Reactive Transport Modeling: Implicit and Sequential strategies

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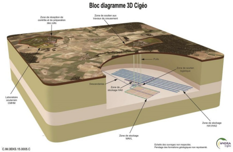
Outline

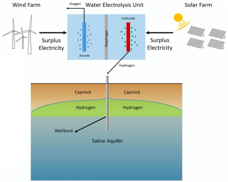
Motivation

- **Goal** is to solve heterogeneous subsurface flow problems: **Thermo-Hydro-Chemical** processes (THC).
- **Applications**: **nuclear waste** management, **geological storage of gas (CO_2, H_2)**



https://www.cigeo.gouv.fr

https://totalenergies.com



https://www.fif.tu-darmstadt.de

Geochemical model

$$\sum_{j=1}^{N_c} \nu_{ij} A_j = 0, \; i = 1, \ldots, N_r$$

Table: Example: 3 reactions and 7 species

$OH^- + H^+ - H_2O$	$=$	0
$HCO_3^- + H^+ - H_2O - CO_{2(l)}$	$=$	0
Calcite $+ H^+ - Ca^{2+} - HCO_3^-$	$=$	0

Equilibrium reactions

Mass action laws:

$$a^j = K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}}, \; j \in I_s / (I_{spe} \cup I_{spk}).$$

Equilibrium dissolution/precipitation reaction:

$$\text{if } K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}} < 1 \text{ then } c_s^j = 0,$$

$$\text{else } K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}} = 1, \; j \in I_{spe},$$

written as $\min(c_s^j, 1 - K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}}) = 0.$

Kinetic reactions

Ordinary differential equation:

$$\frac{d c_s^j}{dt} = -r_j, \; j \in I_{spk}$$

with $r_j = K_j^s A_j^s \left(1 - K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}} \right)$

Geochemical model

$$\sum_{j=1}^{N_c} \nu_{ij} A_j = 0,\ i = 1, \ldots, N_r$$

Table: Example: 3 reactions and 7 species

OH^-	=	H_2O - H^+
HCO_3^-	=	$H_2O + CO_{2(l)}$ - H^+
Calcite	=	$H_2O + Ca^{2+} + CO_{2(l)}$ - $2H^+$

Equilibrium reactions

Mass action laws:

$$a^j = K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}},\ j \in I_s/(I_{spe} \cup I_{spk}).$$

Equilibrium dissolution/precipitation reaction:

$$\text{if } K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}} < 1 \text{ then } c_s^j = 0,$$

$$\text{else } K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}} = 1,\ j \in I_{spe},$$

$$\text{written as} \min(c_s^j, 1 - K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}}) = 0.$$

Kinetic reactions

Ordinary differential equation:

$$\frac{dc_s^j}{dt} = -r_j,\ j \in I_{spk}$$

$$\text{with } r_j = K_j^s A_j^s \left(1 - K_j \prod_{i \in I_p} (a^i)^{\nu_{ji}}\right)$$

Mathematical model for two-phase nonisothermal flow with reactive transport

N_p mass conservation laws:

$$\frac{\partial}{\partial t}\left(\phi S_{\alpha_i} c^i_{\alpha_i} + \sum_{j\in I_{sm}} \phi \nu_{ji} S_{\alpha_j} c^j_{\alpha_j} + \sum_{j\in I_s/I_{sm}} \nu_{ji} c^j_s\right) + L_{\alpha_i}(c^i_{\alpha_i})$$

$$+ \sum_{j\in I_{sm}} \nu_{ji} L_{\alpha_j}(c^j_{\alpha_j}) = 0, \quad i \in I_{pm},$$

$$\text{with } L_\alpha(c^i_\alpha) = -\nabla\cdot(\phi S_\alpha D_\alpha \nabla c^i_\alpha) + \nabla\cdot(c^i_\alpha \overrightarrow{q_\alpha}),$$

$$\frac{\partial}{\partial t}\left(c^i_s + \sum_{j\in I_s/I_{sm}} \nu_{ji} c^j_s\right) = 0, \quad i \in I_{pi},$$

Energy conservation law:

$$\frac{\partial}{\partial t}\left(\phi \sum_\alpha S_\alpha \rho_\alpha u_\alpha + (1-\phi)\rho_S c_h T\right) + \nabla\cdot\left(-\lambda\nabla T + \sum_\alpha \rho_\alpha h_\alpha \overrightarrow{q_\alpha}\right) = 0,$$

Mathematical model for two-phase nonisothermal flow with reactive transport

N_s equations provided by the chemistry

$$a^j_{\alpha_j} = K_j(T) \prod_{i \in I_p} (a^i_{\alpha_i})^{\nu_{ji}}, \quad j \in I_{sm} \cup I_{si},$$

$$\min\left(c^j_s, 1 - K_j(T) \prod_{i \in I_p} (a^i_{\alpha_i})^{\nu_{ji}} \right) = 0, \quad j \in I_{spe},$$

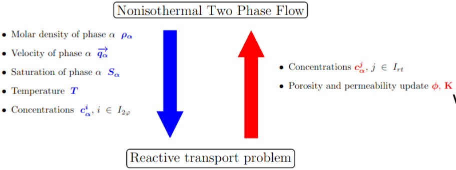
$$\frac{dc^j_s}{dt} = -K^s_j(T) A^s_j \left(1 - K_j(T) \prod_{i \in I_p} (a^i_{\alpha_i})^{\nu_{ji}} \right), \quad j \in I_{spk},$$

+ Capillary pressure law, solubility laws, Equation of states, etc.

