A Coats-Based Formulation for Multiphase Reactive Transport: Application to Hydrogen Storage in Porous Media

Thomas Jacumin – Université Côte d'Azur, Nice, France
Roland Masson – Université Côte d'Azur, Nice, France
Laurent Jeannin – Storengy, La Garenne-Colombes, France
Arthur Dartois – Storengy, La Garenne-Colombes, France

CMWR 2026

July 1, 2026

Objectives

- Extend the Coats formulation to multiphase reactive transport,
- Properly handle phase disappearance (especially the aqueous phase),
- Use a Globally Implicit Approach.

Organization

Notations (Morel's formalism)

- Primary species:

$$\mathcal{E}^{\mathbf{pr}} = \{e_1^{\mathbf{pr}}, \dots, e_M^{\mathbf{pr}}\}.$$

- Secondary species:

$$\mathcal{E}^{\mathbf{sec}} = \{e_1^{\mathbf{sec}}, \dots, e_{N-M}^{\mathbf{sec}}\},$$

such that each secondary species is associated to the chemical reaction:

$$e^{\mathbf{sec}} \leftrightarrows \sum_{e^{\mathbf{pr}} \in \mathcal{E}^{\mathbf{pr}}} E_{e^{\mathbf{pr}},e}\, e^{\mathbf{pr}},$$

where

$$E := [E_{e^{\mathbf{pr}},e}]_{e^{\mathbf{pr}} \in \mathcal{E}^{\mathbf{pr}}, e \in \mathcal{E}} \in \mathbb{R}^{\mathcal{E}^{\mathbf{pr}} \times \mathcal{E}}.$$

- We set $\mathcal{E} := \mathcal{E}^{\mathbf{pr}} \cup \mathcal{E}^{\mathbf{sec}}$.

Notations (Morel's formalism)

- Primary species:

$$\mathcal{E}^{\mathbf{pr}} = \{e_1^{\mathbf{pr}}, \dots, e_M^{\mathbf{pr}}\}.$$

- Secondary species:

$$\mathcal{E}^{\mathbf{sec}} = \{e_1^{\mathbf{sec}}, \dots, e_{N-M}^{\mathbf{sec}}\},$$

such that each secondary species is associated to the chemical reaction:

$$e^{\mathbf{sec}} \leftrightarrows \sum_{e^{\mathbf{pr}} \in \mathcal{E}^{\mathbf{pr}}} E_{e^{\mathbf{pr}},e}\, e^{\mathbf{pr}},$$

where

$$E := [E_{e^{\mathbf{pr}},e}]_{e^{\mathbf{pr}} \in \mathcal{E}^{\mathbf{pr}}, e \in \mathcal{E}} \in \mathbb{R}^{\mathcal{E}^{\mathbf{pr}} \times \mathcal{E}}.$$

- We set $\mathcal{E} := \mathcal{E}^{\mathbf{pr}} \cup \mathcal{E}^{\mathbf{sec}}$.
- To link a species $e \in \mathcal{E}$ to its phase $\beta \in \mathcal{P}$:

$$\alpha : e \in \mathcal{E} \mapsto \alpha(e) \in \mathcal{P}.$$

Total conservation equation

Total conservation

$$\sum_{e \in \mathcal{E}} E_{e^{\mathrm{pr}},e} \partial_t n_e - \sum_{e \in \mathcal{E}^{\mathrm{f}}} E_{e^{\mathrm{pr}},e} \operatorname{div}\left(\zeta^{\alpha(e)} C_e \mathrm{u}^{\alpha(e)}\right) = 0, \quad \forall e^{\mathrm{pr}} \in \mathcal{E}^{\mathrm{pr}},$$

where

- n_e $[\mathrm{mol} \cdot \mathrm{m}^{-3}]$: volumetric molar concentration of e, equals to

$$n_e = \phi \zeta^{\alpha(e)} S^{\alpha(e)} C_e, \quad \forall e \in \mathcal{E}^{\mathrm{f}},$$

- ϕ $[-]$: porosity,
- ζ^β $[\mathrm{mol} \cdot \mathrm{m}^{-3}]$: phase molar density,
- S^β $[-]$: phase saturation,
- C_e $[-]$: mole fraction of e in its phase,
- u^β $[\mathrm{m} \cdot \mathrm{s}^{-1}]$: follows the Darcy's law.

