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VALIDATION OF MARTHE-REACT COUPLED SURFACE AND GROUNDWATER REACTIVE TRANSPORT CODE FOR MODELING HYDRO SYSTEMS

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ABSTRACT

This paper presents the validation of the computer code MARTHE-REACT enabling the simulation of reactive transport in hydrosystems. MARTHE-REACT results from coupling the MARTHE code (flow and transport in porous media) with the chemical simulator TOUGHREACT. The resulting coupled model takes advantage of the functionalities already available in each of the two codes. In particular, it is now possible to simulate flow, reactive mass, and energy transfer in both saturated and unsaturated media (vadose zone), taking into account the soil-atmosphere exchange (rainfall, evapo-transpiration), and runoff into rivers and infiltration. Four examples of verification are presented in comparison with calculations using the reference coupled codes TOUGHREACT, PHAST, PHREEQC, and MARTHE-SCS.

- 1) Continuous injection of acidified CO₂-rich aqueous phase into a fictitious limestone core sample. Simulations performed with several transport schemes are compared with results from PHREEQC and MARTHE-SCS.
- 2) Injection of CO₂-saturated water into a Dogger carbonate reservoir (Paris Basin, France). The reservoir is modeled with a 2D radial geometry. Chemical simulations are compared with those obtained using the TOUGHREACT code.
- 3) Diffusion of acidified water within a cap rock overlying the Dogger aquifer, in which (hypothetical) large amounts of CO₂ are stored.
- 4) Carbonated brine percolation through a weathered cement sample for 7 days, accounting for coupled advection-diffusion-reactions having various kinetics. These simulations are compared with those obtained with the TOUGHREACT code.

The coupling in MARTHE-REACT is based on a sequential noniterative algorithm, so that parallelization of the chemical calculations has been easily implemented. Preliminary results on a 64-processor computer show a dramatic decrease of needed CPU time, even with a moderately complex geometry.

INTRODUCTION

To accurately model complex, real-world aquifer systems and their chemical interactions, it is necessary to combine a detailed groundwater flow model with a geochemical model. For instance, the PHREEQC (Parkhurst and Appelo, 1999) public domain code couples a very detailed chemical simulator with a simple 1D transport scheme. In addition, PHREEQC has been coupled to several transport codes. For instance, in PHAST (Parkhurst et al.), it is coupled with a 3D transport scheme. In PHT3D (Prommer et al., 2003), it is coupled with a MODFLOW model. In HP1 (Simunek et al. 2006), it is coupled with the 1D vadose zone transport code HYDRUS_1D. TOUGHREACT (Xu et al. 2004) is a widely used multiphase mass and energy transport code integrating a chemical simulator. To model complex hydrosystems, TOUGHREACT has been integrated into the MARTHE (Thiery, 1990, 1993, 1995a,b, 2007) flow and transport code. This paper presents a validation of this new tool.

NUMERICAL TOOL

The computer code MARTHE-REACT, resulting from the coupling of the flow and transport code MARTHE with the chemical simulator of TOUGHREACT, is briefly described below.

The TOUGHREACT Code

TOUGHREACT is a nonisothermal multicomponent reactive fluid flow and geochemical transport simulator that can be applied under various thermo-hydrological and geochemical conditions of pressure, water saturation, and ionic strength. It is a reference code extensively used for extreme conditions (high temperatures, high pressure, high salinity, etc.).

The MARTHE Flow and Transport Code

MARTHE (Modelling Aquifers with Rectangular cells, Transport and Hydrodynamics) is a 3D code for flow and hydro-dispersive transport in porous media. Mass and energy transfer are modeled in both saturated and unsaturated media using the Richards equation, taking into account soil-atmosphere interactions (rainfall, evapo-transpiration), and runoff into rivers and infiltration. The flow calculations follow a finite volume approach using irregular

parallelepipedic cells, with the possibility of nested grids or radial grids. Based on a kinematic wave approach, flow in river networks is coupled to groundwater flow. Mass and energy transport occur simultaneously in the groundwater system and in the surface network. Several transport schemes are available, which may be selected according to the kind of problem at hand: finite difference transport, method of characteristics (MOC), total variation diminishing (TVD) (Thi ry, 1995a). Temperature and fluid density variations are also taken into account (Thi ry, 2007).

