Numerical modeling of fluid-rock chemical interactions during CO2 saturated water injection into a sandstone reservoir, using the MARTHE-REACT code.
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ABSTRACT
This study describes the numerical modeling of fluid-rock chemical interactions during CO$_2$-saturated water injection into a sandstone reservoir, using the MARTHE-REACT code (Thiéry et al., 2009, presented in the same TOUGH symposium). The reservoir is modeled in a 2D radial geometry with a thickness of 100 m, divided into three horizontal layers. The layers are characterized by contrasting hydrodynamic properties (porosity between 4 to 7%, permeability between $2\times10^{-16}$ m$^2$ and $2.3\times10^{-15}$ m$^2$), but all layers initially contain the same material (mineralogical assemblage and water composition). CO$_2$-saturated water is injected vertically over the entire thickness of the reservoir.

The simulation results confirm the high reactivity of CO$_2$-saturated water with respect to carbonate and sulphate minerals, which are totally dissolved in the water-saturated zone of the near-well field. Reactions occur to a larger extent in the upper layer, where the permeability is higher. Dissolution of calcite, dolomite, and anhydrite induces some pH buffering and a significant increase in porosity, reaching 41% in the first few meters of the water-saturated zone after ten years. Just behind the dissolution front, one can observe precipitation of dolomite, kaolinite, and quartz. Albite dissolution presents the first step in destabilization of the alumino-silicates. This can be explained by the slow kinetics of alumino-silicate mineral dissolution compared to the faster kinetics of carbonates. Consequently, the porosity evolution of the reservoir is essentially constrained by the magnitude of carbonate- and sulphate-mineral dissolution-precipitation reactions.

This study is a first step in the assessment of CO$_2$-saturated water leakage from the reservoir to the surface in a sedimentary basin, where physical-functionality approaches implemented in the MARTHE simulator are essential for modeling complex hydrodynamic systems (supporting the link between hydrogeology and hydrology, including, for instance, mass exchanges with the atmosphere and river subsystems).

INTRODUCTION
We describe physical and chemical phenomena occurring during the injection of acidic solutions (CO$_2$-rich solutions) with the establishment of reactive and mobile fronts.

Previous studies of geochemical processes occurring during CO$_2$ injection in an aquifer forecast the existence of five contrasting reactive zones extending radially from the injector (Figure 1): a full drying-out of the medium (Zone 5); a highly saline aqueous solution (Zone 4); a multiphase system with pH controlled by CO$_2$ (Zone 3); a saturated and acidified (CO$_2$-rich solution) aqueous solution (Zone 2); and an aqueous solution at equilibrium with reservoir minerals at reservoir pH (Zone 1) (Gaus et al., 2008; André et al., 2007; Azaroual et al., 2007).

![Figure 1. Conceptual diagram of the geochemical processes believed to occur during CO$_2$ injection in an aquifer.](image)

These reactions may change the porosity and connectivity of the porous/fractured medium, and therefore have an impact on the performance of the injection. This study is focused on Zone 1 and Zone 2, which have single-phase flow. In our study, we assume the point zero is located at the interface between supercritical CO$_2$ and water (Zone 3-Zone 2). We analyze the main physical chemical processes involved with injection of CO$_2$ and saturated water into the deep Keuper aquifer in the Paris Basin.
(France), using a reactive transport modeling approach.

**NUMERICAL TOOLS**

The simulations presented in this study were performed using the MARTHE-REACT code (Thiéry et al., 2009, presented in the same TOUGH symposium), which was formed by coupling the MARTHE code (flow and transport in porous media) with the chemical part of the TOUGHREACT code.

**TOUGHREACT reactive code**

TOUGHREACT is a nonisothermal multicomponent reactive fluid flow and geochemical transport simulator (Xu et al, 2004) that can be applied under various thermohydrological and geochemical conditions of pressure (1 bar to several hundred bars), temperature (0–300°C), water saturation (dry to saturated), and ionic strength (up to 6 mol/kg \( \text{H}_2\text{O} \) for NaCl-dominant solutions). Note that only the chemical part of TOUGHREACT is taken into account for the coupling with MARTHE.

