A sequential numerical simulator for two-phase multicomponent flow with reactive transport in porous media

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Outline

1. Introduction
2. Mathematical model
3. Methodology
4. Numerical simulation
5. Conclusion and perspectives
6. Acknowledgments
Introduction

Problematic:
- Reactive transport in multiphase flow occurs in many applications: sequestration of CO₂ in saline aquifers, geological storage of nuclear waste, soil remediation in hydrogeology...
- Necessity to take into account interactions between chemical species and rock matrix.

Goals:
- Numerical simulation of two-phase multicomponent flow with reactive transport in porous media.
- Implementation of a reactive transport module in DuMu⁶.


**Introduction**

Simplified Chemical system for CO$_2$ sequestration example

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**Table:** Chemical components.

<table>
<thead>
<tr>
<th>Liquid phase (l)</th>
<th>Gas phase (g)</th>
<th>Solid phase (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O, CO$_2$(l), H$^+$, CO$_2$(g)</td>
<td>OH$^-$, HCO$_3^-$, Ca$^{2+}$</td>
<td>CaCO$_3$</td>
</tr>
</tbody>
</table>

**Table:** Chemical reactions.

\[
\begin{align*}
\text{OH}^- + \text{H}^+ & \rightleftharpoons \text{H}_2\text{O} \\
\text{HCO}_3^- + \text{H}^+ & \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2\text{(l)} \\
\text{CO}_2\text{(g)} & \rightleftharpoons \text{CO}_2\text{(l)} \\
\text{CaCO}_3 + 2\text{H}^+ & \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2\text{(l)} + \text{Ca}^{2+}
\end{align*}
\]
Geochemical model

$N_s$ species, $N_r$ reactions ($N_e$ equilibrium reactions and $N_k$ kinetic reactions), $S$ stoichiometric matrix:

$$\sum_{j=1}^{N_s} S_{ij} Y_j \overset{\leftrightarrow}{=} 0, \quad i = 1, \ldots, N_r \overset{\leftrightarrow}{=} SY \overset{\leftrightarrow}{=} 0.$$ 

Matrix $S$ can be written as follows:

$$S = \begin{pmatrix} S^e \\ S^k \end{pmatrix}.$$ 

Example:

$$Y_1 + Y_2 \overset{\leftrightarrow}{=} Y_3 \quad (Eq)$$

$$Y_2 + Y_3 \overset{\leftrightarrow}{=} Y_4 \quad (Eq)$$

$$Y_1 + Y_4 \overset{\leftrightarrow}{=} Y_5 \quad (Kin)$$

$$\begin{pmatrix} 1 & 1 & -1 & 0 & 0 \\ 0 & 1 & 1 & -1 & 0 \\ 1 & 0 & 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} Y_1 \\ Y_2 \\ Y_3 \\ Y_4 \\ Y_5 \end{pmatrix} \overset{\leftrightarrow}{=} 0.$$

$$S^e = \begin{pmatrix} 1 & 1 & -1 & 0 & 0 \\ 0 & 1 & 1 & -1 & 0 \end{pmatrix} \text{ and } S^k = \begin{pmatrix} 1 & 0 & 0 & 1 & -1 \end{pmatrix}.$$
Mathematical model

Geochemical model

Equilibrium reactions

Mass action laws: $S^e \log a = \log K$.

The set of chemical species is divided into primary and secondary species.

$S^e = (-I \ S^e)$.

Mass conservation laws: $c_p + S^e T c_s = T$, $T$ known from transport.

System of non-linear equations.

Kinetic reactions

System of ordinary differential equations.

$$\frac{dc_c}{dt} = -r^k(c_p, c_c)$$

Coupled system of differential algebraic equations
Mathematical model for two-phase multicomponent flow

Notations: $\alpha = l, g, s$ - index of phase (liquid, gas, solid), $i$ - index of component, $\alpha_i$ - index of the phase that contains species $i$.