Solving approach

Sequential approach [1, 2]

Operator splitting



Nonisothermal Two Phase Flow

- Molar density of phase α $\boldsymbol{\rho_\alpha}$
- Velocity of phase α $\overrightarrow{\boldsymbol{q_\alpha}}$
- Saturation of phase α $\boldsymbol{S_\alpha}$
- Temperature $\boldsymbol{T}$
- Concentrations $\boldsymbol{c_\alpha^i}$, $i \in I_{2\varphi}$

- Concentrations $\boldsymbol{c_\alpha^j}$, $j \in I_{rt}$
- Porosity and permeability update ϕ, $\mathbf{K}$

Reactive transport problem

Implicit approach [3]

Fully coupled fully implicit scheme using direct substitution approach (DSA)

$$c_\alpha^j = \mathbb{C}_\alpha^j(\mathbf{c_p}),\ j \in I_{sm} \cup I_{si}$$

where $\mathbf{c_p}$ is concentration of primary species.

[1] E. Ahusborde, M. Kern, V. Vostrikov. Numerical simulation of two-phase multicomponent flow with reactive transport in porous media: application to geological sequestration of CO_2, ESAIM: Proc. 50, 21-39 (2015).

[2] E. Ahusborde, B. Amaziane, M. El Ossmani. Improvement of numerical approximation of coupled multiphase multicomponent flow with reactive geochemical transport in porous media, Oil & Gas Science and Technology 73 (2018).

[3] E. Ahusborde, B. Amaziane, M. Id Moulay. High Performance Computing of 3D reactive multiphase flow in porous media: application to geological storage of CO_2, Computational Geosciences 25 (2021).

Numerical Simulation of Thermal-Hydraulic-Chemical coupled processes for CO_2 geological storage

E. Ahusborde, B. Amaziane, F. Croccolo, N. Pillardou

[1] N. Pillardou. Modeling and Multiscale HPC Simulations of CO_2 Storage in Saline Aquifers, PhD thesis, University of Pau and Pays de l'Adour (2023).

[2] E. Ahusborde, B. Amaziane, F. Croccolo, N. Pillardou. Numerical Simulation of a Thermal-Hydraulic-Chemical Multiphase Flow Model for Sequestration in Saline Aquifers. Mathematical Geosciences 56, 541–572 (2024).

Finite Volume Discretization

- Cell-centred finite volume approach for spatial discretization.
- **BDF2** scheme for time discretization.

- Mass conservation law:

$$
\begin{aligned}
&\frac{|V_k|}{\Delta t^n}\left(\beta_1\left\{\phi S_\alpha c_\alpha^i\right\}_k^{n+1}+\beta_0\left\{\phi S_\alpha c_\alpha^i+\right\}_k^{n}+\beta_{-1}\left\{\phi S_\alpha c_\alpha^i+\right\}_k^{n-1}\right)\\
&+\sum_{j\in I_{sm}}\nu_{ji}\frac{|V_k|}{\Delta t^n}\left(\beta_1\left\{\phi S_\alpha \mathbb{C}_\alpha^j(\mathbf{c_p})\right\}_k^{n+1}+\beta_0\left\{\phi S_\alpha \mathbb{C}_\alpha^j(\mathbf{c_p})\right\}_k^{n}+\beta_{-1}\left\{\phi S_\alpha \mathbb{C}_\alpha^j(\mathbf{c_p})\right\}_k^{n-1}\right)\\
&+\sum_{j\in I_s\setminus I_{sm}}\nu_{ji}\frac{|V_k|}{\Delta t^n}\left(\beta_1\left\{\mathbb{C}_s^j(\mathbf{c_p})\right\}_k^{n+1}+\beta_0\left\{\mathbb{C}_s^j(\mathbf{c_p})\right\}_k^{n}+\beta_{-1}\left\{\mathbb{C}_s^j(\mathbf{c_p})\right\}_k^{n-1}\right)\\
&+\sum_{l\in V(k)}|\gamma_{kl}|\left(\left\{c_\alpha^i\right\}_{kl}^{n+1}\left\{\vec{q}_\alpha\right\}_{kl}^{n+1}-\left\{D_\alpha\right\}_{kl}^{n+1,harm}\left\{\nabla c_\alpha^i\right\}_{kl}^{n+1}\right)\cdot\vec{n}_{kl}\\
&+\sum_{j\in I_{sm}}\nu_{ji}\sum_{l\in V(k)}|\gamma_{kl}|\left(\left\{\mathbb{C}_\alpha^j(\mathbf{c_p})\right\}_{kl}^{n+1}\left\{\vec{q}_\alpha\right\}_{kl}^{n+1}-\left\{D_\alpha\right\}_{kl}^{n+1,harm}\left\{\nabla\mathbb{C}_\alpha^j(\mathbf{c_p})\right\}_{kl}^{n+1}\right)\cdot\vec{n}_{kl}\\
&=0,\ i\in I_{pm}
\end{aligned}
$$

Finite Volume Discretization

- Darcy's law:

$$\left\{\vec{q}_\alpha\right\}_{kl}^{n+1} = -\left\{\mathbb{K}\right\}_{kl}^{harm}\left\{\frac{k_{r\alpha}(S_\alpha)}{\mu_\alpha}\right\}_{kl}^{n+1,up}\left(\left\{\nabla P_\alpha\right\}_{kl}^{n+1} - \left\{\rho_\alpha^{mass}\right\}_{kl}^{n+1,ari}\vec{g}\right),$$

