

Numerical simulation of flows with reactive transport in porous media: towards a validation for two-phase flow

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Outline

- 1 Introduction
- 2 Mathematical model
- 3 Methodology
- 4 Numerical simulation
- 5 Conclusion and perspectives
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Introduction

Problem setup:

- **Reactive transport in multiphase flow** occurs in many applications: sequestration of CO_2 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 **DuMu^X**.



DuMu^X web-page : <http://www.dumux.org>.



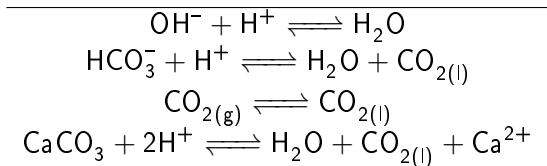
E. Ahusborde, M. Kern and V. Vostrikov. Numerical simulation of two-phase multicomponent flow with reactive transport in porous media: application to geological sequestration of CO_2 . ESAIM: Proceedings and Surveys, 50, 21–39, 2015.

Simplified Chemical system for CO₂ sequestration example

Table : Chemical components.

Liquid phase (l)	Gas phase (g)	Solid phase (s)
H ₂ O, CO _{2(l)} , OH ⁻ , HCO ₃ ⁻ , Ca ²⁺	H ⁺ , CO _{2(g)}	CaCO ₃

Table : Chemical reactions.



Mathematical model for two-phase multicomponent flow

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

N_s species, N_r reactions (N_e equilibrium reactions and N_k kinetic reactions).

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

$$\frac{\partial}{\partial t}(\phi S_{\alpha_i} c^i) - \nabla \cdot (\phi S_{\alpha_i} D_{\alpha_i}^i \nabla c^i) + \nabla \cdot (c^i \vec{q}_{\alpha_i}) = \sum_j^{N_e} S_{ji}^e r_j^e + \sum_j^{N_k} S_{ji}^k r_j^k, \quad (1)$$

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

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

In the sequel, we use:

$$L_{\alpha}(c) = -\nabla \cdot (\phi S_{\alpha} D_{\alpha}^i \nabla c) + \nabla \cdot (c \vec{q}_{\alpha}).$$

Mathematical model for two-phase multicomponent flow

Equation (1) can be written in concise notation as

$$\frac{\partial \mathbf{N}}{\partial t} + \mathbf{L} = \mathbb{S}^T \mathbf{r}, \quad (2)$$

with $\mathbf{N} = (\phi S_{\alpha_1} c^1, \phi S_{\alpha_2} c^2, \dots, \phi S_{\alpha_{N_s}} c^{N_s})^T$, $\mathbf{r} = (r_1, r_2, \dots, r_{N_r})$ and $\mathbf{L} = (L_{\alpha_1}(c^1), L_{\alpha_2}(c^2), \dots, L_{\alpha_{N_s}}(c^{N_s}))^T$.

To eliminate reaction rates, we multiply (1) by a $(N_s - N_r) \times N_r$ component matrix \mathbf{U} such that $\mathbf{U} \mathbb{S}^T = \mathbf{0}$. After multiplication by \mathbf{U} , equation (2) becomes:

$$\frac{\partial \mathbf{U} \mathbf{N}}{\partial t} + \mathbf{U} \mathbf{L} = \mathbf{0}. \quad (3)$$

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



M. Saaltink, C. Ayora and J. Carrera, A mathematical formulation for reactive transport that eliminates mineral concentrations, *Water Resources Research*, 34, 1649–1656, 1998.