- **Mass conservation law** for each component in each phase:

$$\frac{\partial}{\partial t}(\phi S_{\alpha_i} c^i) - \nabla \cdot (\phi S_{\alpha_i} D_{\alpha_i} \nabla c^i) + \nabla \cdot (c^i \overrightarrow{q_{\alpha_i}}) = \sum_{j} S_{ji} r_j^e + \sum_{j} S_{ji} r_j^k, \quad (1)$$

coupled with Darcy’s Law, capillary pressure law and equations of state.

- **Primary variables**: pressures of each phase $p_{\alpha}$, saturations of each phase $S_{\alpha}$ and concentrations $c^i$.

In the sequel, we use:

$$L_{\alpha}(c) = -\nabla \cdot (\phi S_{\alpha} D_{\alpha} \nabla c) + \nabla \cdot (c \overrightarrow{q_{\alpha}}).$$
Mathematical model for two-phase multicomponent flow

To eliminate reaction rates, we multiply (1) by a $(N_s - N_r) \times N_r$ component matrix $U$ such that $U S^T = 0$.

$$
\sum_{\alpha} \left( \frac{\partial}{\partial t} (\phi S_{\alpha} C_{\alpha}^j) + L_{\alpha}(C_{\alpha}^j) \right) = 0, \quad j = 1, \ldots, N_s - N_r,
$$

with

$$
C_{\alpha}^j = \sum_{i \text{ st } \alpha_i = \alpha} U_{ji} c^i, \quad j = 1, \ldots, N_s - N_r, \quad \alpha \in \{l, g, s\}.
$$

To recover $N_s$ equations, we add $N_e$ mass action laws and $N_k$ ordinary differential equations.

\begin{itemize}
\end{itemize}
Mathematical model

Application to the simplified system

Mass conservation law for each component in each phase:

\[ \begin{align*}
H_2O : & \quad \frac{\partial}{\partial t} (\phi S_l c^{H_2O}) + L_l (c^{H_2O}) = r^e_{OH^-} + r^k_{CaCO_3} + r^e_{HCO_3^-} \\
CO_2(l) : & \quad \frac{\partial}{\partial t} (\phi S_l c^{CO_2(l)}) + L_l (c^{CO_2(l)}) = r^e_{HCO_3^-} + r^e_{CO_2(g)} + r^k_{CaCO_3} \\
H^+ : & \quad \frac{\partial}{\partial t} (\phi S_l c^{H^+}) + L_l (c^{H^+}) = -r^e_{OH^-} - 2r^k_{CaCO_3} - r^e_{HCO_3^-} \\
Ca^{2+} : & \quad \frac{\partial}{\partial t} (\phi S_l c^{Ca^{2+}}) + L_l (c^{Ca^{2+}}) = r^k_{CaCO_3} \\
HCO_3^- : & \quad \frac{\partial}{\partial t} (\phi S_l c^{HCO_3^-}) + L_l (c^{HCO_3^-}) = -r^e_{HCO_3^-} \\
OH^- : & \quad \frac{\partial}{\partial t} (\phi S_l c^{OH^-}) + L_l (c^{OH^-}) = -r^e_{OH^-} \\
CO_2(g) : & \quad \frac{\partial}{\partial t} (\phi S_g c^{CO_2(g)}) + L_g (c^{CO_2(g)}) = -r^e_{CO_2(g)} \\
CaCO_3 : & \quad \frac{d}{dt} c_{CaCO_3} = -r^k_{CaCO_3}
\end{align*} \]
Application to the simplified system

Mass conservation law for each component in each phase:

\[ H_2O : \quad \frac{\partial}{\partial t} (\phi S_l c^{H_2O}) + L_l (c^{H_2O}) = r^{e_{OH^-}} + r^{k_{CaCO_3}} + r^{e_{HCO_3^-}} \]

\[ CO_{2(l)} : \quad \frac{\partial}{\partial t} (\phi S_l c^{CO_{2(l)}}) + L_l (c^{CO_{2(l)}}) = r^{e_{HCO_3^-}} + r^{e_{CO_{2(g)}}} + r^{k_{CaCO_3}} \]

