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

Thomas Jacumin, Roland Masson, Laurent Jeannin, and Arthur Dartois
thomas.jacumin@inria.fr
Inria, Université Côte d'Azur and Storengy

▸ Physical Quantities

Symbol	Description	Unit
S^α	Saturation of phase α	[-]
η^α	Mobility of phase α	[$\mathrm{Pa}^{-1}\mathrm{s}^{-1}$]
ζ^α	Molar density of phase α	[$\mathrm{mol/m}^3$]
ϕ	Volume fraction of fluid phases (porosity)	[-]
C_e^α	Mole fraction of chemical species e in phase α	[-]
n_e^α	Molar concentration of chemical species e in phase α ($n_e^\alpha = \phi\zeta^\alpha S^\alpha C_e^\alpha$)	[$\mathrm{mol/m}^3$]
n_m^s	Molar concentration of mineral m	[$\mathrm{mol/m}^3$]
ϕ_s	Volume fraction of reactive rock	[-]
$1-\phi_T$	Volume fraction of non-reactive rock	[-]
ζ_m	Molar density of mineral m	[$\mathrm{mol/m}^3$]

▸ Coats Formulation

We denote:

- $\mathcal{E}$ the set of chemical species, $\mathcal{E}^{\ell g}$ the set of chemical species in both liquid and gazeous phase, $\mathcal{E}^{gh}$ the set of chemical species in gazeous phase only, $\mathcal{E}^{\ell h}$ the set of chemical species in liquid phase only,
- $\mathcal{E}^{pr}$ the set of primary species (Morel formalism),
- $\alpha(e)$ the phase of $e \in \mathcal{E}$,
- $\mathcal{E}^{\alpha,pr} = \mathcal{E}^{pr} \cap \mathcal{E}^\alpha$, the primary species in phase $\alpha \in \{\ell, g\}$,
- $\mathcal{E}^{\alpha,sec} = \mathcal{E}^\alpha \setminus \mathcal{E}^{\alpha,pr}$ the secondary species, $\alpha \in \{\ell, g\}$,
- $\widetilde{\mathcal{E}}^\ell_{Q^s} \subset \mathcal{E}^{pr} \cap \mathcal{E}^{\ell h}$ the elements that must be added to the set of unknowns in order to make the system non-singular in the absence of the liquid phase.

We define:

- the formula (stoichiometric) matrix $E = (E_{i,e})_{i\in\mathcal{E}^{pr},\, e\in\mathcal{E}}$,
- the set of present phases $Q = (Q^f, Q^s)$,
- the subset of primary species only "present" in absent phases $\widetilde{\mathcal{E}}_Q \subset \mathcal{E}^{pr}$,

$$\widetilde{\mathcal{E}}_Q = \begin{cases} \mathcal{E}^{gh} & \text{if } Q^f = \{\ell\}, \\ \widetilde{\mathcal{E}}^\ell_{Q^s} & \text{if } Q^f = \{g\}, \end{cases}$$

- the additional unknowns: $(\widetilde{n}_e)_{e\in\widetilde{\mathcal{E}}_Q}$ (in order to make the system non-singular and track phase appearance).

System of equations

For $e \in \mathcal{E}^{pr}$,

$$\chi_{\alpha(e)\in Q^f}\partial_t n_e^{\alpha(e)} + \chi_{e\in\widetilde{\mathcal{E}}_Q}\widetilde{n}_e + \sum_{\alpha\in Q^f}\sum_{e'\in\mathcal{E}^{\alpha,sec}} E_{e,e'}\partial_t n_{e'}^\alpha + \sum_{m\in Q^s} E_{e,m}\partial_t n_m^s + \chi_{\alpha(e)\in Q^f}\mathcal{L}^{\alpha(e)}(C_e^{\alpha(e)}\zeta^{\alpha(e)}) + \sum_{\alpha\in Q^f}\sum_{e'\in\mathcal{E}^{\alpha,sec}} E_{e,e'}\mathcal{L}^\alpha(\zeta^\alpha C_{e'}^\alpha) = 0,$$

to which are added:

- the ℓ–g equilibrium laws if both fluid phases are present,
- the mass action laws for homogeneous reactions in the aqueous phase if the aqueous phase is present,
- one mass action law for each mineral $m \in Q^s$,
- four closure equations on S^α, C^α and ϕ_s.

▸ Fully Implicit Scheme

Time discretization:

- implicit Euler scheme,
- adaptive time stepping.