Application to the simplified system

Mass conservation law for each component in each phase:

$$\begin{aligned}
 \text{H}_2\text{O} : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{H}_2\text{O}}) + L_l(c^{\text{H}_2\text{O}}) = r_{\text{OH}^-}^e + r_{\text{CaCO}_3}^k + r_{\text{HCO}_3^-}^e \\
 \text{CO}_{2(l)} : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{CO}_{2(l)}}) + L_l(c^{\text{CO}_{2(l)}}) = r_{\text{HCO}_3^-}^e + r_{\text{CO}_{2(g)}}^e + r_{\text{CaCO}_3}^k \\
 \text{H}^+ : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{H}^+}) + L_l(c^{\text{H}^+}) = -r_{\text{OH}^-}^e - 2r_{\text{CaCO}_3}^k - r_{\text{HCO}_3^-}^e \\
 \text{Ca}^{2+} : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{Ca}^{2+}}) + L_l(c^{\text{Ca}^{2+}}) = r_{\text{CaCO}_3}^k \\
 \text{HCO}_3^- : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{HCO}_3^-}) + L_l(c^{\text{HCO}_3^-}) = -r_{\text{HCO}_3^-}^e \\
 \text{OH}^- : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{OH}^-}) + L_l(c^{\text{OH}^-}) = -r_{\text{OH}^-}^e \\
 \text{CO}_{2(g)} : \quad & \frac{\partial}{\partial t}(\phi S_g c^{\text{CO}_{2(g)}}) + L_g(c^{\text{CO}_{2(g)}}) = -r_{\text{CO}_{2(g)}}^e \\
 \text{CaCO}_3 : \quad & \frac{d}{dt} c^{\text{CaCO}_3} = -r_{\text{CaCO}_3}^k
 \end{aligned}$$

Application to the simplified system

Mass conservation law for each component in each phase:

$$\begin{aligned}
 \text{H}_2\text{O} : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{H}_2\text{O}}) + L_l(c^{\text{H}_2\text{O}}) = r_{\text{OH}^-}^e + r_{\text{CaCO}_3}^k + r_{\text{HCO}_3^-}^e \\
 \text{CO}_{2(l)} : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{CO}_{2(l)}}) + L_l(c^{\text{CO}_{2(l)}}) = r_{\text{HCO}_3^-}^e + r_{\text{CO}_{2(g)}}^e + r_{\text{CaCO}_3}^k \\
 \text{H}^+ : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{H}^+}) + L_l(c^{\text{H}^+}) = -r_{\text{OH}^-}^e - 2r_{\text{CaCO}_3}^k - r_{\text{HCO}_3^-}^e \\
 \text{Ca}^{2+} : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{Ca}^{2+}}) + L_l(c^{\text{Ca}^{2+}}) = r_{\text{CaCO}_3}^k \\
 \text{HCO}_3^- : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{HCO}_3^-}) + L_l(c^{\text{HCO}_3^-}) = -r_{\text{HCO}_3^-}^e \\
 \text{OH}^- : \quad & \frac{\partial}{\partial t}(\phi S_l c^{\text{OH}^-}) + L_l(c^{\text{OH}^-}) = -r_{\text{OH}^-}^e \\
 \text{CO}_{2(g)} : \quad & \frac{\partial}{\partial t}(\phi S_g c^{\text{CO}_{2(g)}}) + L_g(c^{\text{CO}_{2(g)}}) = -r_{\text{CO}_{2(g)}}^e \\
 \text{CaCO}_3 : \quad & \frac{d}{dt} c^{\text{CaCO}_3} = -r_{\text{CaCO}_3}^k
 \end{aligned}$$

Reactions rates will be **eliminated**.

Application to the simplified system

Linear combination to eliminate reaction rates: new conservation laws

$$\text{H}_2\text{O} : T_{\text{H}_2\text{O}} = c^{\text{H}_2\text{O}} + c^{\text{OH}^-} + c^{\text{HCO}_3^-} + c^{\text{CaCO}_3} = C_l^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}) + L_l(C_l^{\text{H}_2\text{O}}) = 0$$

Application to the simplified system

Linear combination to eliminate reaction rates: new conservation laws

$$\text{H}_2\text{O} : T_{\text{H}_2\text{O}} = c^{\text{H}_2\text{O}} + c^{\text{OH}^-} + c^{\text{HCO}_3^-} + c^{\text{CaCO}_3} = C_l^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}) + L_l(C_l^{\text{H}_2\text{O}}) = 0$$

$$\text{CO}_{2(l)} : T_{\text{CO}_{2(l)}} = c^{\text{CO}_{2(l)}} + c^{\text{HCO}_3^-} + c^{\text{CO}_{2(g)}} + c^{\text{CaCO}_3} = C_l^{\text{CO}_{2(l)}} + C_g^{\text{CO}_{2(l)}} + C_s^{\text{CO}_{2(l)}}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{CO}_{2(l)}} + \phi S_g C_g^{\text{CO}_{2(l)}} + C_s^{\text{CO}_{2(l)}}) + L_l(C_l^{\text{CO}_{2(l)}}) + L_g(C_g^{\text{CO}_{2(l)}}) = 0$$