**MARTHE transport code**

The MARTHE code (Modelling Aquifers with Rectangular cells, Transport and Hydrodynamics) is designed by BRGM for the hydrodynamic and hydro-dispersive modeling of groundwater flow in porous media (Thiéry, 1990). Hydrodynamic calculations are carried out by a finite volume algorithm based on a matrix resolution of conjugate gradients with Choleski preconditioning. Several methods can be used for transport calculation (total variation diminishing, finite volumes, MOC, or random walk).

**MARTHE-REACT coupling approach**

MARTHE has already been coupled to specific chemical simulators (SCS) (Thiéry, 1995). The approach used to couple it with the TOUGHREACT chemical simulator is essentially the same as before. Flow calculations and mass and energy transport are performed by the MARTHE code with no modifications. The 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 every 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.

**INJECTION OF CO\(_2\)-SATURATED WATER INTO THE KEUPER AQUIFER**

**Keuper aquifer properties**

The study site is located in the Paris Sedimentary Basin, which includes deposits from the Mesozoic to the Cenozoic on a pre-Permian basement. The Keuper formation within the Paris Basin was recently studied for its CO\(_2\) storage feasibility (Bonijoly et al., 2003; Delmas, 2007). Several aquifers in the east and south-central parts of the Paris Basin could be affected by CO\(_2\) storage; we focus our study on the Donnemarie sandstone formation, a multilayered reservoir located at a depth of around 2,000 m with a thickness of 100 m. The reservoir, which is entirely sealed by anhydritic clays, is still exploited for hydrocarbons deposits and natural gas storage. Three layers (an upper, middle, and lower part) can be distinguished, with thicknesses of 35 m, 20 m, and 45 m, respectively. The upper part of the reservoir is the most permeable layer, whereas the porosity of the three parts is similarly low (Table 1). Water salinity is in the range 30–180 g kg\(^{-1}\)\( \text{H}_2\text{O} \). Temperature and pressure conditions in the reservoir (1,500 to 3,000 m depth) vary respectively from 70 to 120°C and 200 to 300 bars (Bonijoly et al., 2003).

<table>
<thead>
<tr>
<th>Reservoir part</th>
<th>Porosity</th>
<th>Permeability (m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>0.06</td>
<td>2.3 (10^{-15})</td>
</tr>
<tr>
<td>Middle</td>
<td>0.04</td>
<td>0.3 (10^{-15})</td>
</tr>
<tr>
<td>Lower</td>
<td>0.07</td>
<td>0.2 (10^{-15})</td>
</tr>
</tbody>
</table>

**Geometry**

The Keuper aquifer (Donnemarie) is modeled as a sandstone reservoir represented by a cylindrical geometry with three layers, here representing the upper, middle, and lower parts of the reservoir (Figure 2).

![Figure 2. Two-dimensional radial geometry](image)
The grid is composed of 300 cells: along the Y axis, 1 cell with a radius of 0.2 m contains the vertical injection well, whereas 99 cells represent a radius following a logarithmic progression up to 100 km; the Z axes is divided by 3 cells corresponding to the upper (35 m), middle (20 m), and lower (45 m) parts of the Donnemarie sandstone. Each layer is assumed to be homogeneous, isotropic, and without slope.

**Basin mineralogy**

Donnemarie sandstone mineralogy has been chosen and identified through numerous data sets. In the first step, an aqueous speciation calculation of Keuper saltwater (Azaroual et al., 1997) is performed with the geochemical code PHREEQC (Parkhurst and Appelo, 1999). In this way, minerals at thermodynamic equilibrium are hypothesized. For the missing mineralogy, data are taken from the literature. Thus, Renoux (2005) suggests the presence of quartz, feldspar, anhydrite, dolomite, and illite. To attribute relatives quantities for each mineral, proportions (in volume fraction) are determined with help of the El-ghali et al. (2009) study: 52.85% of quartz, 25% of dolomite, 9% of calcite, 8% of albite, 3% of anhydrite, 1% of illite, 0.9% of Fe(OH)₃, and 0.25% of kaolinite.