Chemical reactions

- Phase transition: Fugacity equality.
- Chemical equilibrium: Law of mass action,

$$Q := \frac{1}{a_{e^{\mathbf{sec}}}} \prod_{e^{\mathbf{pr}} \in \mathcal{E}^{\mathbf{pr}}} \left(a_{e^{\mathbf{pr}}}\right)^{E_{e^{\mathbf{pr}},R}} = K_R.$$

- Kinetic reaction: Conservation equation with reaction rate T_e,

$$\partial_t n_e - \operatorname{div}\left(\zeta^{\alpha(e)} C_e \mathbf{u}^{\alpha(e)}\right) = T_e, \text{ if e is a fluid kinetic species,}$$
$$\partial_t n_e = T_e, \text{ if e is a solid kinetic species.}$$

Closure equations

- Total volume conservation:

$$\underbrace{\phi}_{\text{fluid}} + \underbrace{\phi^{\mathbf{s}} + 1 - \phi_{\mathbf{T}}}_{\text{solid}} = 1 \quad \Leftrightarrow \quad \phi + \phi^{\mathbf{s}} = \phi_{\mathbf{T}},$$

where

  - $\phi^{\mathbf{s}}$: volume fraction of reactive rock,
  - $1 - \phi_{\mathbf{T}}$: volume fraction of non-reactive rock.

- Closure relations:

$$\sum_{\beta \in \mathcal{P}^{\mathbf{f}}} S^{\beta} = 1, \qquad \sum_{e \in \alpha^{-\mathbf{1}}(\{\beta\})} C_e = 1, \ \forall \beta \in \mathcal{P}^{\mathbf{f}} \qquad \text{and} \qquad \phi^{\mathbf{s}} = \sum_{m \in \mathcal{P}^{\mathbf{s}}} \frac{n_m}{\zeta^m}.$$

Summary

- $\#\mathcal{E} + \#\mathcal{P}^{\mathbf{f}} + 2$ equations:
  - $\#\mathcal{E}^{\mathbf{pr}}$: the conservation equations for total primary species,
  - $\#\mathcal{E}^{\mathbf{sec}}$: one algebraic or differential equation for each equilibrium or kinetic chemical reaction, respectively,
  - $\#\mathcal{P}^{\mathbf{f}} + 2$: closure equations,

- $\#\mathcal{E} + \#\mathcal{P}^{\mathbf{f}} + 2$ natural variables (Coats formulation):
  - pressure P,
  - saturations $S^{\beta}, \quad \beta \in \mathcal{P}^{\mathbf{f}}$,
  - solid porosity $\phi^{\mathbf{s}}$,
  - molar fractions $C_e, \quad e \in \mathcal{E}^{\mathbf{f}}$,
  - molar concentrations $n_e, \quad e \in \mathcal{E}^{\mathbf{s}}$.

Summary

- $\#\mathcal{E} + \#\mathcal{P}^{\mathbf{f}} + 2$ equations:
  - $\#\mathcal{E}^{\mathbf{pr}}$: the conservation equations for total primary species,
  - $\#\mathcal{E}^{\mathbf{sec}}$: one algebraic or differential equation for each equilibrium or kinetic chemical reaction, respectively,
  - $\#\mathcal{P}^{\mathbf{f}} + 2$: closure equations,

- $\#\mathcal{E} + \#\mathcal{P}^{\mathbf{f}} + 2$ natural variables (Coats formulation):
  - pressure P,
  - saturations $S^{\beta}, \quad \beta \in \mathcal{P}^{\mathbf{f}}$,
  - solid porosity $\phi^{\mathbf{s}}$,
  - molar fractions $C_e, \quad e \in \mathcal{E}^{\mathbf{f}}$,
  - molar concentrations $n_e, \quad e \in \mathcal{E}^{\mathbf{s}}$.

Remark

Here, we assume that all phases are present!

Discretization

- Finite volume with TPFA and upwind scheme,

Discretized conservations of total primary species

for $e \in \mathcal{E}^{\mathrm{pr}}$,

$$\sum_{e' \in \mathcal{E}} \chi_K(e') E_{e,e'} |K| \left(n_{e',K} - n_{e',K}^{n-1}\right) + \Delta t^n \sum_{e' \in \mathcal{E}^{\mathrm{f}}} \sum_{\sigma = K|L \in \mathcal{F}_K \cap \mathcal{F}_h} \chi_{K_\sigma^{\alpha(e')}}(e') E_{e,e'} \left(\zeta^{\alpha(e')} C_{e'} \eta^{\alpha(e')}\right)_{K_\sigma^{\alpha(e')}} V_{KL}^{\alpha(e')} = 0,$$

where

- $\mathcal{Q}_K = (\mathcal{Q}_K^{\mathrm{f}}, \mathcal{Q}_K^{\mathrm{s}})$: set of present fluid/solid phases in K,
- $\chi_K(e) := 1_{\mathcal{Q}_K}(\alpha(e))$.