THE COUPLING APPROACH

MARTHE has already been coupled to specific chemical simulators (SCS) (Kerv van et al., 1998, Thi ry 1995b), and the approach used to couple it with the TOUGHREACT chemical simulator is essentially the same. Flow calculations and mass and energy transport are performed by the MARTHE code with no modifications. Chemical simulations are performed by the chemical part of the TOUGHREACT code. The coupling sequence is the following at each time step: (1) coupled flow calculation in aquifers and river networks integrating evaporation, infiltration, runoff, overflow etc.; (2) transport in aquifer and river networks of each primary dissolved chemical species; (3) chemical reactions in each aquifer cell and river reach using the concentrations at the end of the time step. There is no iteration; hence, it is a SNIA (sequential non iterative algorithm) scheme. The important point is that with this sequential scheme, after transport, the chemical reaction calculations are independent in each cell.

This coupling method has several advantages: because the chemical calculations are independent, the chemical reactor extracted from TOUGHREACT is totally independent of any grid or time sequence. As a matter of fact, on each call, the reactor knows only one mesh and one time step duration. This guarantees the independence of both codes and also enables a very simple parallelization. Another advantage is that several chemical simulators may be implemented independently in MARTHE. The user of the code may then select the chemical simulator that is most appropriate to the problem, or the chemical simulator that he/she knows the best.

VALIDATION TEST 1: CONTINUOUS INJECTION OF ACIDIFIED CO₂-RICH AQUEOUS PHASE INTO A FICTITIOUS LIMESTONE CORE SAMPLE

Problem Description

This validation case simulates the percolation of an aqueous solution enriched with CO₂ into a pure calcite cylindrical core initially saturated with a

solution of water, in equilibrium with calcite in atmospheric pCO₂. The simulations were used for the pre-dimensioning and interpretation of experiences with percolation of water acidified by CO₂ dissolved in a Lavoux limestone core (Kerv van et al., 2007). The core properties are given in Table 1.

Table 1. Calcite core geometry and parameters

Core length	10 cm
Core diameter	4 cm
Kinematic porosity	30 %
Longitudinal dispersivity	1 cm
Temperature	25�C
Injection rate	20 cm ³ .h ⁻¹

The composition of the water initially saturating the core was calculated by equilibrating pure water with calcite under atmospheric conditions (CO₂ pressure of 3.16 10⁻⁴ bar). The composition of the injected water has been calculated by equilibrating pure water containing 5 10⁻⁷ mol.kg_{H₂O}⁻¹ of CaCl₂ with a 1 bar CO₂ pressure.

Simulations

The concentrations after one hour of injection were calculated with PHREEQC and MARTHE-REACT. The calculations performed with PHREEQC correspond to a discretization of the core into 80 cells 1.25 mm long, with a time step of 84.9 seconds. The time step in PHREEQC is constrained by the need for a Courant number equal to 1; therefore, since the filtration velocity is 0.0147 mm/s, the time step must be set at 84.9 seconds.

Calculations with MARTHE-REACT were performed with 100 cells, different transport schemes and different time steps (10 s or 60 s). Figure 1 and Figure 2 show that the pH profile and dissolved calcium profile calculated with PHREEQC and MARTHE-REACT are very similar, except very near the core ends.

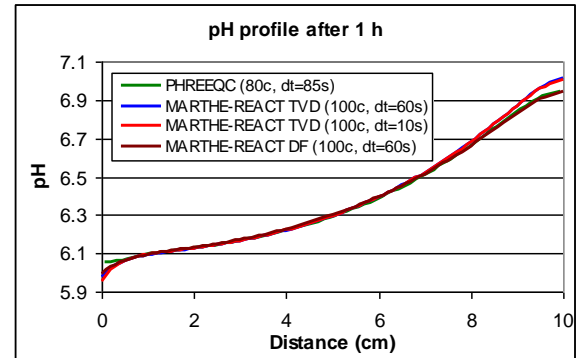


Figure 1. Comparison of pH profile, calculation with PHREEQC and MARTHE-REACT.