**Formation water**

The composition of the Keuper aquifer formation water is calculated at equilibrium with the mineralogy cited above. For the following simulation, the reservoir is assumed to be saturated by saline brine (≈ 150 g/kgH₂O), with the chemical composition given in Table 2 at a temperature of 100°C and 200 bars pressure.

**CO₂-saturated injected water**

CO₂-saturated injected water is created from the equilibrium between initial dilute formation water with a pure CO₂ phase at 100°C and a pressure of 200 bars (equivalent to a CO₂ fugacity of 123.1 bars). As mentioned in André et al. (2007), this reaction produces bicarbonate ions, which gives an acid solution (pH of 3.15).

\[
\text{CO}_2 + H_2O \rightleftharpoons H_2CO_3
\]

\[
H_2CO_3 \rightleftharpoons H^+ + HCO_3^-
\]

The resulting CO₂-saturated solution, with a concentration about 1.3 mol CO₂ kg⁻¹H₂O and a pH of 3.15, is injected into the reservoir (Table 2). A tracer is also injected in the reservoir to show the velocity of a nonreactive compound in the different layers (its concentration is 5×10⁻⁵ mol kg⁻¹H₂O).

**Geochemical approach**

Kinetic rates are taken into account to examine the different mineral behaviors. Mineral (n) dissolution (+)–precipitation (-) rate \( r_n \) in mol/s is expressed by Lasaga et al. (1994):

\[
r_n = \pm k_n A_n \left[ 1 - \Omega_n^{\theta \eta} \right]^{\phi}
\]

with \( k_n \) the rate constant (mol/m²s), \( A_n \) the specific reactive surface area (m²), \( \Omega_n \) the mineral saturation ratio (-) and \( \theta \) and \( \eta \) power terms defined from experiments. Calcite and iron hydroxides are assumed to dissolve-precipitate at equilibrium, because their reaction rates are quite rapid. Other minerals are kinetically controlled by acid, neutral, alkaline (1), and carbonation (2), mechanisms depending on temperature (Lasaga et al., 1994; Palandri and Kharkara, 2004):

\[
k = k_{25} \exp \left[ -\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] k_0 \exp \left[ -\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] n^\alpha
\]

\[
+ \left\{ \begin{array}{l}
\left[ k_{25} \exp \left[ -\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] n^\alpha \right] a_{\mu} \quad 1) \\
\left[ k_{25} \exp \left[ -\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] n^\alpha \right] a_{H} \quad 2)
\end{array} \right.
\]

with \( k_{25} \) the rate constant at 25°C, \( E_a \) the activation energy, \( R \) the gas constant, \( T \) the absolute temperature, \( a \) the activity of species, and \( n \) a power term, where the subscripts \( \mu \) and \( H \) indicate neutral and acid mechanisms respectively.

The acid catalysis is considered only for mineral dissolution. Table 3 provides all parameters defining the kinetic rate constrained for the simulation. For several minerals, the volume fraction is null, because minerals are not initially present in the reservoir, but allowed to precipitate.

**Table 2. Chemical composition of water from the Keuper aquifer (formation water) and of CO₂-saturated water injected into the Keuper aquifer (mol/kgH₂O)**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Formation Water</th>
<th>CO₂-saturated Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>100°C</td>
<td>100°C</td>
</tr>
<tr>
<td>C</td>
<td>3.343e-3</td>
<td>1.3069</td>
</tr>
<tr>
<td>Ca</td>
<td>3.068e-2</td>
<td>3.071e-5</td>
</tr>
<tr>
<td>Mg</td>
<td>8.064e-3</td>
<td>8.061e-6</td>
</tr>
<tr>
<td>Na</td>
<td>2.468</td>
<td>2.468e-3</td>
</tr>
<tr>
<td>K</td>
<td>1.376e-3</td>
<td>1.376e-6</td>
</tr>
<tr>
<td>Fe</td>
<td>1.844e-13</td>
<td>1.010e-13</td>
</tr>
<tr>
<td>H₄SiO₄</td>
<td>8.93e-4</td>
<td>8.932e-7</td>
</tr>
<tr>
<td>SO₄</td>
<td>6.183e-2</td>
<td>8.181e-5</td>
</tr>
<tr>
<td>Al</td>
<td>3.028e-7</td>
<td>3.028e-10</td>
</tr>
<tr>
<td>Cl</td>
<td>2.42</td>
<td>2.42e-3</td>
</tr>
<tr>
<td>Tracer</td>
<td>5.063e-8</td>
<td>5.00e-5</td>
</tr>
</tbody>
</table>