Discretization

- Finite volume with TPFA and upwind scheme,

Discretized conservations of total primary species

for $e \in \mathcal{E}^{\mathrm{pr}}$,

$$\sum_{e' \in \mathcal{E}} \chi_K(e') E_{e,e'} |K| \left(n_{e',K} - n_{e',K}^{n-1}\right) + \Delta t^n \sum_{e' \in \mathcal{E}^{\mathrm{f}}} \sum_{\sigma = K|L \in \mathcal{F}_K \cap \mathcal{F}_h} \chi_{K_\sigma^{\alpha(e')}}(e') E_{e,e'} \left(\zeta^{\alpha(e')} C_{e'} \eta^{\alpha(e')}\right)_{K_\sigma^{\alpha(e')}} V_{KL}^{\alpha(e')} = 0,$$

where

- $\mathcal{Q}_K = (\mathcal{Q}_K^{\mathrm{f}}, \mathcal{Q}_K^{\mathrm{s}})$: set of present fluid/solid phases in K,
- $\chi_K(e) := 1_{\mathcal{Q}_K}(\alpha(e))$.

Problem

Singularity issue if a primary species disappears.

Discretization

- Additional concentration unknowns chosen based on the rank deficiency of the formula matrix restricted to the present species:

$$\widetilde{n}_{e,K}, \quad e \in \widetilde{\mathcal{E}}_{\mathcal{Q}_K},$$

Discretization

- Additional concentration unknowns chosen based on the rank deficiency of the formula matrix restricted to the present species:

$$\widetilde{n}_{e,K}, \quad e \in \widetilde{\mathcal{E}}_{\mathcal{Q}_K},$$

Discretized conservations of total primary species

for $e \in \mathcal{E}^{\mathsf{pr}}$,

$$1_{\widetilde{\mathcal{E}}_{\mathcal{Q}_K}}(e)|K|\ \widetilde{n}_{e,K} + \sum_{e' \in \mathcal{E}} \chi_K(e') E_{e,e'} |K|\ (n_{e',K} - n_{e',K}^{n-1}) + \Delta t^n \sum_{e' \in \mathcal{E}^{\mathsf{f}}} \sum_{\sigma = K|L \in \mathcal{F}_K \cap \mathcal{F}_h} \chi_{K_\sigma^{\alpha(e')}}(e') E_{e,e'} \left(\zeta^{\alpha(e')} C_{e'} \eta^{\alpha(e')} \right)_{K_\sigma^{\alpha(e')}} V_{KL}^{\alpha(e')} = 0.$$

Discretization

- Additional concentration unknowns chosen based on the rank deficiency of the formula matrix restricted to the present species:

$$\widetilde{n}_{e,K}, \quad e \in \widetilde{\mathcal{E}}_{\mathcal{Q}_K},$$

Discretized conservations of total primary species

for $e \in \mathcal{E}^{\mathrm{pr}}$,

$$1_{\widetilde{\mathcal{E}}_{\mathcal{Q}_K}}(e)|K|\ \widetilde{n}_{e,K} + \sum_{e' \in \mathcal{E}} \chi_K(e') E_{e,e'} |K|\ (n_{e',K} - n_{e',K}^{n-1}) + \Delta t^n \sum_{e' \in \mathcal{E}^{\mathbf{f}}} \sum_{\sigma = K|L \in \mathcal{F}_K \cap \mathcal{F}_h} \chi_{K_\sigma^{\alpha(e')}}(e') E_{e,e'} \left(\zeta^{\alpha(e')} C_{e'} \eta^{\alpha(e')}\right)_{K_\sigma^{\alpha(e')}} V_{KL}^{\alpha(e')} = 0.$$

Remarks

- Regularize the Jacobian matrix,
- Track incoming flux from surrounding cells (phases reappearance).

Phase appearance and disappearance

Phase removal

- Fluid phase β disappears if $S^\beta < 0$.
- Mineral phase m disappears if $n_m < 0$.