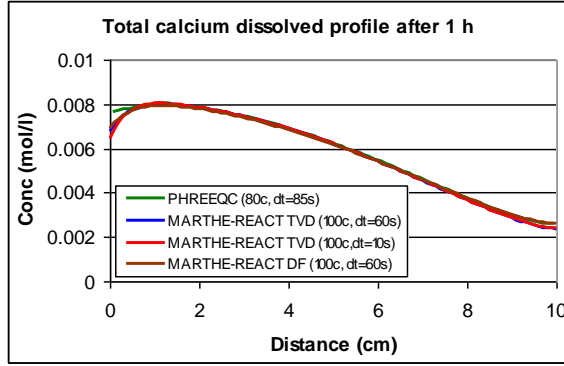


Figure 2. Comparison of total dissolved calcium concentration profile. Calculation with PHREEQC and MARTHE-REACT.

Calculations with MARTHE coupled with specific chemical simulators (MARTHE+SCS) yielded comparable results (Kervévan et al., 2007). Also note that the calculations are much faster with MARTHE-REACT: 1 second of CPU time for 100 cells and 100 time steps, as compared to 600 seconds of CPU time for PHREEQC for 80 cells and 43 time steps.

VALIDATION TEST 2: INJECTION OF CO₂ SATURATED WATER INTO A DOGGER CARBONATE RESERVOIR

Problem Description

This validation case, following the work of André et al. (2007), uses a simple 2-D radial model to simulate the CO₂ behavior near the injection well of the Dogger Reservoir (Paris Basin, France). The well field is modeled (Figure 3) as a circular region of 100,000 m radius and 20 m thickness. At the center, a well injects dissolved CO₂ into the formation water.

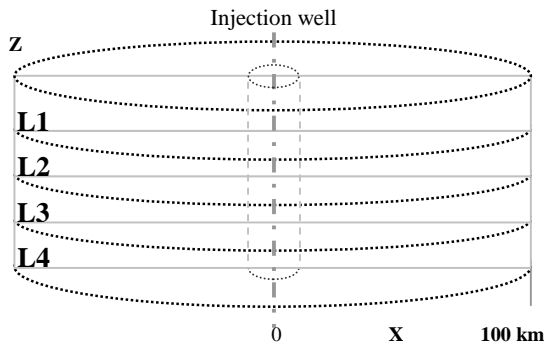


Figure 3. Two-dimensional radial geometry of the Dogger reservoir model with four layers (L1, L2, L3 and L4).

Porosity and permeability are homogeneous. The formation parameters are given in Table 2. The reservoir temperature is assumed to be uniform (75°C), and a hydrostatic pressure is considered

initially as fixed in the outermost column of the grid during the simulation. No exchanges of fluids are considered above or below the system.

Table 2. Injection of CO₂ into the Dogger reservoir: geometry and parameters.

Aquifer thickness	20 m
Permeability	$1 \cdot 10^{-13} \text{ m}^2$
Compressibility	Water compressibility only
Kinematic porosity	15 %
Diffusion	0
Dispersivities	0
Temperature	75°C
Transport method	Finite Differences
Total injected flow	$20 \cdot 10^{-3} \text{ m}^3/\text{s}$

The injected solution corresponds to the formation water in equilibrium at 75°C with a CO₂ pressure of 180 bars (the initial reservoir pressure). Consequently, to be in equilibrium with this gas phase at such pressure, the water contains 1.25 moles of carbonates / kg H₂O.

The reservoir composition is defined in the André et al. simulation (2007) and initially contains a solution at equilibrium with the reservoir rocks at a constant temperature of 75°C. The chemical composition of the formation water and injected CO₂-saturated water are presented in Table 3. The 12 minerals of reservoir rock are similar to the André et al. study, including 70% calcite, 10% dolomite, 5% siderite, 5% illite, 5% albite and 5% K-feldspar (in volume fraction). Kaolinite, chalcedony, magnesite, dawsonite, anhydrite, and halite are not initially present in the reservoir, but are allowed to precipitate. Dissolution and precipitation of minerals follow kinetic laws.