\[ H^+ : \quad \frac{\partial}{\partial t} (\phi S_l c^{H^+}) + L_l (c^{H^+}) = -r^{e_{OH^-}} - 2r^{k_{CaCO_3}} - r^{e_{HCO_3^-}} \]

\[ Ca^{2+} : \quad \frac{\partial}{\partial t} (\phi S_l c^{Ca^{2+}}) + L_l (c^{Ca^{2+}}) = r^{k_{CaCO_3}} \]

\[ HCO_3^- : \quad \frac{\partial}{\partial t} (\phi S_l c^{HCO_3^-}) + L_l (c^{HCO_3^-}) = -r^{e_{HCO_3^-}} \]

\[ OH^- : \quad \frac{\partial}{\partial t} (\phi S_l c^{OH^-}) + L_l (c^{OH^-}) = -r^{e_{OH^-}} \]

\[ CO_{2(g)} : \quad \frac{\partial}{\partial t} (\phi S_g c^{CO_{2(g)}}) + L_g (c^{CO_{2(g)}}) = -r^{e_{CO_{2(g)}}} \]

\[ CaCO_3 : \quad \frac{d}{dt} c^{CaCO_3} = -r^{k_{CaCO_3}} \]

Reactions rates will be eliminated.
Mathematical model

Application to the simplified system

Linear combination to eliminate reaction rates: new conservation laws

$$H_2O : T_{H_2O} = c^{H_2O} + c^{OH^-} + c^{HCO_3^-} + c^{CaCO_3} = C_i^{H_2O} + C_s^{H_2O}$$

$$\frac{\partial}{\partial t}(\phi S_l C_i^{H_2O} + C_s^{H_2O}) + L_l(C_i^{H_2O}) = 0$$
Application to the simplified system

Linear combination to eliminate reaction rates: new conservation laws

$$H_2O : T_{H_2O} = c^{H_2O} + c^{OH^-} + c^{HCO_3^-} + c^{CaCO_3} = C^H_{H_2O} + C^S_{H_2O}$$

$$\frac{\partial}{\partial t}(\phi S_l C^H_{H_2O} + C^S_{H_2O}) + L_l(C^H_{H_2O}) = 0$$

$$CO_{2(l)} : T_{CO_{2(l)}} = c^{CO_{2(l)}} + c^{HCO_3^-} + c^{CO_{2(g)}} + c^{CaCO_3} = C^I_{CO_{2(l)}} + C^G_{CO_{2(l)}} + C^S_{CO_{2(l)}}$$

$$\frac{\partial}{\partial t}(\phi S_l C^I_{CO_{2(l)}} + \phi S_g C^G_{CO_{2(l)}} + C^S_{CO_{2(l)}}) + L_l(C^I_{CO_{2(l)}}) + L_g(C^G_{CO_{2(l)}}) = 0$$
Application to the simplified system

Linear combination to eliminate reaction rates: new conservation laws

\[
\text{H}_2\text{O} : T_{\text{H}_2\text{O}} = c^{\text{H}_2\text{O}} + c^{\text{OH}^-} + c^{\text{HCO}_3^-} + c^{\text{CaCO}_3} = C_j^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}
\]

\[
\frac{\partial}{\partial t} (\phi S_I C_j^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}) + L_I (C_j^{\text{H}_2\text{O}}) = 0
\]

\[
\text{CO}_2^{\text{l}} : T_{\text{CO}_2^{\text{l}}} = c^{\text{CO}_2^{\text{l}}} + c^{\text{HCO}_3^-} + c^{\text{CO}_2^{\text{g}}} + c^{\text{CaCO}_3} = C_j^{\text{CO}_2^{\text{l}}} + C_g^{\text{CO}_2^{\text{l}}} + C_s^{\text{CO}_2^{\text{l}}}
\]

\[
\frac{\partial}{\partial t} (\phi S_I C_j^{\text{CO}_2^{\text{l}}} + \phi S_g C_g^{\text{CO}_2^{\text{l}}} + C_s^{\text{CO}_2^{\text{l}}}) + L_I (C_j^{\text{CO}_2^{\text{l}}}) + L_g (C_g^{\text{CO}_2^{\text{l}}}) = 0
\]