- Energy conservation law:

$$\frac{|V_k|}{\Delta t^n}\left(\beta_1\sum_\alpha\left\{\phi\rho_\alpha u_\alpha S_\alpha\right\}_k^{n+1} + \beta_0\sum_\alpha\left\{\phi\rho_\alpha u_\alpha S_\alpha\right\}_k^{n} + \beta_{-1}\sum_\alpha\left\{\phi\rho_\alpha u_\alpha S_\alpha\right\}_k^{n-1}\right)$$
$$+\frac{|V_k|}{\Delta t^n}\left(\beta_1\left\{(1-\phi)\rho_s c_h T\right\}_k^{n+1} + \beta_0\left\{(1-\phi)\rho_s c_h T\right\}_k^{n} + \beta_{-1}\left\{(1-\phi)\rho_s c_h T\right\}_k^{n-1}\right)$$
$$+\sum_{l\in V(k)}|\gamma_{kl}|\left(-\left\{\lambda_{pm}\right\}_{kl}^{n+1,harm}\left\{\nabla T\right\}_{kl}^{n+1} + \sum_\alpha\left\{\rho_\alpha h_\alpha\right\}_{kl}^{n+1}\left\{\vec{q}_\alpha\right\}_{kl}^{n+1}\right)\cdot\vec{n}_{kl} = 0,$$

- Mass action laws for equilibrium reactions:

$$\left\{a_\alpha^j\right\}_k^{n+1} = K_j(T)\prod_{i\in I_p}\left\{(a_\alpha^i)^{\nu_{ji}}\right\}_k^{n+1}, \; j\in I_s\setminus I_{sk},$$

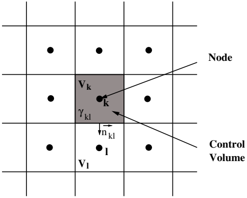
- ODE for kinetic reactions:

$$\left\{c_s^j\right\}_k^{n+1} = \left\{c_s^j\right\}_k^{n} - \Delta t^n K_j^s(T)A_j^s\left(1-K_j(T)\prod_{i\in I_p}\left\{(a_{\alpha_i}^i)^{\nu_{ji}}\right\}_k^{n+1}\right), \; j\in I_{sk}.$$

Finite Volume Discretization

A fully **upwinding** scheme is used to approximate the numerical flux for the convective term. The quantities (S_α, $c^i_{\alpha_i}$, P_α, T and $k_{r\alpha}$) are evaluated implicitly and upstream at the interface γ_{kl} between two adjacent elements as:

$$\{\cdot\}^{n+1,up}_{kl} = \begin{cases} \{\cdot\}^{n+1}_{k} & \text{if} \quad \{\vec{q}_\alpha\}^{n+1}_{kl} \cdot \vec{n}_{kl} > 0, \\ \{\cdot\}^{n+1}_{l} & \text{else.} \end{cases}$$



Flux on interfaces for diffusive terms are computed using Two-Point Flux Approximation (TPFA) or Multiple-Point Flux Approximation (MPFA).

Presentation of DuMu^X

DuMu^X: **Du**ne for **Mu**lti-{phase, component, scale, physics,..} Flow and Transport in Porous Media [1, 2].

- Free and open source simulator for flow and transport in porous media based on DUNE [3].
- Parallel computing using MPI standard and DUNE capacities.
- Newton-Raphson method: to solve the non-linear system:
  - The jacobian matrix is calculated by numerical differentiation,
  - Adaptive time step strategy.
- Linear solver: Krylov space methods: Bi-conjugate Gradient Stabilized + AMG preconditioner.

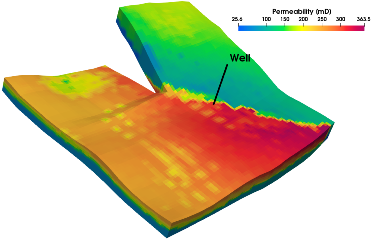
[1] Koch T., Gläser D., Weishaupt K., *et al.*, *DuMu^X 3 - an open-source simulator for solving flow and transport problems in porous media with a focus on model coupling*, Computers and Mathematics with Applications, Vol 81, 423-443, 2021.

[2] DuMu^X webpage: https://dumux.org/

[3] DUNE: Distributed and Unified Numerics Environment. Webpage: https://www.dune-project.org/

3D heterogeneous test case

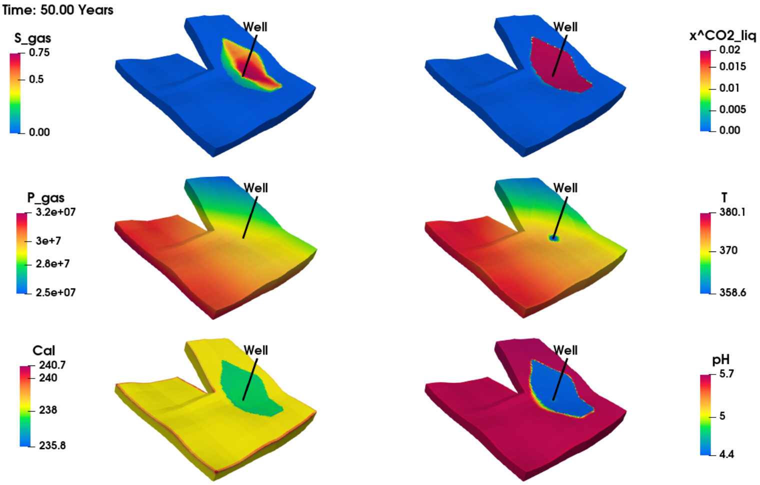
- Test case based on example presented in [1].
- **3D heterogeneous domain**.
- Chemical system composed of 12 **elements** (3 minerals) and 8 **reactions** (3 kinetic reactions and 5 equilibrium).
- $T_{init} = 353K$. Injection at $T = 313K$ during **25 years**.
- Time of simulation = **50 years**.
- Mesh with **54756 elements**.