Application to the simplified system

Linear combination to eliminate reaction rates: new conservation laws

$$\text{H}_2\text{O} : T_{\text{H}_2\text{O}} = c^{\text{H}_2\text{O}} + c^{\text{OH}^-} + c^{\text{HCO}_3^-} + c^{\text{CaCO}_3} = C_l^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}) + L_l(C_l^{\text{H}_2\text{O}}) = 0$$

$$\text{CO}_{2(l)} : T_{\text{CO}_{2(l)}} = c^{\text{CO}_{2(l)}} + c^{\text{HCO}_3^-} + c^{\text{CO}_{2(g)}} + c^{\text{CaCO}_3} = C_l^{\text{CO}_{2(l)}} + C_g^{\text{CO}_{2(l)}} + C_s^{\text{CO}_{2(l)}}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{CO}_{2(l)}} + \phi S_g C_g^{\text{CO}_{2(l)}} + C_s^{\text{CO}_{2(l)}}) + L_l(C_l^{\text{CO}_{2(l)}}) + L_g(C_g^{\text{CO}_{2(l)}}) = 0$$

$$\text{H}^+ : T_{\text{H}^+} = c^{\text{H}^+} - c^{\text{OH}^-} - c^{\text{HCO}_3^-} - 2c^{\text{CaCO}_3} = C_l^{\text{H}^+} + C_s^{\text{H}^+}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{H}^+} + C_s^{\text{H}^+}) + L_l(C_l^{\text{H}^+}) = 0$$

Application to the simplified system

Linear combination to eliminate reaction rates: new conservation laws

$$\text{H}_2\text{O} : T_{\text{H}_2\text{O}} = c^{\text{H}_2\text{O}} + c^{\text{OH}^-} + c^{\text{HCO}_3^-} + c^{\text{CaCO}_3} = C_l^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{H}_2\text{O}} + C_s^{\text{H}_2\text{O}}) + L_l(C_l^{\text{H}_2\text{O}}) = 0$$

$$\text{CO}_2(\text{l}) : T_{\text{CO}_2(\text{l})} = c^{\text{CO}_2(\text{l})} + c^{\text{HCO}_3^-} + c^{\text{CO}_2(\text{g})} + c^{\text{CaCO}_3} = C_l^{\text{CO}_2(\text{l})} + C_g^{\text{CO}_2(\text{l})} + C_s^{\text{CO}_2(\text{l})}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{CO}_2(\text{l})} + \phi S_g C_g^{\text{CO}_2(\text{l})} + C_s^{\text{CO}_2(\text{l})}) + L_l(C_l^{\text{CO}_2(\text{l})}) + L_g(C_g^{\text{CO}_2(\text{l})}) = 0$$

$$\text{H}^+ : T_{\text{H}^+} = c^{\text{H}^+} - c^{\text{OH}^-} - c^{\text{HCO}_3^-} - 2c^{\text{CaCO}_3} = C_l^{\text{H}^+} + C_s^{\text{H}^+}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{H}^+} + C_s^{\text{H}^+}) + L_l(C_l^{\text{H}^+}) = 0$$

$$\text{Ca}^{2+} : T_{\text{Ca}^{2+}} = c^{\text{Ca}^{2+}} + c^{\text{CaCO}_3} = C_l^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}$$

$$\frac{\partial}{\partial t}(\phi S_l C_l^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}) + L_l(C_l^{\text{Ca}^{2+}}) = 0$$

Application to the simplified system

Ordinary differential equation

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

Mass action laws

$$\text{CO}_{2(\text{g})} : a^{\text{CO}_{2(\text{g})}} = K_{\text{CO}_2} a^{\text{CO}_{2(1)}}$$

$$\text{OH}^- : a^{\text{OH}^-} = K_{\text{OH}^-} a^{\text{H}^{+ - 1}}$$

$$\text{HCO}_3^- : a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^{+ - 1}} a^{\text{CO}_{2(1)}}$$

Coupled system: PDE + ODE + algebraic equations

Strategy for solving

- Fully implicit approach

The full system of equations is solved with all the unknowns: pressures p_α , saturations S_α and concentrations c^i (Fan 2012).