Table 3. Chemical composition of formation water and injected water (in mol/kgH₂O)

Formation water		CO ₂ -saturated water	
Temperature	75 °C	Temperature	75 °C
pH	6.7	pH	3.0
Alkalinity	427.0	Total Carbon	1.080
Na	$7.734 \cdot 10^{-2}$	Na	$7.734 \cdot 10^{-5}$
K	$9.051 \cdot 10^{-4}$	K	$9.051 \cdot 10^{-7}$
Ca	$2.860 \cdot 10^{-3}$	Ca	$2.860 \cdot 10^{-6}$
Mg	$2.777 \cdot 10^{-3}$	Mg	$2.777 \cdot 10^{-6}$
Al	$1.976 \cdot 10^{-7}$	Al	$1.976 \cdot 10^{-10}$
Fe	$2.856 \cdot 10^{-5}$	Fe	$2.856 \cdot 10^{-8}$
Cl	$7.049 \cdot 10^{-2}$	Cl	$7.049 \cdot 10^{-5}$
SO ₄	$6.985 \cdot 10^{-3}$	SO ₄	$6.985 \cdot 10^{-6}$
SiO ₂	$8.476 \cdot 10^{-4}$	SiO ₂	$8.476 \cdot 10^{-7}$

Simulations

The geologic formation is assumed to be infinite-acting and homogeneous, with a total thickness of 20 m. A 2D radial grid (X, Z) has been chosen. The aquifer thickness (Z axis) is divided into four layers

(L1, L2, L3 and L4), and the radial direction (X axis) is divided into 100 columns, with radius following a logarithmic progression starting from 0.2 m for the injection well to 10.115 m at the outmost limit, 100,000 m away. The total grid then has 400 cells.

Simulations are realized for 1 year of CO₂-saturated water injection with MARTHE-REACT and TOUGHREACT. Effects of temperature on flow are taken into account in both simulations. Due to the water compressibility, the hydraulic calculation is performed in a transient state. Because of the small size of the injection cell, a time step of 24 seconds was selected for the entire simulation (after some smaller time steps at the very beginning).

Simulation results (Figure 4) are compared in terms of pH (A), porosity (B) and variation of minerals—(C) carbonates and (D): alumino-silicates. The results are identical in the four layers; only the first layer profiles along the radial distance from the injected well are presented. One can observe an acidification of the reservoir in the first few meters around the well (pH = 3) involving total dissolution of carbonates (calcite and dolomite) and minor dissolution of alumino-silicates (Albite, K-feldspar and illite). This high dissolution has an impact on porosity, which increases (15% initially and 87% after 1 year).

Further within the reservoir, pH is controlled by calco-carbonic equilibrium (pH = 4.8) where carbonates are still present. In the nonaffected zone, minor chemical reactions occur where formation water is at near-equilibrium with mineralogical assemblage. Within these simulations all the observations related to chemical reactivity are similar to André et al results (2007). MARTHE-REACT and TOUGHREACT results are identical.