**Table 3. Kinetic rate parameters of each mineral for neutral and acid mechanism and associated volume fraction**
Dissolve and precipitate at equilibrium.

<table>
<thead>
<tr>
<th>Minerals volume fraction (Vmin/Vs)</th>
<th>Acid Mechanism</th>
<th>Neutral Mechanism</th>
<th>Carbonation Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log k</td>
<td>Ea</td>
<td>n</td>
</tr>
<tr>
<td>Dolomite</td>
<td>-3.19</td>
<td>36.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Siderite</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dawsonite</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Magnesite</td>
<td>-6.38</td>
<td>14.4</td>
<td>1</td>
</tr>
<tr>
<td>Calcite*</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(OH)₃*</td>
<td>0.009</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The scenario is a hypothetical injection of a CO₂-saturated water conducted to test the reactive geochemical model in Zone 2 (acidified zone) and observe the dissolution-precipitation phenomena on Keuper mineralogy. Injection rate of CO₂-saturated water is chosen to have an increase in pressure lower than 20% of the initial pressure (200 bars) in each layer. Deduced injection rates correspond to $8.4 \times 10^{-4}$ m$^3$/s, $6 \times 10^{-5}$ m$^3$/s, and $9.45 \times 10^{-5}$ m$^3$/s into upper, middle, and lower layers respectively. An amount of 300,000 m$^3$ of CO₂-saturated water flows over 10 years, which corresponds to 18,720 tons of dissolved CO$₂$ considering 1.3 mol CO$₂$ kg$^{-1}$H$₂$O. A hydrostatic pressure is considered initially and is fixed in the outermost column of the grid during the simulation. No exchanges of fluids are considered under and above the system.

Simulation results

Hydrodynamics

The tracer included within the CO₂-saturated water is represented on a profile (Figure 3) from 0 to 350 m after 10 years of injection. Its behavior confirms different flow velocities for the three layers, with the fastest transport in the upper layer (the most permeable). After 10 years, originally injected CO₂-saturated water reaches a radius of 150 m in the upper layer, 70 m in the middle layer, and 45 m in the lower layer. We can expect preferential geochemical reactivity in these zones.

Geochemical reactivity

As original injected CO₂-saturated water reaches a radius of 150 m in the upper layer, we could expect a pH of 3.15 in this area. But the pH of 3.15 exists only in the first few meters around the injection well (Figure 4). Further into the upper layer (radius 3–150 m), the pH is 4.8, which indicates that geochemical reactivity is buffering the pH. Estimated changes in porosity and permeability are located in the same area as well (Figure 5).
Figure 3. Profile of tracer after 10 years of CO₂-saturated water injection. Initial concentration of tracer is equal to $5 \times 10^{-8} \text{ mol.kg}^{-1} \text{H}_2\text{O}$ and injected tracer concentration is equal to $5 \times 10^{-5} \text{ mol.kg}^{-1} \text{H}_2\text{O}$.

Figure 4. Profile of pH after 10 years of CO₂-saturated water injection. The pH of injected CO₂-saturated water and formation water are equal to 3.15 and 6.46 respectively.

Figure 5. Profile of potential impact on porosity and permeability (red zone) after 10 years of CO₂-saturated water injection. Maximal porosity is estimated around 0.41 and maximal permeability is deduced equal to $7 \times 10^{-13} \text{ m}^2$.

For a better understanding, we focus on the geochemical reactivity of the upper layer (Figure 6). As observed previously, the pH of 3.15 extends a few meters (0 to 2.5 m), forming an acidic front: Zone 2a (A). The total dissolution of dolomite, calcite (B), and anhydrite (C) is observed in the same area.