- Sequential approach

We consider that one dominant species exists in each phase: H₂O in liquid phase and CO₂ in gas phase (Zhang 2012, Steefel 2015).

- ① We compute the pressures p_α , the velocities \vec{q}_α , the saturations S_α and the concentrations of dominant species, solutions of a simplified two-phase flow with two components (H₂O and CO₂).
- ② Using p_α , \vec{q}_α and S_α , we solve a reactive transport problem with concentrations of the other species c^i .



Y. Fan, L. J. Durlofsky and H. A. Tchelepi, A fully-coupled flow-reactive-transport formulation based on element conservation, with application to CO₂ storage simulations, *Advances in Water Resources*, 42, 47–61, 2012.



F. Zhang, G.-T. Yeh and J.C. Parker, *Groundwater reactive transport models*, Bentham Science Publishers Ltd, 2012.



C. I. Steefel *et al.*, Reactive transport codes for subsurface environmental simulation, *Computational Geosciences*, 19, 445–478, 2015.

Sequential approach

$$\text{H}_2\text{O} : \frac{\partial}{\partial t}(\phi S_l c^{\text{H}_2\text{O}}) + L_l(c^{\text{H}_2\text{O}}) = \Psi_1(c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(l)} : \frac{\partial}{\partial t}(\phi S_l c^{\text{CO}_{2(l)}} + \phi S_g c^{\text{CO}_{2(g)}}) + L_l(c^{\text{CO}_{2(l)}}) + L_g(c^{\text{CO}_{2(g)}}) = \Psi_2(c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(g)} : a^{\text{CO}_{2(g)}} = K_{\text{CO}_2} a^{\text{CO}_{2(l)}}$$

$$\text{H}^+ : \frac{\partial}{\partial t}(\phi S_l C_l^{\text{H}^+} + C_s^{\text{H}^+}) + L_l(C_l^{\text{H}^+}) = 0$$

$$\text{Ca}^{2+} : \frac{\partial}{\partial t}(\phi S_l C_l^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}) + L_l(C_l^{\text{Ca}^{2+}}) = 0$$

$$\text{OH}^- : a^{\text{OH}^-} = K_{\text{OH}^-} a^{\text{H}^+ - 1}$$

$$\text{HCO}_3^- : a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^+ - 1} a^{\text{CO}_{2(l)}}$$

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

Sequential approach

$$\text{H}_2\text{O} : \frac{\partial}{\partial t}(\phi S_l c^{\text{H}_2\text{O}}) + L_l(c^{\text{H}_2\text{O}}) = \Psi_1(c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(l)} : \frac{\partial}{\partial t}(\phi S_l c^{\text{CO}_{2(l)}} + \phi S_g c^{\text{CO}_{2(g)}}) + L_l(c^{\text{CO}_{2(l)}}) + L_g(c^{\text{CO}_{2(g)}}) = \Psi_2(c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(g)} : a^{\text{CO}_{2(g)}} = K_{\text{CO}_2} a^{\text{CO}_{2(l)}}$$

$$\text{H}^+ : \frac{\partial}{\partial t}(\phi S_l C_l^{\text{H}^+} + C_s^{\text{H}^+}) + L_l(C_l^{\text{H}^+}) = 0$$

$$\text{Ca}^{2+} : \frac{\partial}{\partial t}(\phi S_l C_l^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}) + L_l(C_l^{\text{Ca}^{2+}}) = 0$$

$$\text{OH}^- : a^{\text{OH}^-} = K_{\text{OH}^-} a^{\text{H}^+ - 1}$$

$$\text{HCO}_3^- : a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^+ - 1} a^{\text{CO}_{2(l)}}$$