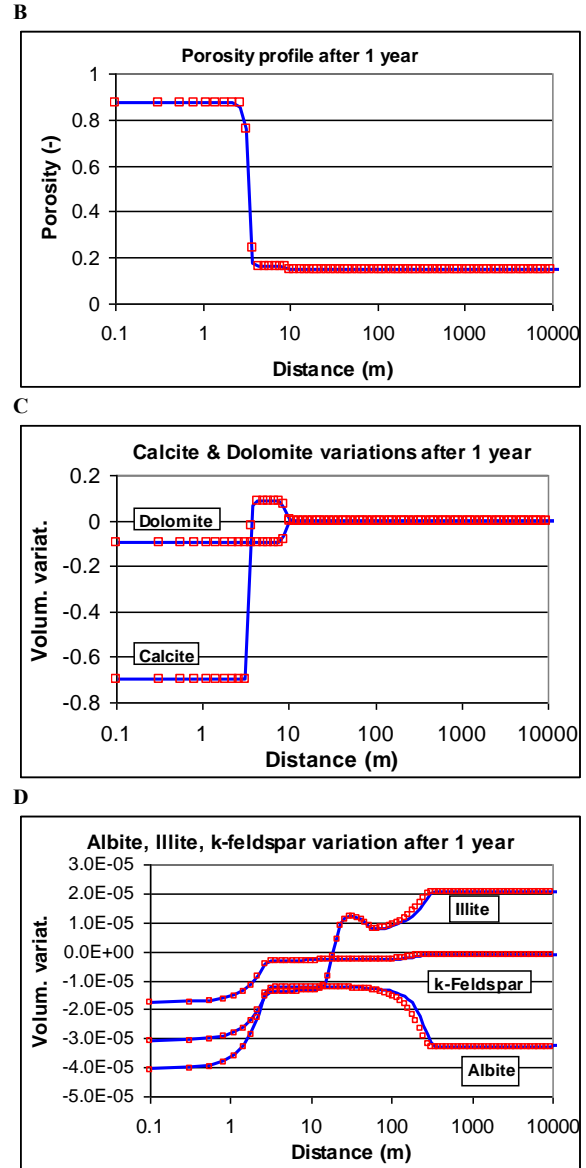
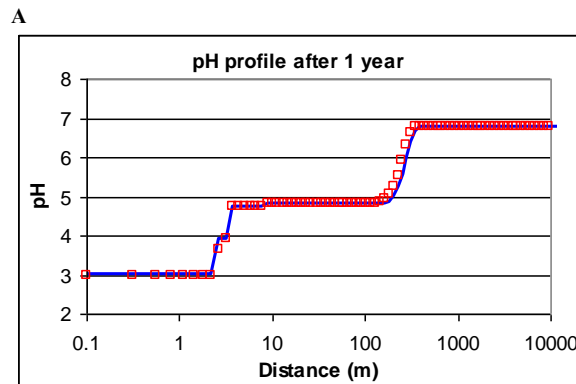


Figure 4. Variation of pH, porosity and mineral volume fractions (V_{min}/V_s) in the first layer of Dogger aquifer from the injection cell to the outermost after 1 year of CO₂-saturated water injection. MARTHE-REACT (solid line) and TOUGHREACT (open squares).

Similarly, simulations have been done for a reactivity study of the Keuper sandstone aquifer, using the MARTHE-REACT simulator. The work is described by Picot-Colbeaux et al. (2009, in the same Tough Symposium) where the aquifer is represented by a 2D radial geometry with three layers, each layer having their own permeability and porosity. In this case, flow, chemical reactivities, and transport vary between layers, from the injected well to the outermost column.

VALIDATION TEST 3: DIFFUSION OF ACIDIFIED WATER WITHIN A CAP ROCK OVERLYING THE DOGGER AQUIFER

Problem Description

This validation case hypothetically simulates the vertical diffusion of acidified water from the Dogger aquifer into its overlying clay cap rock (Kervévan et al., 2009). The cap-rock formation is mainly composed of calcite, montmorillonite-Na, and quartz. There are eight primary minerals, initially present in the formation, and four secondary minerals. Because the permeability is very low, the advection flow is considered as negligible, and only molecular diffusion is taken into account. The system is modeled as a vertical 1D domain, with vertical dimension large enough to be considered as semi-infinite during the simulation duration of 10,000 years (Table 4).

Table 4. Clay caprock geometry and parameters.

Domain length	10 m
Kinematic porosity	15 %
Diffusion	$10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$
Temperature	80°C
Transport method	Finite Differences

The acidified water in the Dogger aquifer, at the lower end of the domain, is a brine at 80 °C, with a CO₂ pressure of 150 bars and pH of approximately 4.8. The initial brine in the cap rock, mainly composed of NaCl (0.26 mol/kgw), has a pH of approximately 6.5. The detailed mineralogy and brine compositions assumed, as well as the kinetic laws used for describing dissolution and precipitation processes, lead to a relatively complex coupled problem that includes 12 mineral phases.