Phase appearance and disappearance

Phase removal

- Fluid phase β disappears if $S^\beta < 0$.
- Mineral phase m disappears if $n_m < 0$.

Phase appearance with liquid phase

- A mineral phase appears when its solubility product exceeds equilibrium.
- A gas phase appears if

$$\widetilde{n}_e > 0$$

for some gas species, or if

$$\sum_e \widetilde{C}_e > 1.$$

Phase appearance and disappearance

Phase removal

- Fluid phase β disappears if $S^\beta < 0$.
- Mineral phase m disappears if $n_m < 0$.

Phase appearance with liquid phase

- A mineral phase appears when its solubility product exceeds equilibrium.
- A gas phase appears if

$$\widetilde{n}_e > 0$$

for some gas species, or if

$$\sum_e \widetilde{C}_e > 1.$$

Without liquid phase

A multiphase flash calculation is performed at fixed total composition.

Organization

Settings

- Primary species (4):

$$\mathcal{E}^{\mathrm{pr}} = \{H_2O^\ell, CO_2^\ell, H^+, Ca^{2+}\},$$

- Reactions (6):

$$\begin{aligned}
HCO_3^- &\leftrightarrows H_2O^\ell + CO_2^\ell - H^+, && \text{(equilibrium aq-aq)}\\
OH^- &\leftrightarrows H_2O^\ell - H^+, && \text{(equilibrium aq-aq)}\\
CO_3^{2-} &\leftrightarrows H_2O^\ell + CO_2^\ell - 2H^+, && \text{(equilibrium aq-aq)}\\
H_2O^g &\leftrightarrows H_2O^\ell, && \text{(phase change)}\\
CO_2^g &\leftrightarrows CO_2^\ell, && \text{(phase change)}\\
CaCO_3 &\leftrightarrows Ca^{2+} + H_2O^\ell + CO_2^\ell - 2H^+, && \text{(kinetic min-aq)}
\end{aligned}$$

- Phases: $\mathcal{P} = \{\ell, g, m_{CaCO_3}\}$,

Additional unknowns (CO_2 test case)

$$E := \left(\begin{array}{cccc|cccccc} H_2O^\ell & CO_2^\ell & H^+ & Ca^{2+} & HCO_3^- & OH^- & CO_3^{2-} & H_2O^g & CO_2^g & CaCO_3 & \\ 1 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & 1 & H_2O^\ell \\ 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 1 & CO_2^\ell \\ 0 & 0 & 1 & 0 & -1 & -1 & -2 & 0 & 0 & -2 & H^+ \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & Ca^{2+} \end{array}\right).$$

Additional unknowns (CO_2 test case)

$$E := \begin{array}{c} \begin{array}{cccc|cccccc} H_2O^\ell & CO_2^\ell & H^+ & Ca^{2+} & HCO_3^- & OH^- & CO_3^{2-} & H_2O^g & CO_2^g & CaCO_3 \end{array} \\ \left(\begin{array}{cccc|cccccc} 1 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & 1 \\ 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 & -1 & -1 & -2 & 0 & 0 & -2 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \end{array}\right) \end{array} \begin{array}{c} H_2O^\ell \\ CO_2^\ell \\ H^+ \\ Ca^{2+} \end{array}.$$

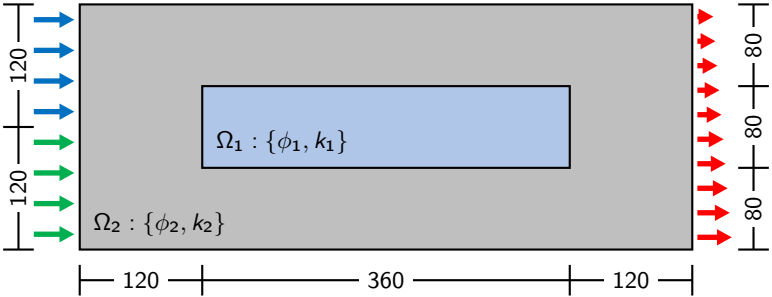
$$E_Q = \begin{array}{c} \begin{array}{cc} H_2O^g & CO_2^g \end{array} \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \end{array}, \text{ if } Q = \{g\}.$$

$$E_Q = \begin{array}{c} \begin{array}{ccc} H_2O^g & CO_2^g & CaCO_3 \end{array} \\ \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 0 & 0 & -2 \\ 0 & 0 & 1 \end{pmatrix} \end{array}, \text{ if } Q = \{g, m_{CaCO_3}\}.$$

- Rank: 2,
- Two additional unknowns: $\widetilde{n}_{H^+}$ and $\widetilde{n}_{Ca^{2+}}$.