$$
\begin{aligned}
&H_2O_{(g)} = H_2O_{(l)}\\
&CO_{2(g)} = CO_{2(l)}\\
&CO_{2(l)} + H_2O = H^+ + HCO_3^-\\
&CO_3^{2-} + H^+ = HCO_3^-\\
&OH^- + H^+ = H_2O\\
&\text{Ano} + 8\,H^+ = 4\,H_2O + Ca^{2+} + 2\,Al^{3+} + 2\,SiO_{2(l)}\\
&\text{Cal} + H^+ = Ca^{2+} + HCO_3{}^-\\
&\text{Kao} + 6\,H^+ = 5\,H_2O + 2\,Al^{3+} + 2\,SiO_{2(l)}
\end{aligned}
$$

[1] H. Class, A. Ebigbo, R. Helmig, H. K. Dahle, J. M. Nordbotten, et al. A benchmark study on problems related to CO_2 storage in geologic formations. Computational Geosciences, Springer Verlag, 2009, 13 (4), p. 409-434.

3D heterogeneous test case



Comparison fully implicit/ sequential schemes

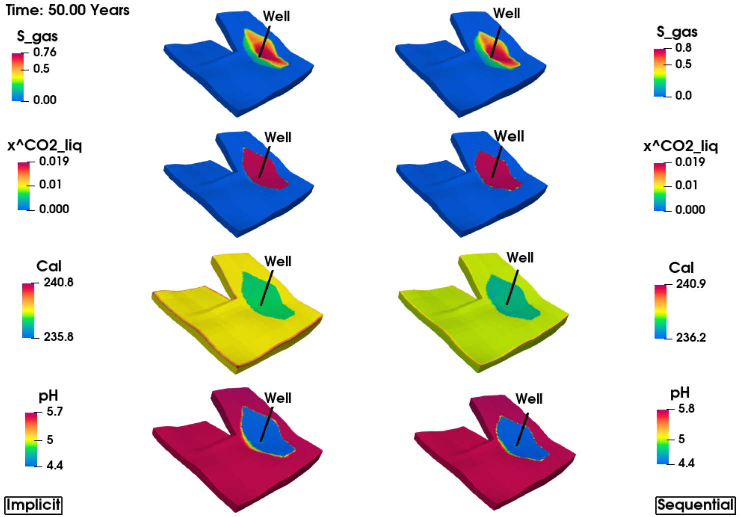


Figure: Comparison of the solutions between the fully implicit and the sequential scheme at t=50 years.

Comparison fully implicit/ sequential schemes

Loss of mass: 3.5%

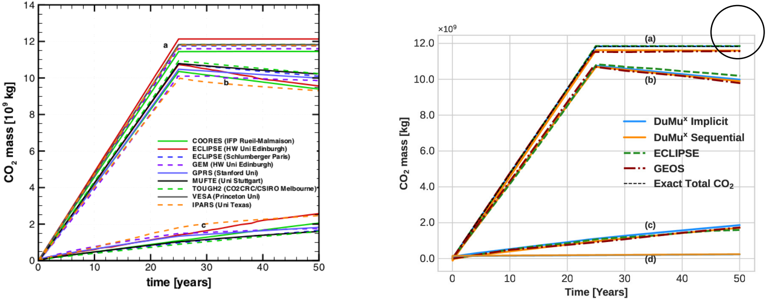


Figure: Evolution of CO_2 quantities as a function of time. (a) total injected mass of CO_2, (b) mass of CO_2 in gas phase, (c) mass of CO_2 dissolved in liquid phase, (d) mass of CO_2 in mineral phase

Maximum time step size effect

$$\epsilon_{\mathrm{CO}_2} = \frac{|Tot_{inj}^{End} - Tot_{\mathrm{CO}_2}^{End} - Tot_{\Gamma_{Dir}}^{End}|}{Tot_{inj}^{End}}$$

Method	dt_{max} [s]	CPU	TS	NI	LI/NI	ϵ_{CO_2}
Imp	1×10^7	9h20min	236	6.37	15.89	1.20×10^{-14}
Imp	5×10^6	12h03min	376	5.25	15.55	2.99×10^{-14}
Imp	1×10^6	35h42min	1626	3.64	15.61	1.4×10^{-13}
Seq	1×10^7	5h50min	222	8.63	9.41	2.73×10^{-2}
Seq	5×10^6	7h19min	373	8.34	8.41	1.89×10^{-2}
Seq	1×10^6	24h27min	1620	6.18	8.26	1.39×10^{-2}

Table: Numerical performances. CPU: elapsed time, TS: number of time steps, NI: Average number of nonlinear iterations per time step, LI / NI: average number of linear iterations per Newton iteration

Maximum time step size effect

$$\epsilon_{\mathrm{CO_2}} = \frac{\left| Tot_{inj}^{End} - Tot_{\mathrm{CO_2}}^{End} - Tot_{\Gamma_{Dir}}^{End} \right|}{Tot_{inj}^{End}}$$