\[
\text{H}^+ : T_{\text{H}^+} = c^{\text{H}^+} - c^{\text{OH}^-} - c^{\text{HCO}_3^-} - 2c^{\text{CaCO}_3} = C_j^{\text{H}^+} + C_s^{\text{H}^+}
\]

\[
\frac{\partial}{\partial t} (\phi S_I C_j^{\text{H}^+} + C_s^{\text{H}^+}) + L_I (C_j^{\text{H}^+}) = 0
\]
Application to the simplified system

Linear combination to eliminate reaction rates: new conservation laws

**H₂O:** \( T_{H₂O} = c^{H₂O} + c^{OH⁻} + c^{HCO₃⁻} + c^{CaCO₃} = C_i^{H₂O} + C_s^{H₂O} \)

\[
\frac{\partial}{\partial t} (\phi S_l C_i^{H₂O} + C_s^{H₂O}) + L_i (C_i^{H₂O}) = 0
\]

**CO₂(l):** \( T_{CO₂(l)} = c^{CO₂(l)} + c^{HCO₃⁻} + c^{CO₂(g)} + c^{CaCO₃} = C_i^{CO₂(l)} + C_g^{CO₂(l)} + C_s^{CO₂(l)} \)

\[
\frac{\partial}{\partial t} (\phi S_l C_i^{CO₂(l)} + \phi S_g C_g^{CO₂(l)} + C_s^{CO₂(l)}) + L_i (C_i^{CO₂(l)}) + L_g (C_g^{CO₂(l)}) = 0
\]

**H⁺:** \( T_{H⁺} = c^{H⁺} - c^{OH⁻} - c^{HCO₃⁻} - 2c^{CaCO₃} = C_i^{H⁺} + C_s^{H⁺} \)

\[
\frac{\partial}{\partial t} (\phi S_l C_i^{H⁺} + C_s^{H⁺}) + L_i (C_i^{H⁺}) = 0
\]

**Ca²⁺:** \( T_{Ca²⁺} = c^{Ca²⁺} + c^{CaCO₃} = C_i^{Ca²⁺} + C_s^{Ca²⁺} \)

\[
\frac{\partial}{\partial t} (\phi S_l C_i^{Ca²⁺} + C_s^{Ca²⁺}) + L_i (C_i^{Ca²⁺}) = 0
\]
Mathematical model

Application to the simplified system

Ordinary differential equation

\[
\text{CaCO}_3 : \frac{d}{dt} c_{\text{CaCO}_3} = -K_s A_s \left( 1 - \frac{a^{H^+} a^{\text{CO}_2(l)} a^{\text{Ca}^{2+}}}{K_{\text{CaCO}_3}} \right)
\]

Mass action laws

\[
\begin{align*}
\text{CO}_2(g) : a^{\text{CO}_2(g)} &= K_{\text{CO}_2} a^{\text{CO}_2(l)} \\
\text{OH}^- : a^{\text{OH}^-} &= K_{\text{OH}^-} a^{H^+} a^{-1} \\
\text{HCO}_3^- : a^{\text{HCO}_3^-} &= K_{\text{HCO}_3^-} a^{H^+} a^{\text{CO}_2(l)}
\end{align*}
\]

Coupled system: PDE + ODE + algebraic equations
Methodology

Strategy for solving

- **Fully implicit approach**
  The full system of equations is solved with all the unknowns: pressures $p_{\alpha}$, saturations $S_{\alpha}$ and concentrations $c^i$ (Fan 2012).

- **Sequential approach**
  We consider that one dominant species exists in each phase: H$_2$O in liquid phase and CO$_2$ in gas phase (Zhang 2012).
  1. We compute the pressures $p_{\alpha}$, the velocities $\vec{q}_{\alpha}$, the saturations $S_{\alpha}$ and the concentrations of dominant species, solutions of a simplified two-phase flow with two components (H$_2$O and CO$_2$).
  2. Using $p_{\alpha}$, $\vec{q}_{\alpha}$ and $S_{\alpha}$, we solve a reactive transport problem with concentrations of the other species $c^i$.