- Rank: 3,
- One additional unknown: $\widetilde{n}_{H^+}$ (or $\widetilde{n}_{Ca^{2+}}$).

Settings



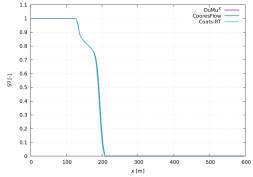
Gas stream (pure CO_2^g): Q_{gas} [m^3/day]

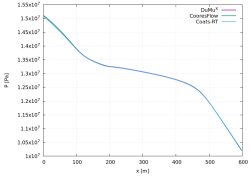
Water stream (pure H_2O^ℓ): Q_{wat} [m^3/day]

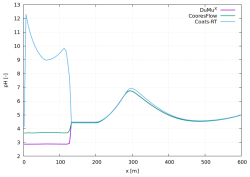
Outflow (hydrostatic pressure): p_{out} [bar]

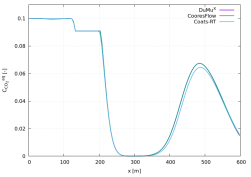
Results

Code team	TS (failed)	NI	LI / NI	F (failed)	CPU	Architecture
DuMu^X	17571 (2937)	3.45	8.37	-	66124	Intel i7-8565U @1.8 GHz
CooresFlow	2008 (0)	4.1	not available	-	10224	Intel Xeon E5-1620 v3 @3.5 GHz
Coats-RT	2032 (8)	5.2	11.76	206939 (0)	6361	Intel Core Ultra 7 255H @2.0 GHz









Settings

- Primary species (7):

$$\mathcal{E}^{\text{pr}} := \{H_2S^\ell, H_2^\ell, CO_2^\ell, H_2O, H^+, Ca^{2+}, Na^+\}.$$

- Reactions (9):

$$\begin{aligned}
SO_4^{2-} &\leftrightarrows H_2S^\ell - 4H_2^\ell + 4H_2O - 2H^+, && \text{(kinetic aq-aq)}\\
HS^- &\leftrightarrows H_2S^\ell - H^+, && \text{(equilibrium aq-aq)}\\
OH^- &\leftrightarrows H_2O - H^+, && \text{(equilibrium aq-aq)}\\
HCO_3^- &\leftrightarrows CO_2^\ell - H^+ + H_2O, && \text{(equilibrium aq-aq)}\\
CO_3^{2-} &\leftrightarrows CO_2^\ell - 2H^+ + H_2O, && \text{(equilibrium aq-aq)}\\
H_2S^g &\leftrightarrows H_2S^\ell, && \text{(phase change)}\\
H_2^g &\leftrightarrows H_2^\ell, && \text{(phase change)}\\
CO_2^g &\leftrightarrows CO_2^\ell, && \text{(phase change)}\\
CaCO_3 &\leftrightarrows Ca^{2+} + CO_2^\ell - 2H^+ + H_2O, && \text{(equilibrium min-aq)}
\end{aligned}$$

- Phases: $\mathcal{P} = \{\ell, g, m_{CaCO_3}\}$.

Settings

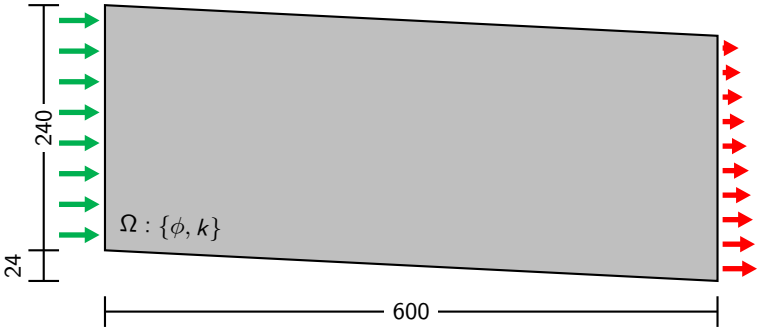


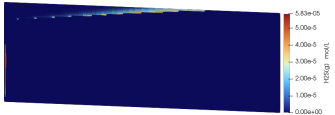
Figure: Radial geometry.