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Comparison fully implicit/ sequential schemes

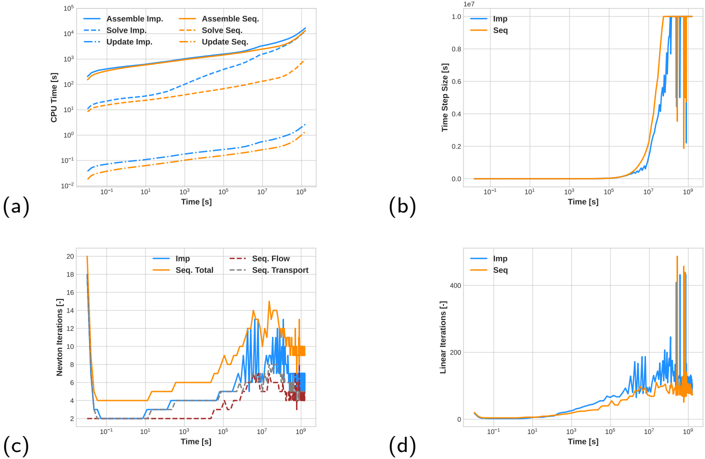
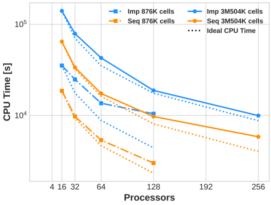
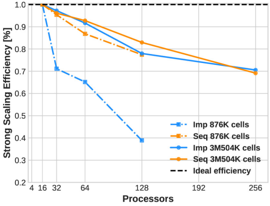


Figure: (a) CPU time evolution as a function of the simulation time for different stages of the computation, (b) timestep, (c) Number of Newton iterations per timestep, (d) Total number of linear iterations per timestep

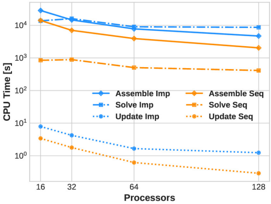
Parallel performance computations



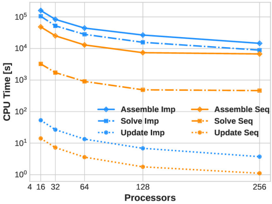
(a) CPU time



(b) Strong efficiency



(c) Detailed CPU time for the mesh composed of 876096 elements



(d) Detailed CPU time for the mesh composed of 3504384 elements

Sequential methodology for Reactive transport modelling using PHREEQC

E. Ahusborde, S. Tabrizinejadas

[1] E. Ahusborde, S. Tabrizinejadas. Sequential methodology for reactive transport modeling utilizing PHREEQC. Submitted for publications in Environmental Earth Sciences (2024).

Element-based mathematical formulation

$$\frac{\partial(\phi c_i)}{\partial t} + \nabla\cdot(c_i \vec{q} - D\nabla c_i) = \sum_{k=1}^{n_k} v_{ik}\ r_k + \sum_{q=1}^{n_q} v_{iq}\ r_q, i \in I_f,$$

$$\frac{\partial c_m}{\partial t} = \sum_{k=1}^{n_k} v_{mk}\ r_k + \sum_{q=1}^{n_q} v_{mq}\ r_q, m \in I_s,$$

We introduce L as the advective diffusive operator:

$$L(c_i) = \nabla\cdot(c_i \vec{q} - D\nabla c_i),$$

and S the stoichiometric matrix as follows:

$$S_{n_c\times n_r} = \begin{bmatrix} v_{11} & \dots & v_{1n_r} \\ \dots & v_{ij} & \dots \\ v_{n_c 1} & \dots & v_{n_c n_r} \end{bmatrix}.$$

Element-based mathematical formulation

The mass conservation laws can be written in consive form:

$$\frac{\partial \mathbf{N}}{\partial t} + \mathbf{L} = \mathbf{S} \times \mathbf{r}.$$

In this system, **r** is the vector containing reaction rates. **N** and **L** are defined as follows:

$$\mathbf{N}_{n_c \times 1} = \begin{pmatrix} \phi c_1 \\ \vdots \\ \phi c_{n_f} \\ c_{n_f+1} \\ \vdots \\ c_{n_f+n_s} \end{pmatrix}, \mathbf{L}_{n_c \times 1} = \begin{pmatrix} L(c_1) \\ \vdots \\ L(c_{n_f}) \\ 0 \\ \vdots \\ 0 \end{pmatrix}.$$

Element-based mathematical formulation

We define the element stoichiometric matrix as follows:

$$\mathbf{E}_{n_e \times n_c} = \begin{bmatrix} E_{11} & \dots & E_{1n_c} \\ \dots & E_{ei} & \dots \\ E_{n_e 1} & \dots & E_{n_e n_c} \end{bmatrix},$$

where E_{ei} is the number of element e in species i.
$\mathbf{E}$ is such that $\mathbf{E}_{n_e \times n_c} \mathbf{S}_{n_c \times n_r} = \mathbf{0}_{n_e \times n_r}$.