Sequential approach

\[
\frac{\partial}{\partial t} (\phi_S l c_{\text{H}_2\text{O}}) + L_{l} (c_{\text{H}_2\text{O}}) = \Psi_1 (c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})
\]

\[
\frac{\partial}{\partial t} (\phi_S l c^{\text{CO}_2(l)} + \phi_S g c^{\text{CO}_2(g)}) + L_{l} (c^{\text{CO}_2(l)}) + L_g (c^{\text{CO}_2(g)}) = \Psi_2 (c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})
\]

\[
\frac{\partial}{\partial t} \left[ \frac{\partial}{\partial x} (\phi_S l c_{\text{H}_2\text{O}}) \right] + L_{l} (c_{\text{H}_2\text{O}}) = \Psi_1 (c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})
\]

\[
\frac{\partial}{\partial t} (\phi_S l c^{\text{CO}_2(g)}) = K_{\text{CO}_2} a^{\text{CO}_2(l)}
\]

\[
\frac{\partial}{\partial t} (\phi_S l c^{\text{H}^+} + C_s^{\text{H}^+}) + L_{l} (C_s^{\text{H}^+}) = 0
\]

\[
\frac{\partial}{\partial t} (\phi_S l c^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}) + L_{l} (C_s^{\text{Ca}^{2+}}) = 0
\]

\[
a^{\text{OH}^-} = K_{\text{OH}^-} a^{\text{H}^+} - 1
\]

\[
a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^+} - 1 a^{\text{CO}_2(l)}
\]

\[
\frac{d}{dt} c^{\text{CaCO}_3} = -K_s A_s (1 - \frac{a^{\text{H}^+} - 2 a^{\text{CO}_2(l)} a^{\text{Ca}^{2+}}}{K_{\text{CaCO}_3}})
\]
Methodology

Sequential approach

\[ \frac{\partial}{\partial t} (\phi_S l c^{H_2O} + L_I c^{H_2O}) = \Psi_1 (c^{OH^-}, c^{HCO_3^-}, c^{CaCO_3}) \]

\[ \frac{\partial}{\partial t} (\phi_S l c^{CO_2(l)} + \phi_S g c^{CO_2(g)}) + L_I (c^{CO_2(l)}) + L_g (c^{CO_2(g)}) = \Psi_2 (c^{HCO_3^-}, c^{CaCO_3}) \]

\[ a^{CO_2(g)} = K_{CO_2} a^{CO_2(l)} \]

\[ \frac{\partial}{\partial t} (\phi_S l c^{H^+} + C_s c^{H^+}) + L_I (c^{H^+}) = 0 \]

\[ \frac{\partial}{\partial t} (\phi_S l c^{Ca^{2+}} + C_s c^{Ca^{2+}}) + L_I (c^{Ca^{2+}}) = 0 \]

\[ a^{OH^-} = K_{OH^-} a^{H^+} - 1 \]

\[ a^{HCO_3^-} = K_{HCO_3} a^{H^+} - 1 a^{CO_2(l)} \]

\[ \frac{d}{dt} c^{CaCO_3} = -K_s A_s (1 - \frac{a^{H^+} - 2 a^{CO_2(l)} a^{Ca^{2+}}}{K_{CaCO_3}}) \]
Sequential approach

Two-phase two-component flow

\[ \frac{\partial}{\partial t} \left( \phi S_I c^{H_2O} \right) + L_I \left( c^{H_2O} \right) = \Psi_1 \left( c^{OH^-}, c^{HCO_3^-}, c^{CaCO_3} \right) \]

\[ \frac{\partial}{\partial t} \left( \phi S_I c^{CO_2(1)} + \phi S_g c^{CO_2(g)} \right) + L_I \left( c^{CO_2(1)} \right) + L_g \left( c^{CO_2(g)} \right) = \Psi_2 \left( c^{HCO_3^-}, c^{CaCO_3} \right) \]

