

## CAPROCK INTEGRITY ASSESSMENT BY REACTIVE TRANSPORT MODELING: A CODE INTERCOMPARISON APPROACH

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### **ABSTRACT**

In the framework of the recently launched ULTimate-CO<sub>2</sub> Project, funded by the European Commission (FP7 Program), we have conducted reactive transport simulations to assess the containment properties of an idealized clay-rich, impermeable rock. The caprock formation considered for the simulations has a mineralogical composition similar to clays of the Charmotte area, Paris Basin, France. Idealized geometries have been employed to explore likely mineralogical processes expected after prolonged exposure of the cap rock to CO<sub>2</sub>-rich fluids. We have investigated the effects of both advection- and diffusion-dominated mass-transport conditions, and have performed numerical simulations in parallel, using TOUGHREACT and the Elmer/PhreeqC simulator. A comparison between the outputs of the two codes indicates that minor mineralogical transformations are expected in the Charmotte claystone over a time span of 100–200 years.

### **INTRODUCTION**

The deep geological storage of CO<sub>2</sub> is currently considered a promising technology for reducing CO<sub>2</sub> emissions in the atmosphere. The assessment of leakage risk from such storage is a primary prerequisite for site approval, public acceptance, and the awarding of credits for stored CO<sub>2</sub> quantities. Numerical simulations are usually employed to demonstrate that a geological reservoir offers the confinement properties required for safe and durable geological storage of CO<sub>2</sub>. Among the so-called containment issues is the potential impact on cap-rock-mineral integrity resulting from prolonged exposure to CO<sub>2</sub>-rich fluids—an issue of some concern with respect to the long-term effectiveness of CO<sub>2</sub> storage in geological formations.

In the framework of the recently launched ULTimate-CO<sub>2</sub> Project, funded by the European Commission (FP7 Program), exploratory numerical simulations have been performed to predict major mineralogical patterns in selected areas of potential interest for CO<sub>2</sub> geological storage in France. The caprock formation considered for this study has a mineralogical composition similar to the clays of the Charmotte area, France (Bildstein et al., 2010).

The present study has two main objectives. First, we want to set up a reactive transport model for evaluating the mineralogical transformations induced in the caprock of a candidate site for CO<sub>2</sub> geological storage in France—a model that could simulate the propagation of a CO<sub>2</sub>-rich aqueous solution likely migrating from the injection target reservoir. Secondly, we want to make an intercomparison between the reactive transport simulator Elmer/PhreeqC and one of the most proven, widely used reactive transport simulators, TOUGHREACT (Xu and Pruess, 1998).

### **MODEL SETUP**

For the sake of simplification and interpretation of results, we considered an idealized homogeneous rock medium having fixed initial porosity (0.15) and absolute permeability ( $10^{-18}$  m<sup>2</sup>). With TOUGHREACT, we simulated a vertical column of 20 m, discretized in 100 cells for the two codes and with uniform spacing of 0.2 m and an interface area of 0.01 m<sup>2</sup>. Based on field evidence, we assumed isothermal (T = 80°C) and aqueous saturated conditions (S<sub>l</sub> = 1.0). The maximum simulation time considered is 200 years.

Two mass transport conditions have been explored: (1) a pure diffusion case (labeled “D”

in the figures), with dissolved species migrating according to a single average effective diffusion coefficient of  $10^{-11}$  m<sup>2</sup>/s; and (2) a mixed case (labeled “A”), i.e., advection-controlled conditions, with an average Darcy velocity of  $8.4 \times 10^{-9}$  m/s.

Table 1. Caprock mineralogical composition and kinetic parameters of minerals considered in the simulations ( $k_{25}$  is the kinetic dissolution/precipitation rate at 25°C;  $E_a$  the activation energy in kJ/mol; SSA the reactive surface area in cm<sup>2</sup>/g-mineral;  $V_f$  being the initial volume fraction)