Example

Table: Example: 2 reactions, 5 species (OH^-, H^+, H_2O, HCO_3^-, $CO_{2(l)}$) and 3 elements (O, H, C)

$OH^- + H^+ - H_2O$	=	0
$HCO_3^- + H^+ - H_2O - CO_{2(l)}$	=	0

$$\mathbf{A}_{5\times 1} = \begin{bmatrix} OH^- \\ H^+ \\ H_2O \\ HCO_3^- \\ CO_{2(l)} \end{bmatrix}, \mathbf{S}_{5\times 2} = \begin{bmatrix} 1 & 0 \\ 1 & 1 \\ -1 & -1 \\ 0 & 1 \\ 0 & -1 \end{bmatrix}, \mathbf{E}_{3\times 5} = \begin{bmatrix} 1 & 0 & 1 & 3 & 2 \\ 1 & 1 & 2 & 1 & 0 \\ 0 & 0 & 0 & 1 & 1 \end{bmatrix}$$

In this case:

$$\mathbf{ES} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}.$$

Element-based mathematical formulation

Then we multiply by $\mathbf{E}$ the mass conservation laws:

$$\frac{\partial \mathbf{N}}{\partial t} + \mathbf{L} = \mathbf{S} \times \mathbf{r}.$$

It eliminates the chemical rates on the right-hand side and leads to:

$$\boxed{\frac{\partial (\mathbf{EN})}{\partial t} + \mathbf{EL} = \mathbf{0}.}$$

Element-based mathematical formulation

First, we introduce $\mathbf{U} = \mathbf{EN}$ as the total concentration of elements. $\mathbf{U}$ can be decomposed as follows:

$$\mathbf{U} = \phi \mathbf{U}_m + \mathbf{U}_f = \phi \mathbf{U}_m + \mathbf{U}_f^{eq} + \mathbf{U}_f^{kin},$$

By definition, $\mathbf{U}_f^{kin}$ is such that:

$$\frac{d\mathbf{U}_f^{kin}}{dt} = -\mathbf{r}_k.$$

It can be shown that

$$\mathbf{EL} = L(\mathbf{U}_m).$$

Finally, the mass conservation for each element can be written as:

$$\boxed{\frac{\partial \phi \mathbf{U}_m}{\partial t} + \frac{\partial \mathbf{U}_f^{eq}}{\partial t} + L(\mathbf{U}_m) = \mathbf{r}_k.}$$

Decoupling between hydrological and geochemical processes

Following [1], a geochemical PHREEQC [2] batch calculation can be conceptualized as a system of differential algebraic equations (DAE):

$$\begin{cases} \dfrac{d\phi\mathbf{U}_m}{dt} + \dfrac{d\mathbf{U}_f^{eq}}{dt} = \mathbf{r}_k, \\[2ex] f(\mathbf{U}_m + \mathbf{U}_f^{eq}, \mathbf{c}, \mathbf{r}_k) = 0. \end{cases}$$

[1] A. Nardi , A. Idiart, P. Trinchero, L. de Vries, J. Molinero. Interface COMSOL-PHREEQC (iCP), an efficient numerical framework for the solution of coupled multiphysics and geochemistry. Computers & Geosciences 69, 10-21 (2014).

[2] D.L. Parkhurst, C.A.J. Appelo. Description of input and examples for PHREEQC version 3–a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Technical report, US Geological Survey (2013).

Operator splitting strategy: SNIA

Coupling between hydrological and geochemical problems during one time step Δt between the times t^n and t^{n+1} to solve $\boxed{\dfrac{\partial \phi \mathbf{U}_m}{\partial t} + \dfrac{\partial \mathbf{U}_f^{eq}}{\partial t} + L(\mathbf{U}_m) = \mathbf{r}_k}$.

- Hydrological step:
  Mass conservation of the total mobile concentration for each element:

$$\frac{\partial \phi \mathbf{V}_m}{\partial t} + L(\mathbf{V}_m) = 0, \quad \mathbf{V}_m(0) = \mathbf{U}_m^n,$$

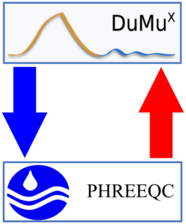
- Geochemical step: $\mathbf{V}_m(\Delta t)$, the output of the hydrological step as the total mobile concentration after Δt, is used to initialize the total mobile concentration in n_r equations corresponding to each chemical reaction.

$$\begin{cases} \dfrac{d\phi \mathbf{W}_m}{dt} + \dfrac{d\mathbf{W}_f^{eq}}{dt} = \mathbf{r_k}, \ \mathbf{W}_m(0) = \mathbf{V}_m(\Delta t), \\ f(\mathbf{W}_m + \mathbf{W}_f^{eq}, \mathbf{C}, \mathbf{r_k}) = 0, \end{cases} \tag{1}$$

- Update step:

$$\mathbf{U}_m^{n+1} = \mathbf{W}_m(\Delta t). \tag{2}$$

Coupling structure between DuMu^X and PHREEQC



Hydrological step:

$$\frac{\partial \phi \mathbf{V}_m}{\partial t} + L(\mathbf{V}_m) = 0,\ \mathbf{V}_m(0) = \mathbf{U}_m(t^n)$$

$\mathbf{V}_m(\Delta t)$

Update step:

$$\mathbf{U}_m(t^{n+1}) = \mathbf{W}_m(\Delta t)$$

Geochemical step:

$$\begin{cases} \dfrac{d\mathbf{W}_m}{dt} + \dfrac{d\mathbf{W}_f^{eq}}{dt} = \mathbf{r_k},\ \mathbf{W}_m(0) = \mathbf{V}_m(\Delta t) \\ f(\mathbf{W}_m + \mathbf{W}_f^{eq}, C, \mathbf{r_k}, T) = 0 \end{cases}$$

Numerical results: calcite dissolution benchmark

Motivation
Mathematical formulation for reactive flows
Numerical Simulation of THC processes for CO_2 storage
Sequential methodology for RTM utilizing PHREEQC
Conclusions

- Injection of $MgCl_2$ into a Calcite column in equilibrium with Calcium.
- Calcite ($CaCO_3$) dissolves and Dolomite ($CaMg(CO_3)_2$) precipitates.