Results

(a) H_2^g at $t = 500$ days

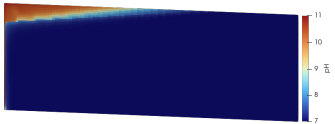
(b) H_2^g at $t = 1000$ days

(c) H_2S^g at $t = 500$ days



(d) H_2S^g at $t = 1000$ days

(e) pH at $t = 500$ days



(f) pH at $t = 1000$ days

Conclusion and perspectives

Conclusion

- Fully implicit multiphase reactive transport model based on Morel's and Coats' formulations.
- Robust handling of phase appearance/disappearance, including the aqueous phase.
- Validate the method and the implementation on the CO_2 benchmark.
- Application to a 2D axisymmetric hydrogen injection scenario.

Future work

- Clay-fluid reactions for pH buffering.
- Injection and production well models.

Thank you for your attention!

Globally Implicit Approach

- At each time step n, the nonlinear system is solved using Newton's method.
- Adaptive time stepping: If Newton converges,

$$\Delta t^{n+1} = \min\{1.1\,\Delta t^n, \Delta t_{\max}\}.$$

  If Newton fails, the time step is halved and recomputed.
- At each Newton iteration:
  - assembly of the Jacobian and residual,
  - relaxed Newton update,
  - weighted ℓ^∞ norm residual based on pressure, saturations, fluid compositions and mineral concentrations.
- Convergence criteria:

$$\|R\|_\infty < 10^{-7} \qquad \text{or} \qquad \|\delta U\|_\infty < 10^{-10}.$$

- Linear systems are solved using CPR-AMG. Convergence is reached when

$$\frac{\|r_k\|_2}{\|r_0\|_2} < 10^{-7}.$$

Settings (H_2^g)

- Monod-type law:

$$T_{SO_4^{2-}} = -v_{max} \frac{10^{-3}\zeta^\ell C_{SO_4^{2-}}}{10^{-3}\zeta^\ell C_{SO_4^{2-}} + K_{SO_4^{2-}}} \frac{10^{-3}\zeta^\ell C_{H_2^\ell}}{10^{-3}\zeta^\ell C_{H_2^\ell} + K_{H_2^\ell}},$$

with

  - $v_{max} = 1.45 \times 10^{-5}\ \mathrm{mol \cdot L^{-1} \cdot year^{-1}}$,
  - $K_{SO_4^{2-}} = 10^{-4}\ \mathrm{mol \cdot L^{-1}}$, and $K_{H_2^\ell} = \varepsilon\ \mathrm{mol \cdot L^{-1}}$.

- Additional unknowns:

$$\widetilde{\mathcal{E}}_Q = \begin{cases} \{H_2O, H^+, Ca^{2+}, Na^+\} & \text{if } Q^s = \emptyset \text{ and } Q^f = \{g\}, \\ \{H_2O, H^+, Na^+\} & \text{if } Q^s = \{m_{CaCO_3}\} \text{ and } Q^f = \{g\}. \end{cases}$$

Discretization

- $\mathcal{M}_h$: Conforming polytopal mesh of Ω, with cell volumes $|K|$,
- $\mathcal{F}_h$: Set of interior faces and $\mathcal{F}_K$ the set of faces of cell K,
- $\sigma = K|L$: Interior face shared by two neighboring cells,
- Time discretization:

$$0 = t^0 < t^1 < \cdots < t^n < \cdots < t^m = T_{\text{end}}, \qquad \Delta t^n = t^n - t^{n-1}.$$

Discretization

- The Darcy flux of phase β across $\sigma = K|L$ is approximated by

$$V_{KL}^{\beta} \approx \int_{\sigma} -\mathbb{K}\left(\nabla P + \rho^{\beta} \mathrm{g}\right) \cdot \mathrm{n}_{KL},$$

  with the conservation property $V_{KL}^{\beta} + V_{LK}^{\beta} = 0$,

- Mobility terms $\zeta^{\beta} C_e \eta^{\beta}$ are evaluated by phase-based upwinding:

$$\left(\zeta^{\beta} C_e \eta^{\beta}\right)_{K_{\sigma}^{\beta}}, \qquad K_{\sigma}^{\beta} = \begin{cases} K, & V_{KL}^{\beta} \geq 0, \\ L, & V_{KL}^{\beta} < 0. \end{cases}$$