Simulations

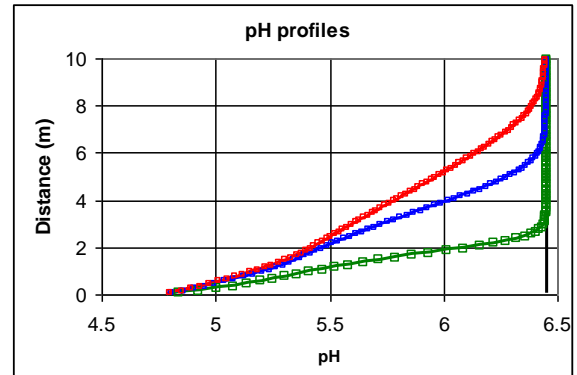
Coupled transport and reactions have been simulated with MARTHE-REACT, TOUGHREACT, PHREEQC, and PHAST. The domain was discretized into 100 cells of 10 cm length. For MARTHE-REACT simulations, the 10,000-year simulation period was divided into 6 small time steps, followed by 1,999 time steps of 5 years duration. TOUGHREACT also used time steps of 5 years after 30 times steps increasing progressively. Figure 5 and Figure 6 compare, for some dissolved elements and some minerals, the concentration profiles calculated with MARTHE-REACT (solid line) and with TOUGHREACT (open squares). These figures show that the simulations results are identical. Simulations were also performed with PHREEQC and PHAST codes, with chemical formulations and water compositions approximately the same. The results with PHAST, described in Kervévan et al. (2009), are comparable with MARTHE-REACT (or TOUGHREACT) for the pH and dissolved carbon

profiles—reasonably close for some minerals and quite different for others. The discrepancies are most probably due to the differences in the TOUGHREACT and PHREEQC chemical reactors.

Parallelization

A simple parallelization of the chemical calculations has been implemented in MARTHE-REACT code. This same simulation on a cluster of 16 processors resulted in a reduction of the CPU time by a factor of 11, compared to a nonparallel simulation on the same computer.

A



B

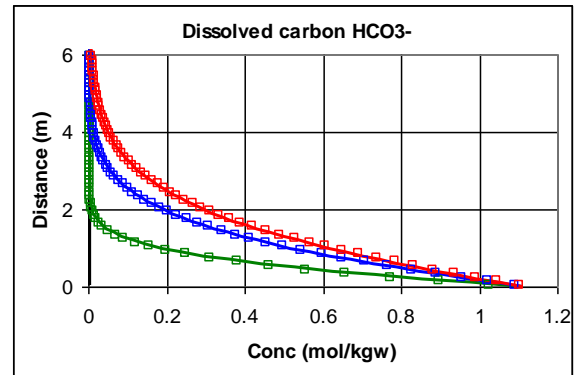


Figure 5. Diffusion in clay caprock: Profiles after 1000 years (green), 5000 years (blue) and 10000 years (red). A: pH, B: Dissolved carbon. MARTHE-REACT (solid line) and TOUGHREACT (open squares)