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

Sequential approach

Two-phase two-component flow

$$\text{H}_2\text{O} : \frac{\partial}{\partial t} (\phi S_l c^{\text{H}_2\text{O}}) + L_l (c^{\text{H}_2\text{O}}) = \Psi_1 (c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(l)} : \frac{\partial}{\partial t} (\phi S_l c^{\text{CO}_{2(l)}} + \phi S_g c^{\text{CO}_{2(g)}}) + L_l (c^{\text{CO}_{2(l)}}) + L_g (c^{\text{CO}_{2(g)}}) = \Psi_2 (c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(g)} : a^{\text{CO}_{2(g)}} = K_{\text{CO}_2} a^{\text{CO}_{2(l)}}$$

$$\text{H}^+ : \frac{\partial}{\partial t} (\phi S_l C_l^{\text{H}^+} + C_s^{\text{H}^+}) + L_l (C_l^{\text{H}^+}) = 0$$

$$\text{Ca}^{2+} : \frac{\partial}{\partial t} (\phi S_l C_l^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}) + L_l (C_l^{\text{Ca}^{2+}}) = 0$$

$$\text{OH}^- : a^{\text{OH}^-} = K_{\text{OH}^-} a^{\text{H}^+ - 1}$$

$$\text{HCO}_3^- : a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^+ - 1} a^{\text{CO}_{2(l)}}$$

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

Sequential approach

Two-phase two-component flow

$$\text{H}_2\text{O} : \frac{\partial}{\partial t} (\phi S_l c^{\text{H}_2\text{O}}) + L_l (c^{\text{H}_2\text{O}}) = \Psi_1 (c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(l)} : \frac{\partial}{\partial t} (\phi S_l c^{\text{CO}_{2(l)}} + \phi S_g c^{\text{CO}_{2(g)}}) + L_l (c^{\text{CO}_{2(l)}}) + L_g (c^{\text{CO}_{2(g)}}) = \Psi_2 (c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(g)} : a^{\text{CO}_{2(g)}} = K_{\text{CO}_2} a^{\text{CO}_{2(l)}}$$

$$\text{H}^+ : \frac{\partial}{\partial t} (\phi S_l C_l^{\text{H}^+} + C_s^{\text{H}^+}) + L_l (C_l^{\text{H}^+}) = 0$$

$$\text{Ca}^{2+} : \frac{\partial}{\partial t} (\phi S_l C_l^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}) + L_l (C_l^{\text{Ca}^{2+}}) = 0$$

$$\text{OH}^- : a^{\text{OH}^-} = K_{\text{OH}^-} a^{\text{H}^+ - 1}$$

$$\text{HCO}_3^- : a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^+ - 1} a^{\text{CO}_{2(l)}}$$

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

Sequential approach

Two-phase two-component flow

$$\text{H}_2\text{O} : \frac{\partial}{\partial t} (\phi S_l c^{\text{H}_2\text{O}}) + L_l (c^{\text{H}_2\text{O}}) = \Psi_1 (c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(l)} : \frac{\partial}{\partial t} (\phi S_l c^{\text{CO}_{2(l)}} + \phi S_g c^{\text{CO}_{2(g)}}) + L_l (c^{\text{CO}_{2(l)}}) + L_g (c^{\text{CO}_{2(g)}}) = \Psi_2 (c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(g)} : a^{\text{CO}_{2(g)}} = K_{\text{CO}_2} a^{\text{CO}_{2(l)}}$$

Reactive transport problem

$$\text{H}^+ : \frac{\partial}{\partial t} (\phi S_l C_l^{\text{H}^+} + C_s^{\text{H}^+}) + L_l (C_l^{\text{H}^+}) = 0$$

$$\text{Ca}^{2+} : \frac{\partial}{\partial t} (\phi S_l C_l^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}) + L_l (C_l^{\text{Ca}^{2+}}) = 0$$

$$\text{OH}^- : a^{\text{OH}^-} = K_{\text{OH}^-} a^{\text{H}^+} - 1$$

$$\text{HCO}_3^- : a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^+} - 1 a^{\text{CO}_{2(l)}}$$