Aqueous reactions	$\log_{10}(K^{eq})$
$2\,H^+ + 2\,e^- = H_2$	-3.1055
$2\,H_2O - 4\,H^+ - 4\,e^- = O_2$	-85.9862
$HCO_3^- + 9\,H^+ + 8\,e^- - 3\,H_2O = CH_4$	27.8493
$H_2O - H^+ = OH^-$	-13.9995
$H^+ - H_2O + HCO_3 = CO_2$	6.3519
$HCO_3{}^- - H^+ = CO_3^{2-}$	-10.3289
$Ca^{+2} - H^+ + HCO_3{}^- = CaCO_3$	-7.1048
$Ca^{+2} + H_2O - H^+ = CaOH^+$	-12.78
$Mg^{+2} - H^+ + HCO_3{}^- = MgCO_3$	-7.3492
$Mg^{+2} + HCO_3{}^- = MgHCO_3{}^+$	1.0682
$Mg^{+2} + H_2O - H^+ = MgOH^+$	-11.44
Mineral reactions	
$CaCO_{3(s)} = Ca^{2+} - H^+ + HCO_3{}^-$	1.849
$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} - 2\,H^+ + 2\,HCO_3{}^-$	4.118

[1] D. Jara, J. de Dreuzy, B. TReacLab: An object-oriented implementation of non-intrusive splitting methods to couple independent transport and geochemical software. Computers & Geosciences, Vol 109, 281-294, 2017.

Numerical results: Calcite dissolution benchmark

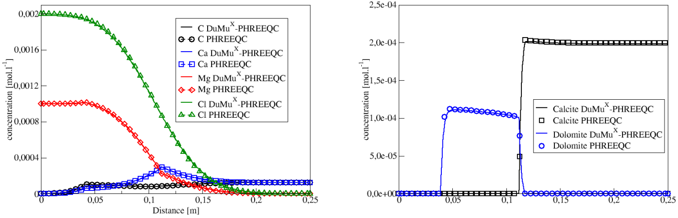
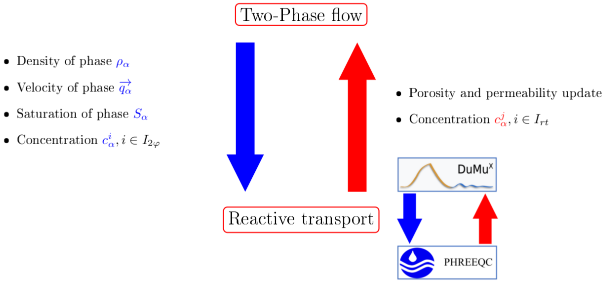


Figure: Profiles of concentrations for mobile elements (top) and minerals (bottom) at $t = 10000\,s$ for the calcite dissolution benchmark.

Number of cells	DuMu^X-PHREEQC	PHREEQC
100	4.5	10.9
200	11.5	83.0
400	35.8	567.8

Table: CPU time (s) comparison between the newly developed model and the reference PHREEQC model.

Extension to reactive two-phase flow



Two-Phase flow

- Density of phase ρ_α
- Velocity of phase $\overrightarrow{q_\alpha}$
- Saturation of phase S_α
- Concentration $c_\alpha^i, i \in I_{2\varphi}$

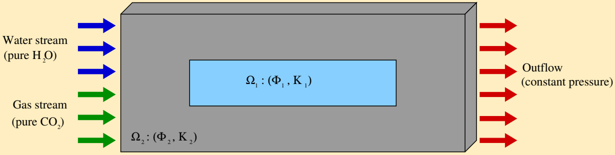
- Porosity and permeability update
- Concentration $c_\alpha^j, i \in I_{rt}$

Reactive transport

Figure: Coupling procedure between flow and reactive transport modules.

Numerical results: Benchmark for reactive two-phase flow

2D Geometry + boundary conditions



Reactions	$log_{10}(K^{eq})$
$CO_{2(l)} = CO_{2(g)}$	–
$H_2O_{(l)} = H_2O_{(g)}$	–
$H_2O - H^+ = OH^-$	-13.95
$H^+ - H_2O + HCO_3 = CO_2$	6.293
$HCO_3{}^- - H^+ = CO_3^{2-}$	-10.279
$CaCO_{3(s)} = Ca^{2+} - H^+ + HCO_3{}^-$	1.889

[1] S. de Hoop, D. Voskov, E. Ahusborde, B. Amaziane, M. Kern. A benchmark study on reactive two-phase flow in porous media: Part I -model description. Computational Geosciences, https://doi.org/10.1007/s10596-024-10268-z, 2024.

[2] E. Ahusborde, B. Amaziane, S. de Hoop, M. El Ossmani, E. Flauraud, F.P. Hamon, M. Kern, A. Socié, D. Su, K.U. Mayer, M. Tóth, D. Voskov. A benchmark study on reactive two-phase flow in porous media: Part II -results and discussion. Computational Geosciences, https://doi.org/10.1007/s10596-024-10269-y, 2024.