Mineral	$k_{25}$	$E_a$	SSA	$V_f$
Anhydrite	<i>equilibrium</i>	-	-	0.047
Calcite	$1.6 \times 10^{-6}$	23.5	10	0.482
Dolomite	$3.0 \times 10^{-12}$	52.2	10	0.024
Siderite	$1.3 \times 10^{-9}$	62.8	10	0.012
Magnesite	$4.5 \times 10^{-10}$	63.0	10	0
Pyrite	$4.0 \times 10^{-11}$	62.8	10	0.024
Dawsonite	$1.3 \times 10^{-9}$	62.8	10	0
Ankerite	$1.3 \times 10^{-9}$	62.8	1	0
			0	
Kaolinite	6.9	2	5	0
	×	2	0	.
	$10^{-14}$	.	0	1
		2	0	0
				6
Illite	8.8	1	5	0
	×	4	0	.
	$10^{-16}$	.	0	1
		0	0	2
				9
Montmor	3.9	4	5	0
	×	8	0	.
	$10^{-15}$	.	0	0
		0	0	2
				4
Quartz	1.0	8	1	0
	×	7	0	.
	$10^{-14}$	.		1
		7		0
				6

Table 2. Chemical formulas and thermodynamic constants of minerals considered in the simulations (log K values are calculated at 80°C)

Mineral	Formula	Log K
Anhydrite	CaSO <sub>4</sub>	-5.20
Calcite	CaCO <sub>3</sub>	1.06
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	1.58
Siderite	FeCO <sub>3</sub>	-1.30
Magnesite	MgCO <sub>3</sub>	0.97
Pyrite	FeS <sub>2</sub>	-90.90
Dawsonite	NaAlCO <sub>3</sub> (OH) <sub>2</sub>	-15.87
Ankerite	CaFe <sub>0.7</sub> Mg <sub>0.3</sub> (CO <sub>3</sub> ) <sub>2</sub>	0.40
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	-34.24
Illite	K <sub>0.85</sub> Mg <sub>0.25</sub> Al <sub>2.35</sub> Si <sub>3.4</sub> O <sub>10</sub> (OH) <sub>2</sub>	-38.38
Montmor.	Na <sub>0.33</sub> Mg <sub>0.33</sub> Al <sub>1.67</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	-31.20
Quartz	SiO <sub>2</sub>	-3.17

The mineralogical system is described in terms of nine primary phases (Table 1). Dissolution and precipitation rates for the minerals are calculated with a general kinetic formulation based on the Theory of the Transition State (Aagaard and Helgeson, 1982; Lasaga, 1981, 1984). Kinetic parameters are taken from the compilation of Palandri and Kharaka (2004). Initial mineralogical composition and the kinetic parameters employed in the simulations are listed in Table 1.

Thermodynamic data are mostly from the Thermoddem database (thermoddem.brgm.fr), an internally consistent and thoroughly revised compilation of thermodynamic data prepared at the French Geological Survey (BRGM). Log K values for relevant minerals are listed in Table 2. The initial chemical composition of cap rock and acidic reservoir pore waters has been taken from Bildstein et al. (2010). Clay-rock pore waters have been slightly modified by iterative batch modeling in order to achieve near-steady-state conditions with the mineralogical assemblage of Table 1. These chemical compositions are listed in Table 3.

Table 3. Elemental chemical composition of reservoir and caprock porewaters. Total concentrations are in mol/kgw. Chemical components (or basis species) are in brackets.

Parameter	Caprock	Reservoir
pH	6.08	4.65
redox (as H <sub>2(aq)</sub> )	$3.95 \times 10^{-24}$	$8.15 \times 10^{-8}$
Ca (as Ca <sup>+2</sup> )	$2.08 \times 10^{-2}$	$5.93 \times 10^{-2}$
Mg (as Mg <sup>+2</sup> )	$6.48 \times 10^{-3}$	$1.67 \times 10^{-2}$
Na (as Na <sup>+</sup> )	$2.46 \times 10^{-1}$	$2.50 \times 10^{-1}$
K (as K <sup>+</sup> )	$2.97 \times 10^{-3}$	$4.52 \times 10^{-3}$
Fe (as Fe <sup>+2</sup> )	$9.53 \times 10^{-5}$	$9.36 \times 10^{-6}$
Si (as SiO <sub>2(aq)</sub> )	$6.95 \times 10^{-4}$	$2.48 \times 10^{-4}$
Al (as AlO <sub>2</sub> <sup>-</sup> )	$2.78 \times 10^{-8}$	$1.21 \times 10^{-8}$
Cl (as Cl <sup>-</sup> )	$2.68 \times 10^{-1}$	$3.44 \times 10^{-1}$
C (as HCO <sub>3</sub> <sup>-</sup> )	$8.73 \times 10^{-3}$	$1.02 \times 10^{+0}$
S (as SO <sub>4</sub> <sup>-2</sup> )	$1.61 \times 10^{-2}$	$1.06 \times 10^{-2}$