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

Sequential approach

Two-phase two-component flow

$$\text{H}_2\text{O} : \frac{\partial}{\partial t} (\phi S_l c^{\text{H}_2\text{O}}) + L_l (c^{\text{H}_2\text{O}}) = \Psi_1 (c^{\text{OH}^-}, c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(l)} : \frac{\partial}{\partial t} (\phi S_l c^{\text{CO}_{2(l)}} + \phi S_g c^{\text{CO}_{2(g)}}) + L_l (c^{\text{CO}_{2(l)}}) + L_g (c^{\text{CO}_{2(g)}}) = \Psi_2 (c^{\text{HCO}_3^-}, c^{\text{CaCO}_3})$$

$$\text{CO}_{2(g)} : a^{\text{CO}_{2(g)}} = K_{\text{CO}_2} a^{\text{CO}_{2(l)}}$$

Reactive transport problem

$$\text{H}^+ : \frac{\partial}{\partial t} (\phi S_l C_l^{\text{H}^+} + C_s^{\text{H}^+}) + L_l (C_l^{\text{H}^+}) = 0$$

$$\text{Ca}^{2+} : \frac{\partial}{\partial t} (\phi S_l C_l^{\text{Ca}^{2+}} + C_s^{\text{Ca}^{2+}}) + L_l (C_l^{\text{Ca}^{2+}}) = 0$$

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$$\text{HCO}_3^- : a^{\text{HCO}_3^-} = K_{\text{HCO}_3^-} a^{\text{H}^+ - 1} a^{\text{CO}_{2(l)}}$$

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

Sequential approach

Two-phase two-component flow problem

- Liquid phase density ρ_l
- Liquid phase velocity \vec{q}_l
- Liquid phase saturation S_l
- Concentrations $c_l^{\text{H}_2\text{O}}$, $c_l^{\text{CO}_2(l)}$



- Update of porosity ϕ
- Concentrations $c_l^{\text{H}^+}$, $c_l^{\text{OH}^-}$,
 $c_l^{\text{Ca}^{2+}}$, $c_l^{\text{HCO}_3^-}$, $c_s^{\text{CaCO}_3}$

Reactive transport problem

Figure : Coupling procedure between flow and reactive transport problems.

Numerical simulation

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

Flow:

- **2p2c** module 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**.



Reactive transport

The reactive transport problem can be written as follows:

$$\begin{aligned} \frac{\partial(\phi S_l C_l + C_s)}{\partial t} + L_l(C_l) &= 0, \\ T &= \phi S_l C_l + C_s, \\ C_s &= \Psi_C(T). \end{aligned}$$

- **Operator Splitting** (Yeh and Tripathi 1989, Carrayrou 2004),
- **Direct Substitution** (Hammond and Valocchi 2005, Saaltink 1998),
- **DAE Formulation** (Erhel and de Dieuleveult 2008),
- **Elimination Technique** (Kraütle and Knabner 2005),
- **Implicit Formulation** (Amir and Kern 2010),
- **Space-time domain decomposition** (Haeberlein, Michel and Caetano 2010).

SIA method

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

$$\begin{aligned} \phi^n \frac{S_I^{n+1} C_I^{n+1,k+1} - S_I^n C_I^n}{\Delta t} + \frac{C_S^{n+1,k} - C_S^n}{\Delta t} + L_I(C_I^{n+1,k+1}) &= 0, \\ T^{n+1,k+1} &= \phi^n S_I^{n+1} C_I^{n+1,k+1} + C_S^{n+1,k}, \\ C_S^{n+1,k+1} &= \Psi_C(T^{n+1,k+1}). \end{aligned}$$

The algorithm is stopped when:

$$\frac{\|C_I^{n+1,k+1} - C_I^{n+1,k}\|}{\|C_I^{n+1,k+1}\|} + \frac{\|C_S^{n+1,k+1} - C_S^{n+1,k}\|}{\|C_S^{n+1,k+1}\|} < \epsilon.$$



G.T. Yeh and V.S. Tripathi. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multi-chemical components. *Water Resources Research*, 25, 93–108, 1989.