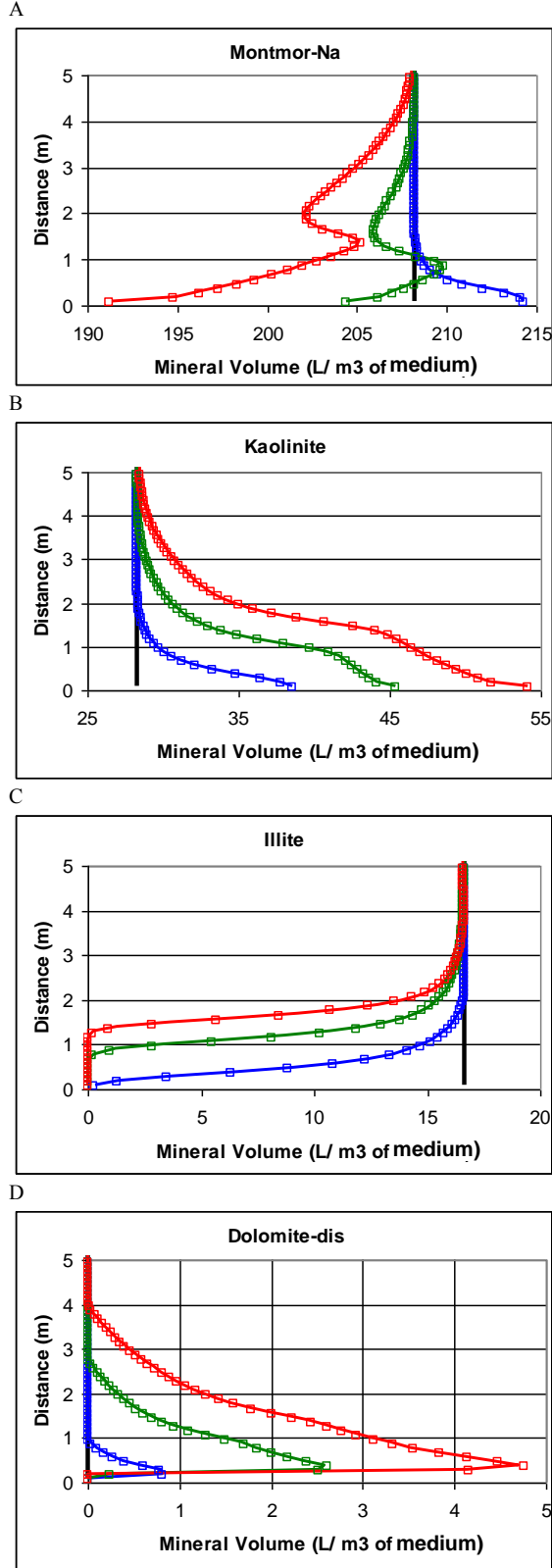


Figure 6. Diffusion in clay caprock: Profiles after 1000 years (blue), 5000 years (green) and 10000 years (red). A to D: minerals. MARTHE-REACT (solid line) and TOUGHREACT (open squares)

VALIDATION TEST 4: CARBONATED BRINE PERCOLATION THROUGH A POROUS CEMENT

Leakage via the cement sheath of the wells is an issue for the long-term safety of CO₂ geological storage. The reactivity of cement with the fluids (gas, brine) occurring in the host reservoir at high pressure and high temperature can result in their alteration. Well cement-CO₂ interactions in the context of CO₂ geological storage have been investigated via reactive transport modeling (Jacquemet, 2006; Carey and Lichtner, 2007) with the aim of reproducing *in situ* or experimental observations. As a test, we modeled, with MARTHE-REACT, the percolation of a carbonated brine through a cementitious porous channel. This feature represents a defect in a well cement sheath. The model is based on an experiment by IFP (French Institute of Petroleum). This percolation experiment has already been modeled with TOUGHREACT by Jacquemet (2009) in the framework of the CO₂GEONET project (Rochelle et al., 2009).

Problem Description

An acid brine percolates over 7 days through a 40 mm long cementitious porous channel, whose properties are given in Table 5. The cement is initially composed of four primary minerals, and later, of 5 potential secondary minerals (Table 6). The initial interstitial cement water results from the equilibrium of pure water with the primary cement minerals, and hence is very basic: its pH is 10.8. The injected water is composed of a NaCl solution (0.4 mol/kgw) equilibrated with a CO₂ pressure of 5 bar at a temperature of 80°C: its pH is 3.5.

Table 5. Cement porous channel geometry and parameters.

Length	40 mm
Permeability	$3.5 \cdot 10^{-15} \text{ m}^2$
Kinematic porosity	60 %
Diffusion	0
Longitudinal dispersivity	0
Temperature	80°C
Transport method	Finite Diff.

Table 6. Initial cement mineral assemblage.

Mineral	% Volume
Calcium Silicate Hydrates (CSH 1.6, C/S=1.6)	60
Portlandite (CH)	20
Katoite	10
Calcium monosulfoaluminate (AFm)	10
CSH 1.2 (C/S=1.2)	0
CSH 0.8 (C/S=0.8)	0
Amorphous silica, calcite and aragonite	0

Simulations

The coupled transport and reaction was simulated with MARTHE-REACT and TOUGHREACT. The core was discretized into 100 cells of 0.4 mm length. The 7-day simulation period was divided into time steps of 2 seconds duration. This time-step duration was chosen because it corresponds to a reasonable Courant number of 1.02.

Figure 7 and Figure 8 compare profiles calculated with MARTHE-REACT and with TOUGHREACT. The profiles show that the simulation results are very close. A small discrepancy appears: the reactions with TOUGHREACT are slightly faster (around 1 or 2%), which might result from a small difference in the hydraulic parameter definition. The models predict very similar evolutions. Because of the slow reaction kinetics compared to the quick advection, the pH decreases dramatically, which results in a strong dissolution of the cement. Porosity increases from 60% to ~100% after 3 days of injection.