Comparison of results

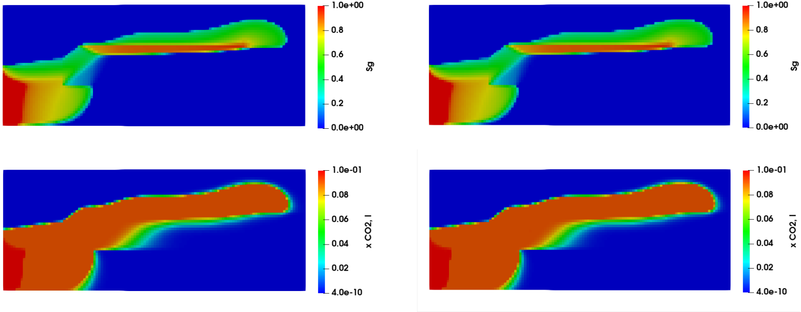


Figure: Comparison of different quantities at $t = 1$ year. Left: DuMu^X-PHREEQC. Right: fully implicit strategy

Comparison of results

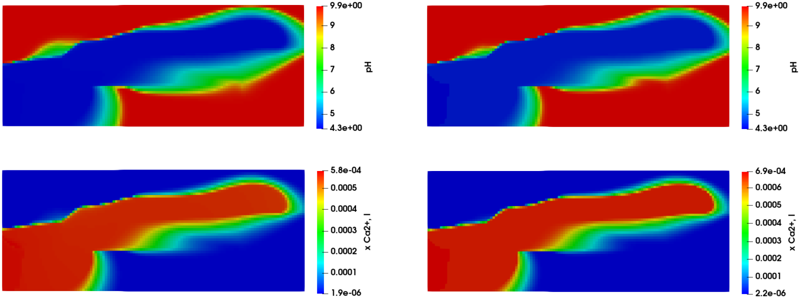


Figure: Comparison of different quantities at $t = 1$ year. Left: DuMu^X-PHREEQC. Right: fully implicit strategy

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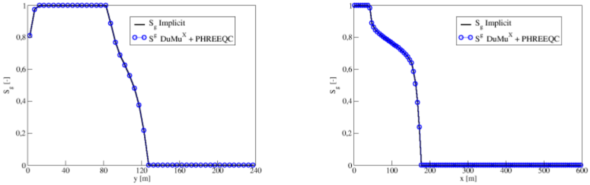
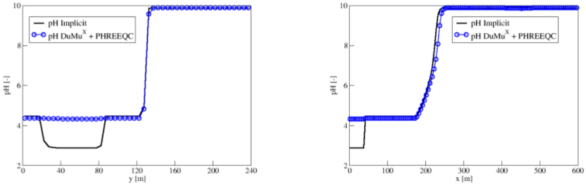
Comparison of results



(a) Gas saturation S_g (a) Gas saturation S_g

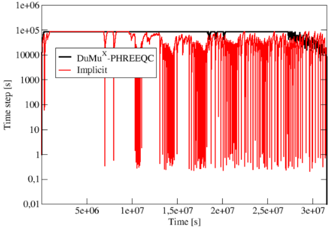


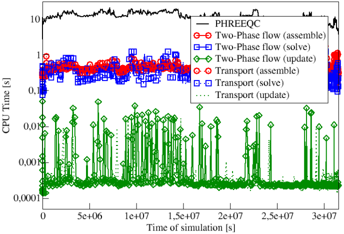
(b) pH (b) pH

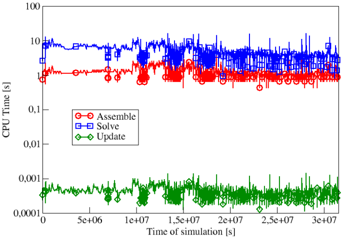
Figure: Comparison of different quantities at $t = 1$ year on vertical line $x = 40$ (left) and horizontal line $y = 50$ (right).

Comparison of performances

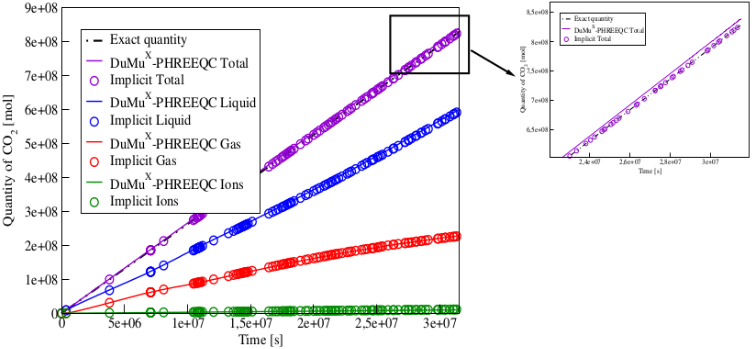
Times [s]	$DuMu^X$ -PHREEQC	Fully implicit
Total CPU	6238	21886
Assembly	249 (2P) 200 (TR)	4882
Solve	160 (2P) 135 (TR)	17002
Update	1.1 (2P) 0.25 (TR)	2
PHREEQC	5492	-
Timesteps	528	5312







Comparison of the distribution of CO_2



Conclusions

Implementation of fully implicit and sequential strategies for THC modelling including HPC.

- Fully implicit strategies:
  - ✓ totally mass-conservative,
  - ✗ time-consuming.
- Sequential strategies:
  - ✓ faster, integration of specialized software,
  - ✗ possible splitting errors.

Acknowledgements

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