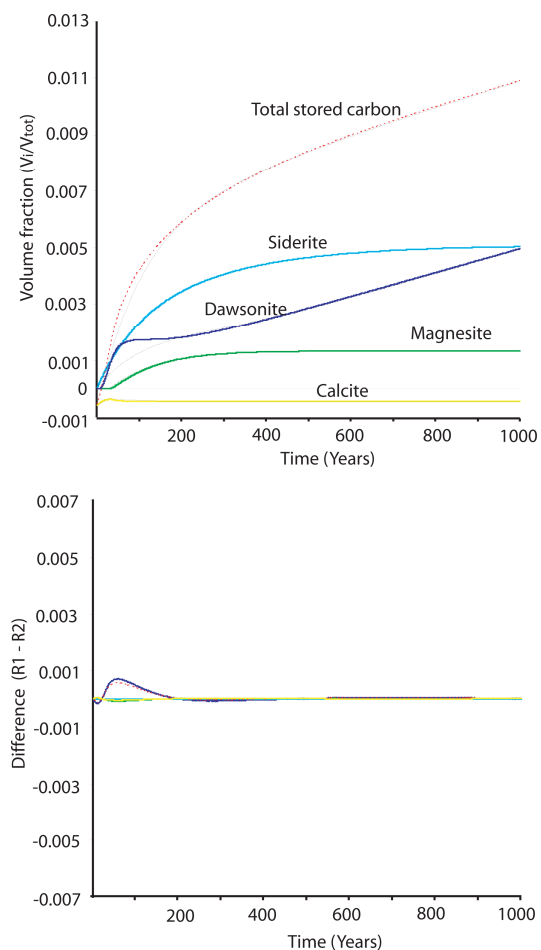


Fig. 4. Comparison between the first simulation (R1) and the third simulation (R2), the latter with the variable aluminium replaced by a constant value.



## 4 Conclusion

Solving reactive transport equations, like equation (1), commonly involve a reaction term that can cause some degree of stiffness. This creates a bottleneck for solving the reactive transport equations. This work presents a typical problem that involves solving stiff systems of ODE. This kind of problems is usually solved by some implicit routine like a BDF solver. In this report the ACCRETE geochemistry code attempts to solve the reaction term using simple explicit routines. The report presents both painstakingly slow calculations integrating the mineral reactions over short time steps, and fast simulations with large time step sizes. By comparing the different simulations, aqueous aluminium is identified as the cause of instability for this system. By replacing the variable aluminium with an independent function or constant, we can reproduce the long-term reactivity of CO<sub>2</sub> at a low CPU cost. A 1000 years single-grid batch simulation becomes possible in a few seconds or even less.

### Acknowledgements

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