- Calcite + $H^+ \rightleftharpoons HCO_3^- + Ca^{2+}$
- Anhydrite + $H^+ \rightleftharpoons HSO_4^- + Ca^{2+}$
- Dolomite + $2H^+ \rightleftharpoons 2HCO_3^- + Ca^{2+} + Mg^{2+}$

Dissolution of albite (D) is observed in lower quantities as a result of smaller kinetic rates.

Albite + $4H^+ + 4H_2O \rightleftharpoons 3H_2SiO_4 + Al^{3+} + Na^+$

The potential impact of mineral dissolution on porosity is estimated (A), but not taken into account in the flow calculation. A maximal increase in porosity (41% from 6% initially) is estimated, which corresponds to the total dissolution of carbonate and sulphate minerals.
These dissolutions release Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, HSO$_4^-$, Al$^{3+}$, and H$_2$SiO$_4$ in solution, allowing precipitation of kaolinite and dolomite just after the acidic zone (2.5 to 3 m).

$$2\text{Al}^{3+} + \text{H}_2\text{O} + 2\text{H}_2\text{SiO}_4 \Leftrightarrow \text{Kaolinite}$$

Further (3 to 150 m), we can observe a second area where the pH is buffered by carbonate and sulphate, and where kaolinite and quartz precipitate (zone 2b = buffering zone).

$$\text{H}_4\text{SiO}_4 \Leftrightarrow \text{Quartz} + \text{H}_2\text{O}$$

Precipitations of kaolinite and quartz have a minor impact on porosity changes compared to dissolution of carbonates. But at this time scale (10 years), porosity changes are limited by the amount of carbonate, because of the slow reactivity of silicates. Further, in the buffered zone (from 150 m to 100 km), pH increases to reach the pH of formation water, and any dissolution-precipitations are observed because of the equilibrium between minerals and formation water (zone 1 = initial zone).

The simulation results confirm the high reactivity of CO$_2$-saturated water with respect to the carbonate minerals (André et al., 2007), which are totally dissolved in the water-saturated zone of the near-well field. Reactions occur on a larger extent in the superior layer, where the permeability is higher. Dissolution of calcite, dolomite, and anhydrite induces some pH buffering and a significant increase in porosity, reaching 41% in the first meters of the water-saturated zone after ten years, when the dissolution is total. Albite dissolution presents the first step in destabilization of the alumino-silicates in lower quantities. This can be explained by the slow kinetics of dissolution for alumino-silicate minerals compared to that for carbonates. This is in accordance with observations by Audigane et al. (2007), who simulate CO$_2$ injection into sandstone. Just behind the acidic zone, one can observe precipitation of dolomite, kaolinite, and quartz. The porosity evolution of the reservoir is essentially constrained by the magnitude of carbonate and sulphate mineral dissolution, and the impact on injectivity still depends on the location of mineral dissolution-precipitation (connected pores or not).

**CONCLUSION**

A 2D-radial numerical model of CO$_2$-saturated water injection into the sandstone Keuper aquifer in the Paris Basin has been presented using the MARTHE-REACT code. The simulation was performed over 10 years of continuous injection considered as a high reactivity level compared to supercritical CO$_2$ injection as studied by André et al (2007). Three reactive zones were identified:

1) An **acidic zone** where dolomite, calcite, and anhydrite are totally dissolved, and where albite starts to dissolve from the acidic conditions (pH
A buffered zone where carbonate and sulphate minerals buffer the acidic injection (pH = 4.8) and where transported ions allow precipitation of kaolinite, quartz, and dolomite with minor impact on porosity.

An initial zone where minerals are in equilibrium with formation water (pH = 6.46) without changes in porosity.

The results obtained confirm similar findings from other studies on the reactivity of carbonate and sandstone aquifers, and provides further confidence in the coupling tool.

This study is a first step before the assessment of CO$_2$-saturated water leakage from a reservoir to the surface in a sedimentary basin, where functionalities of the MARTHE simulator are essential for modeling complex hydrodynamic systems (providing a link between hydrogeology and hydrology, including, for example, atmosphere and river subsystems).

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