### CODE COMPARISON

The intercomparison study we conducted relied on the resolution of the geochemical-transport equation:

$$\frac{\partial \omega C_i}{\partial t} = -\nabla \cdot (\omega v C_i) + \nabla \cdot (\omega D \nabla C_i) - \frac{\partial q_i}{\partial t},$$

the source term  $\frac{\partial q_i}{\partial t}$  being determined by the geochemical equilibrium.

The ELMER/PHREEQC environment is based on the operator splitting approach described in Strang (1968). Elmer is a multiphysics software code that can account for flow, ion transport, temperature, and mechanics; it was developed by the CSC-IT (<http://www.csc.fi/english>), a Finnish institute. This software is based on finite element technologies; while written mainly in fortran90, it also uses C and C++. In its 6.2 version, Elmer is distributed under the GNU license (GPL 2.). The use of Elmer gives access to up-to-date algebraic solvers. For direct methods, Lapack or Umfpack libraries are made accessible; for iterative methods, preconditioned Krylov subspace or multilevel methods can be accessed. The code can also be run parallel using MPI tools, using domain decomposition to distribute the load to multiple processes that are being run either on different cores or CPUs.

Here, mesh partitioning can be made using Metis (<http://glaros.dtc.umn.edu>). In association with Elmer, we use PhreeqC (Parkhurst & Appelo 1999) as geochemical batch solver, here in its 2.17.5 version.

The coupling is carried out in Python for a NI or a CC algorithm, Elmer and phreeqC being shared objects within the environment with memory access to code structure to reach an efficient coupling of the tools. Validation of the coupling algorithm is achieved with ~50 standard geophysical tests. Chemical equilibrium can be distributed on a node-by-node basis over system CPUs to shorten simulation times.

TOUGHREACT (Xu and Pruess, 1998) was developed by introducing reactive chemistry into the framework of the existing multiphase fluid and heat flow code TOUGH2 (Pruess, 1991). Spatial discretization in TOUGHREACT is achieved by means of integral finite differencing (Narasimhan and Witherspoon, 1976). An implicit time-weighting scheme is used to solve equations for flow, transport, and geochemical reactions.

Simulations were performed following a sequential noniterative approach similar for the two tools. After solution of the flow equations, we used the fluid velocities and phase saturations for aqueous-chemical transport simulation, which is solved on a species-component basis. The resulting aqueous concentrations calculated from the transport simulation are substituted into the chemical reaction model. Then the system of chemical reaction equations is solved on a gridblock basis by the Newton-Raphson method.

### BENCHMARKING EXERCISE

For this exercise, we used TOUGHREACT version 1.2; for phreeqC, we used version 2.17.5 coupled to Elmer 6.2. The goal of the comparison was to construct a geochemical model to be used with confidence using either of the two simulators, before dealing with unsaturated media.

## MODEL RESULTS

Despite two quite similar initial chemical systems, we have not yet been able to reach the same spatial geochemical evolution of the system on the two codes. Figure 1 shows the extension of a tracer within the system (see Figure 1 to relate to porosity variations). Small variations in the pH are noted (Figure 2), but with respect to precipitation/dissolution phenomena, we find differences that induce further differences in the simulated porosity evolution (Figure 3). The porosity evolution rate for Elmer/phreeqC is about two times that calculated with TOUGHREACT. As an example, for the geochemical simulation using phreeqC, no dissolution of the quartz occurs, in contrast with what is determined with the TOUGHREACT solver. In addition, for minerals like calcite or Mg-Na-montmorillonite, dissolution rates are quite different. Parameters such as time integration were studied, but they did not explain the noted differences. Further investigations will be conducted not only on model parameters (such as activity) but also on numerical parameters such as differential integration.