GSL library. Multidimensional root-finding (<http://www.gnu.org/software/gsl/>).

MoMaS Benchmark

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

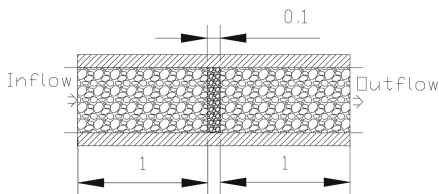


Figure : Scheme for the 1D problem



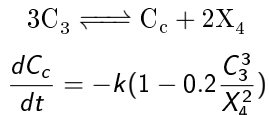
J. Carayrou, M. Kern, P. Knabner. Reactive transport benchmark of MoMaS, *Comput Geosci*, 14, 385–392, 2010.

MoMaS Benchmark: Chemical system

Equilibrium reactions:

	X_1	X_2	X_3	X_4	X_5	S	K
C_1	0	-1	0	0	0	0	1.00E-12
C_2	0	1	1	0	0	0	1
C_3	0	-1	0	1	0	0	1
C_4	0	-4	1	3	0	0	0.1
C_5	0	4	3	1	0	0	1.00E+35
C_6	0	10	3	0	0	0	1.00E+32
C_7	0	-8	0	2	0	0	1.00E-04
CS_1	0	3	1	0	0	1	1.00E+6
CS_2	0	-3	0	1	0	2	1.00E-01
CP_1	0	3	1	0	0	0	8.00E+10
CP_2	0	1	0	0	1	0	20

Kinetic reaction:



MoMaS Benchmark: Numerical results

- Mesh with **1027 elements** (finest in the center of the domain).
- Variable time step: $dt_{max} = 0.05s$.
- **Dissolution/Precipitation**: for each precipitated species CP_i , a solubility product must be respected:

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

Reformulation as a **complementarity problem**:

$$\min(CP_i, 1 - K_p \prod_{j=1}^{N_s} X_j^{apj}) = 0.$$

MoMaS Benchmark: Numerical results

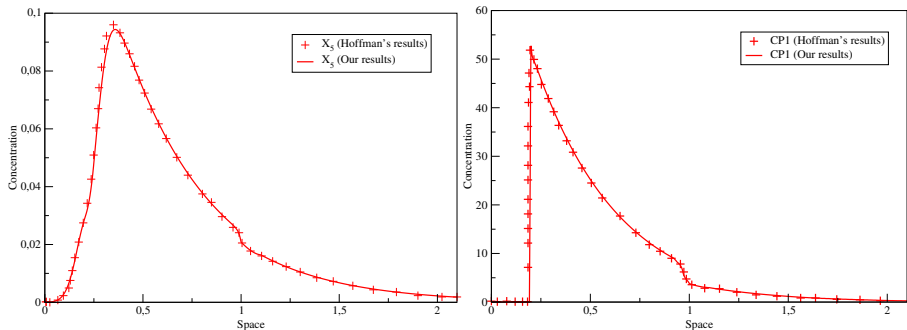


Figure : Concentration profile at $t = 5010$ for X_5 (Left) and for the mineral $CP1$ (Right) for the 1D advective Hard Test Case.



J. Hoffmann, S. Kräutle, P. Knabner, A parallel global-implicit 2-D solver for reactive transport problems in porous media based on a reduction scheme and its application to the momas benchmark problem, *Computational Geosciences* 14 (2010) 421–433.

Test of Saaltink et al

- Injection of CO_2 in a deep saline aquifer in Hontomin.
- 2D axisymmetric domain of thickness = 100m and length = 5km.
- Injection well in the centre of the domain.
- Same chemical as defined previously but equilibrium reaction or calcite dissolution/precipitation.
- Variable porosity : $\phi = 1 - \frac{c_s^{\text{CaCO}_3} M^{\text{CaCO}_3}}{\rho^s}$ with $M^{\text{CaCO}_3} = 0.1$ kg.mol⁻¹ and $\rho^s = 2700$ kg.m⁻³.
- Time of simulation = 1 year.
- Mesh with 10000 elements (500 × 20).