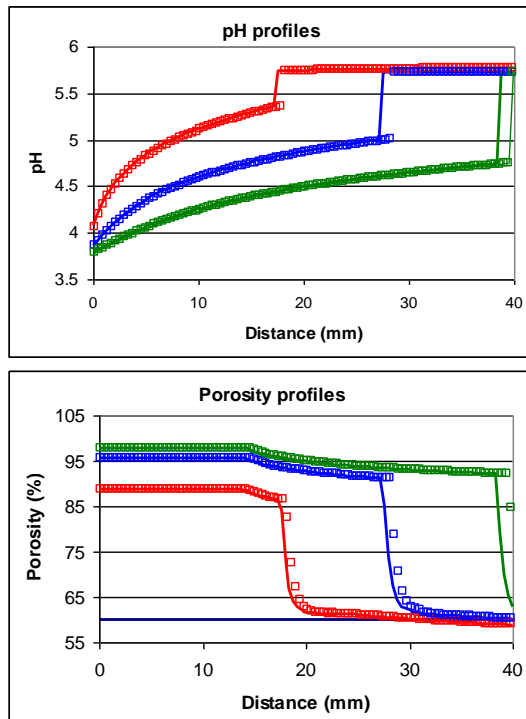


Figure 7. Carbonated brine percolation through a cement. Profiles after 1 day (red), 2 days (blue) and 3 days (green). Top: pH, bottom: porosity. MARTHE-REACT (solid line) and TOUGHREACT (open squares).

Note that a transient calcite precipitation (up to 3 days) allows the initial porosity to be conserved in the second half of the channel. Amorphous silica deposits quickly at a distance of 14 mm and reaches a 6% volume fraction, without the possibility of dissolving. This is the only mineral significantly

present at the end of the simulation, and the resultant porosity is 94 %.

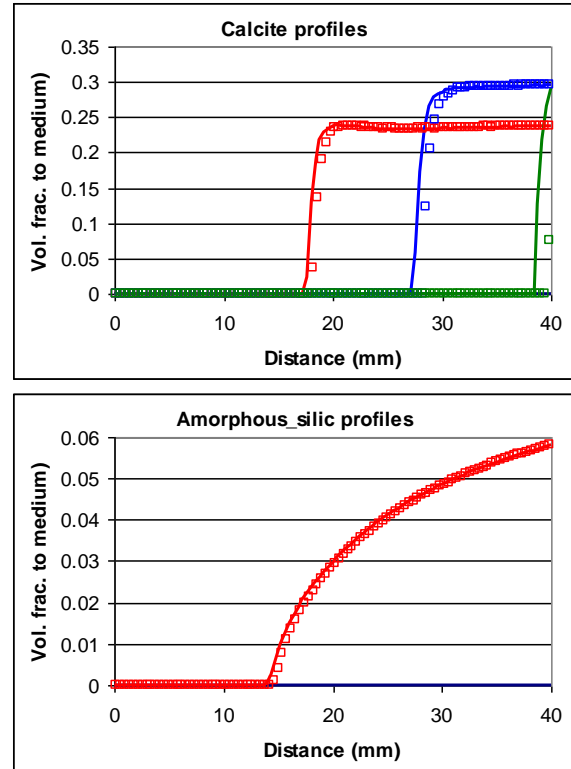


Figure 8. Carbonated brine percolation through a cement. Profiles after 1 day (red), 2 days (blue) and 3 days (green). Top: calcite, bottom: amorphous silica. MARTHE-REACT (solid line) and TOUGHREACT (open squares).

CONCLUSIONS

A set of coupled reactive transport simulations performed with the MARTHE-REACT code was compared with TOUGHREACT and other codes. It appears that the results are the same, which is a verification of the coupling of TOUGHREACT chemical simulator with the MARTHE code. The value of MARTHE-REACT is that it integrates efficient transport schemes and is adapted to the simulation of unconfined aquifers and complex hydrosystems. Validation of reactive transport simulations through the vadose zone are scheduled.

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