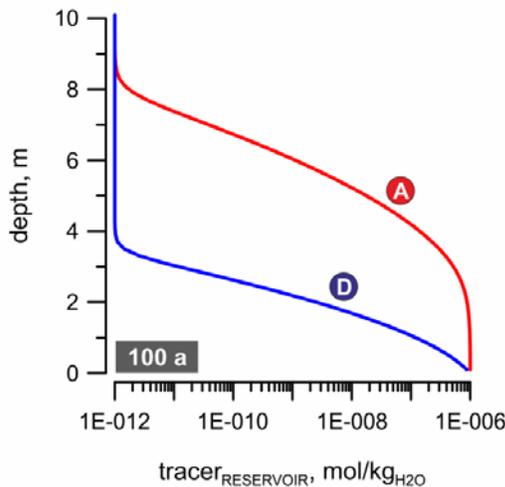


Figure 1. Spatial variation of aqueous tracer concentration in the caprock (10m vertical column) after 100 years. The red and blue curves labeled “A” and “D” are representative of calculations under advection- and diffusion-controlled mass transport conditions, respectively (results from TOUGHREACT simulation).

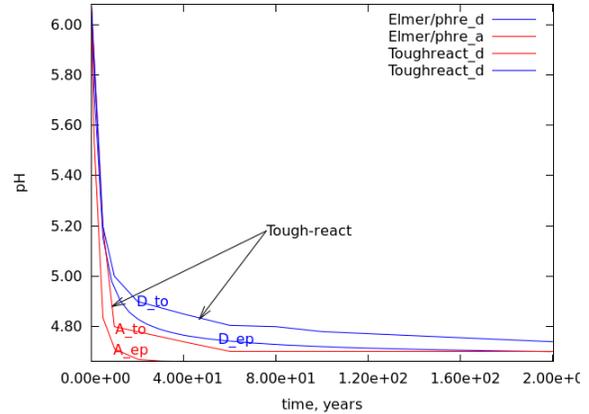


Figure 2. Temporal (0 to 200 years) variation of pH in the first cell of the caprock.

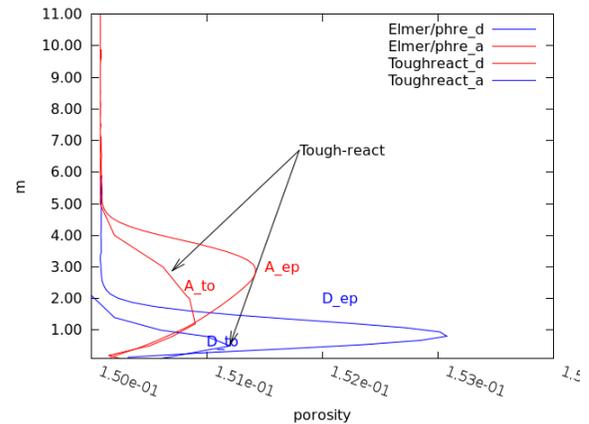


Figure 3. Spatial variation of the porosity after 200 years for TOUGHREACT and Elmer/phreeqC coupling

With respect to numerical integration, the TOUGHREACT solver is about four times faster than Elmer/PhreeqC. For Elmer/PhreeqC, about 95% of the CPU time is dedicated to the numerical integration of the differential equations. That integration is made through the cvoid solver, whose numerical parameters have been optimized in terms of CPU time.

## CONCLUSIONS

Within the frame of the exercise, we were not able to reach the same evolution for the geochemical system using the two tools. Our time span was too short to make a thorough analysis of all elements potentially explaining the discrepancies. Nevertheless, the two tools

delivered results that can be identified as similar in terms of safety.

Considering CPU times, without making use of any parallel distribution of the chemistry equilibrium states over the CPU architecture, we find that TOUGHREACT is about 4 times faster than the Elmer/phreeqC coupling, with the ccode solver (used within phreeqC for kinetically driven precipitation/dissolution minerals) the primary cause of that difference.

The comparison between the codes will be pursued over the next few months, as we try to match one code's evolution of cap-rock chemistry with the other, in order to get definitive elements of comparison in terms of performance.

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