M. W. Saaltink, V. Vilarrasa, F. De Gaspari, O. Silva, J. Carrera, and T.S. Rötting. A method for incorporating equilibrium chemical reactions into multiphase flow models for CO_2 storage, *Advances in Water Resources*, 62, 431–441, 2013.

Test of Saaltink et al



Figure : Saturation S_g after 100 days (top) and 1 year (bas) CO_2 injection.



Figure : Precipitated/dissolved calcite volume fraction after 100 days of CO_2 injection.

Test of Saaltink et al

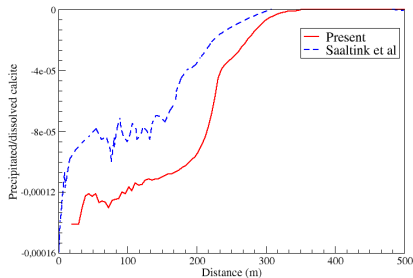
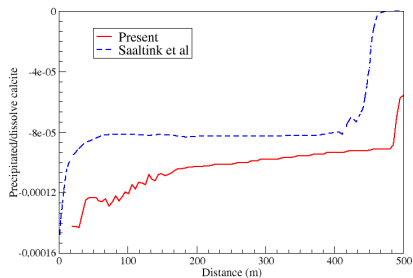


Figure : Precipitated/dissolved calcite volume fraction after 100 days of CO_2 injection at two depth (left: 10 and right: 50m).

Test of Fan *et al*

- **CO₂ injection** in deep saline aquifer.
- **3D domain** , 100m of thickness, 15km of length and 15km of width.
- **Injection well** at 25m 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).



Y. Fan, L. J. Durlofsky, and H. A. Tchelepi. A fully-coupled flow-reactive-transport formulation based on element conservation, with application to CO₂ storage simulations. *Advances in Water Resources*, 42:47–61, 2012.

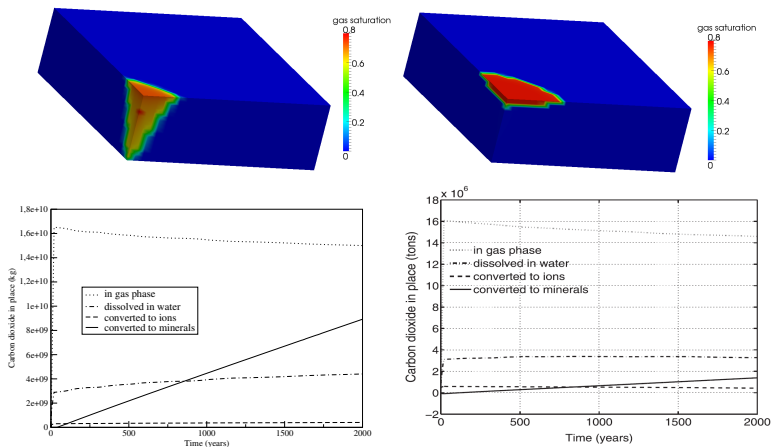
Test of Fan *et al*: Numerical results

Figure : Gas saturation evolution (top left: 20 years, top right: 2000 years). Distribution of CO₂ (bottom left: our results, bottom right: Fan's results).

Test of Fan *et al*: Missing data

Parameters	Taken values
Relative permeabilities	$k_{rl} = (S_l^*)^4$ $k_{rg} = 0.4(1 - S_l^*)^2(1 - (S_l^*)^2)$ $S_l^* = \frac{S_l - 0.2}{1 - 0.2}$
Liquid diffusivity	$D = 10^{-9} m^2.s^{-1}$
Kinetic reactions rates	$r_k = -K_s A_s S_l (1 - Q/K_k)$
Initial conditions for six-element case	Initial conditions for nine-element case

Table : Missing data.

Necessity to have a **reliable and well documented benchmark**.



Y. Fan. Chemical reaction modeling in a subsurface flow simulator with application to in-situ upgrading and CO₂ mineralization (Ph.D. dissertation), Stanford University, 2010.

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.

We are interested in the emergence of a group aiming at the elaboration of a benchmark for two-phase multicomponent flow with reactive transport in porous media.

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

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