\[ a^{CO_2(g)} = K_{CO_2} a^{CO_2(1)} \]

\[ \frac{\partial}{\partial t} \left( \phi S_I C^H + C_s^{H^+} \right) + L_I \left( C_s^{H^+} \right) = 0 \]

\[ \frac{\partial}{\partial t} \left( \phi S_I C^{Ca^2+} + C_s^{Ca^2+} \right) + L_I \left( C_s^{Ca^2+} \right) = 0 \]

\[ a^{OH^-} = K_{OH^-} a^{H^+} - 1 \]

\[ a^{HCO_3^-} = K_{HCO_3} a^{H^+} - 1 a^{CO_2(1)} \]

\[ \frac{d}{dt} c^{CaCO_3} = -K_s A_s \left( 1 - \frac{a^{H^+} - 2 a^{CO_2(1)} a^{Ca^2+}}{K_{CaCO_3}} \right) \]
Sequential approach

Two-phase two-component flow

\[
\begin{align*}
\text{H}_2\text{O} & : \frac{\partial}{\partial t} (\phi S_l c^{\text{H}_2\text{O}}) + L_l(c^{\text{H}_2\text{O}}) = \Psi_1(c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3}) \\
\text{CO}_2(\text{l}) & : \frac{\partial}{\partial t} (\phi S_l c^{\text{CO}_2(\text{l})} + \phi S_g c^{\text{CO}_2(\text{g})}) + L_l(c^{\text{CO}_2(\text{l})}) + L_g(c^{\text{CO}_2(\text{g})}) = \Psi_2(c^{\text{HCO}_3^-}, c^{\text{CaCO}_3}) \\
\text{CO}_2(\text{g}) & : a^{\text{CO}_2(\text{g})} = K_{\text{CO}_2} a^{\text{CO}_2(\text{l})}
\end{align*}
\]

\[
\begin{align*}
\text{H}^+ & : \frac{\partial}{\partial t} (\phi S_l c^{\text{H}^+} + c^{\text{H}^+}) + L_l(c^{\text{H}^+}) = 0 \\
\text{Ca}^{2+} & : \frac{\partial}{\partial t} (\phi S_l c^{\text{Ca}^{2+}} + c^{\text{Ca}^{2+}}) + L_l(c^{\text{Ca}^{2+}}) = 0 \\
\text{OH}^- & : a^{\text{OH}^-} = K_{\text{OH}^-} a^{\text{H}^+} - 1 \\
\text{HCO}_3^- & : a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^+} - 1 a^{\text{CO}_2(\text{l})} \\
\text{CaCO}_3 & : \frac{d}{dt} c^{\text{CaCO}_3} = -K_s A_s (1 - \frac{a^{\text{H}^+} - 2 a^{\text{CO}_2(\text{l})} a^{\text{Ca}^{2+}}}{K_{\text{CaCO}_3}})
\end{align*}
\]
Sequential approach

Two-phase two-component flow

\[
\begin{align*}
\text{H}_2\text{O} : & \quad \frac{\partial}{\partial t}(\phi S_l c^{\text{H}_2\text{O}}) + L_l(c^{\text{H}_2\text{O}}) = \Psi_1(c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3}) \\
\text{CO}_2(l) : & \quad \frac{\partial}{\partial t}(\phi S_l c^{\text{CO}_2(l)} + \phi S_g c^{\text{CO}_2(g)}) + L_l(c^{\text{CO}_2(l)}) + L_g(c^{\text{CO}_2(g)}) = \Psi_2(c^{\text{HCO}_3^-}, c^{\text{CaCO}_3}) \\
\text{CO}_2(g) : & \quad a^{\text{CO}_2(g)} = K_{\text{CO}_2} a^{\text{CO}_2(l)}
\end{align*}
\]

Reactive transport problem

\[
\begin{align*}
\text{H}^+ : & \quad \frac{\partial}{\partial t}(\phi S_l C_l^{\text{H}^+} + C_s^{\text{H}^+}) + L_l(C_l^{\text{H}^+}) = 0 \\
\text{Ca}^{2+} : & \quad \frac{\partial}{\partial t}(\phi S_l C_l^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}) + L_l(C_l^{\text{Ca}^{2+}}) = 0 \\
\text{OH}^- : & \quad a^{\text{OH}^-} = K_{\text{OH}^-} a^{\text{H}^+} - 1 \\
\text{HCO}_3^- : & \quad a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^+} - 1 a^{\text{CO}_2(l)} \\
\text{CaCO}_3 : & \quad \frac{d}{dt} c^{\text{CaCO}_3} = -K_s A_s (1 - \frac{a^{\text{H}^+} - 2 a^{\text{CO}_2(l)} a^{\text{Ca}^{2+}}}{K_{\text{CaCO}_3}})
\end{align*}
\]
Sequential approach

Two-phase two-component flow

\[ \frac{\partial}{\partial t} \left( \phi_S c_{H_2O} \right) + L_l (c_{H_2O}) = \Psi_1 (c^{OH^-}, c^{HCO_3^-}, c^{CaCO_3}) \]

\[ \frac{\partial}{\partial t} \left( \phi_S c^{CO_2(l)} + \phi_S c^{CO_2(g)} \right) + L_l (c^{CO_2(l)}) + L_g (c^{CO_2(g)}) = \Psi_2 (c^{HCO_3^-}, c^{CaCO_3}) \]

\[ a^{CO_2(g)} = K_{CO_2} a^{CO_2(l)} \]

Reactive transport problem

\[ \frac{\partial}{\partial t} \left( \phi_S c_{H^+} + C_s c_{H^+} \right) + L_l (c_{H^+}) = 0 \]

\[ \frac{\partial}{\partial t} \left( \phi_S c_{Ca^{2+}} + C_s c_{Ca^{2+}} \right) + L_l (c_{Ca^{2+}}) = 0 \]

\[ a^{OH^-} = K_{OH^-} a^{H^+} - 1 \]

\[ a^{HCO_3^-} = K_{HCO_3} a^{H^+} - 1 a^{CO_2(l)} \]

\[ \frac{d}{dt} c^{CaCO_3} = -K_s A_s \left( 1 - \frac{a^{H^+} - 2 a^{CO_2(l)} a^{Ca^{2+}}}{K_{CaCO_3}} \right) \]
Sequential approach

- Density of phase $\rho_\alpha$
- Velocity of phase $\vec{q}_\alpha$
- Saturation of phase $S_\alpha$
- Concentration of dominant species
- Update of porosity $\phi$
- Concentration of minor species

**Figure**: Coupling procedure between flow and reactive transport modules.
Numerical simulation

Simulator: **DuMu**\(^X\), DUNE for Multi-\{Phase, Component, Scale, Physics, ...\} flow and transport in porous media.

**Flow:**
- **2p2c** model to compute two-phase two-component flow.
- **Fully implicit** approach.
- Spatial discretization: **cell-centred finite-volume**.
- Time discretization: **Implicit Euler scheme**.

**Reactive transport**
- Development and integration of a **reactive transport module** in DuMu\(^X\) framework: **1pNc-react**.

\[ \text{DuMu}^X \]

http://dune-project.org/
Reactive transport

The reactive transport problem can be written as follows:

\[
\frac{\partial (\phi S_l C_l + C_s)}{\partial t} + L_l(C_l) = 0,
\]

\[
T = \phi S_l C_l + C_s,
\]

\[
C_s = \Psi_C(T).
\]

- **Operator Splitting** (Yeh and Tripathi 1989, Carayrou 2004),
- **Direct Substitution** (Hammond and Valocchi 2005, Saaltink 1998),
- **DAE Formulation** (Erhel and de Dieuleveult, 2008),
- **Elimination Technique** (Knabner, Kraeutle 2006),
- **Implicit Formulation** (Amir and Kern 2010),
- **Space-time domain decomposition** (Haeberlein et al 2010).
**SIA method**

We use a sequential iterative approach (Yeh and Tripathi 1989). Supposing $T^n, T^{n+1,k}, C^j_n, C^{n+1,k}_l, C^n_s, C^{n+1,k}_s$ are known, $T^{n+1,k+1}, C^{n+1,k+1}_s, C^{n+1,k+1}_l$ are computed thanks to the following iterative scheme:

\[
\phi^n S^n \frac{C^{n+1,k+1}_l - S^n C^n_l}{\Delta t} + \frac{C^{n+1,k}_s - C^n_s}{\Delta t} + L_l(C^{n+1,k+1}_l) = 0,
\]
\[
T^{n+1,k+1} = \phi^n S^{n+1}_l C^{n+1,k+1}_l + C^{n+1,k}_s,
\]
\[
C^{n+1,k+1}_s = \Psi_C(T^{n+1,k+1}).
\]

The algorithm is stopped when:

\[
\frac{||C^{n+1,k+1}_l - C^{n+1,k}_l||}{||C^{n+1,k+1}_l||} + \frac{||C^{n+1,k+1}_s - C^{n+1,k}_s||}{||C^{n+1,k+1}_s||} < \varepsilon.
\]

---


MoMaS Benchmark

- 1D Hard Advective Case.
- Heterogeneous media.
- 18 components, 12 reactions (11 equilibrium and 1 kinetic).

Figure: Scheme for the 1D problem

Equilibrium reactions:

<table>
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<tr>
<th></th>
<th>X₁</th>
<th>X₂</th>
<th>X₃</th>
<th>X₄</th>
<th>X₅</th>
<th>S</th>
<th>K</th>
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<td>1</td>
</tr>
<tr>
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<td>1</td>
<td>3</td>
<td>0</td>
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<td>0.1</td>
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<tr>
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</tr>
<tr>
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<td>0</td>
<td>2</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>20</td>
</tr>
</tbody>
</table>

Kinetic reaction:

$$3C₃ \rightleftharpoons C_c + 2X_4$$

$$\frac{dC_c}{dt} = -k(1 - 0.2 \frac{C_3^3}{X_4^2})$$
Mesh with 1027 elements (finest in the center of the domain).

Variable time step: $dt_{\text{max}} = 0.05s$.

Dissolution/Precipitation: for each precipitated species $CP_i$, a solubility product must be respected:

$$\text{if } K_p \prod_{j=1}^{N_s} X_j^{ap_j} < 1 \text{ then } CP_i = 0 \text{ else } K_p \prod_{j=1}^{N_s} X_j^{ap_j} = 1.$$ 

Reformulation as a complementarity problem:

$$\min(CP_i, 1 - K_p \prod_{j=1}^{N_s} X_j^{ap_j}) = 0.$$
Figure: Concentration profile at $t = 5010$ for $X5$ (Left) and for the mineral $CP1$ (Right) for the 1D advective Hard Test Case.

Numerical simulation

Test of Fan et al

- CO$_2$ injection in deep saline aquifer.
- 3D domain, 100 m of thickness, 15 km of length and 15 km of width.
- Injection well at 25 m of the top of the aquifer.
- Chemical system with 12 components (3 minerals) and 6 reactions (3 kinetic reactions and 3 equilibrium).
- Injection during 20 years. Time of simulation = 2000 years.
- Mesh with 10000 elements (25 × 25 × 16).

Test of Fan et al: Numerical results

Figure: Gas saturation evolution. Top left: 20 years. Top right: 500 years. Bottom left: 1200 years. Bottom right: 2000 years.
Numerical simulation

Test of Fan et al: Numerical results

Figure: Mineral changes (left) and evolution of the distribution of CO$_2$ (right). Top: our results. Bottom: Fan’s results.
Conclusion and perspectives

- Sequential approach for two-phase multicomponent flow with reactive transport.
- Both kinetic and equilibrium chemical reactions taken into account.
- Validation on several examples but necessity to have a reliable and well documented benchmark.

- Parallel implementation of the method.
- New algorithms to improve accuracy and robustness.
- New application: alteration of bentonite in geological storage of nuclear waste.

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