Space discretization:

- cell-centered Finite Volume (FV) scheme,
- $K \in \mathcal{M}_h$ the cells with volume $|K|$,
- $\sigma = K|L$ the faces shared by cells K and L,
- V_{KL}^α denotes the Two-Point Flux Approximation (TPFA) of Darcy fluxes (without mobility),
- K_σ^α the upstream cell associated with the face σ and the phase α w.r.t. the sign of V_{KL}^α.

Unknowns for each $K \in \mathcal{M}_h$ which depend on the set of present phases $Q_K = (Q_K^f, Q_K^s)$ in K:

$$p_K, S_K^\ell, S_K^g, \phi_{s,K}, (C_{e,K}^\alpha)_{e\in\mathcal{E}^\alpha,\, \alpha\in Q_K^f}, (n_{m,K}^s)_{m\in Q_K^s}, (\widetilde{n}_{e,K})_{e\in\widetilde{\mathcal{E}}_{Q_K}}.$$

System of equations

For each cell $K \in \mathcal{M}_h$ and for each primary species $e \in \mathcal{E}^{pr}$:

$$\chi_{\alpha(e)\in Q_K^f}|K|\partial_t n_{e,K}^{\alpha(e)} + \chi_{e\in\widetilde{\mathcal{E}}_{Q_K}}|K|\partial_t\widetilde{n}_{e,K} + \sum_{\alpha\in Q_K^f}\sum_{e'\in\mathcal{E}^{\alpha,sec}} E_{e,e'}|K|\partial_t n_{e',K}^\alpha + \sum_{m\in Q_K^s} E_{e,m}|K|\partial_t n_{m,K}^s + \sum_{\sigma=K|L}\chi_{\alpha(e)\in Q^f_{K_\sigma^{\alpha(e)}}}(C_e^{\alpha(e)}\zeta^{\alpha(e)}\eta^{\alpha(e)})_{K_\sigma^{\alpha(e)}}V_{KL}^{\alpha(e)} + \sum_{\sigma=K|L}\sum_{\alpha\in Q^f_{K_\sigma^\alpha}}\sum_{e'\in\mathcal{E}^{\alpha,sec}} E_{e,e'}(\zeta^\alpha C_{e'}^\alpha\eta^\alpha)_{K_\sigma^\alpha}V_{KL}^\alpha = 0.$$

▸ Phase Appearance and Disappearance

The set of present phases Q is updated at each Newton iteration.

- Disappearance:
  - Fluid phase: if its saturation after the Newton update is negative,
  - Mineral phase m: if $n_m^s < 0$.
- Appearance (liquid present):
  - Absent mineral phase: if its solubility product exceeds the equilibrium constant,
  - Gas phase: if $\widetilde{n}_e^g > 0$ for some $e \in \mathcal{E}^{gh}$ or if $\sum_{e\in\mathcal{E}^{\ell g}} C_e^g > 1$, where the C_e^g are the mole fractions at equilibrium with the liquid phase.
- Appearance (liquid absent):
  - Multiphase (negative) flash at fixed z^T: if the mole fraction of the liquid phase is positive.

▸ CO_2 Benchmark

A choice of primary species:

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

Reactive system in canonical (Morel) form:

$$\begin{aligned}
H_2O^{(g)} &\leftrightarrows H_2O^{(\ell)} && \text{(phase change)}\\
CO_2^{(g)} &\leftrightarrows CO_2^{(\ell)} && \text{(phase change)}\\
OH^- &\leftrightarrows H_2O^{(\ell)} - H^+ && \text{(aqueous–aqueous reaction)}\\
HCO_3^- &\leftrightarrows H_2O^{(\ell)} + CO_2^{(\ell)} - H^+ && \text{(aqueous–aqueous reaction)}\\
CO_3^{2-} &\leftrightarrows H_2O^{(\ell)} + CO_2^{(\ell)} - 2H^+ && \text{(aqueous–aqueous reaction)}\\
CaCO_3 &\leftrightarrows Ca^{2+} + H_2O^{(\ell)} + CO_2^{(\ell)} - 2H^+ && \text{(aqueous–mineral reaction)}
\end{aligned}$$

Thus,

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

Liquid phase disappearance:

$$\widetilde{\mathcal{E}}^\ell_{Q^s} = \begin{cases} \{H^+, Ca^{2+}\} & \text{if } Q_s = \emptyset, \\ \{H^+\} & \text{if } Q_s = \{CaCO_3\}. \end{cases}$$

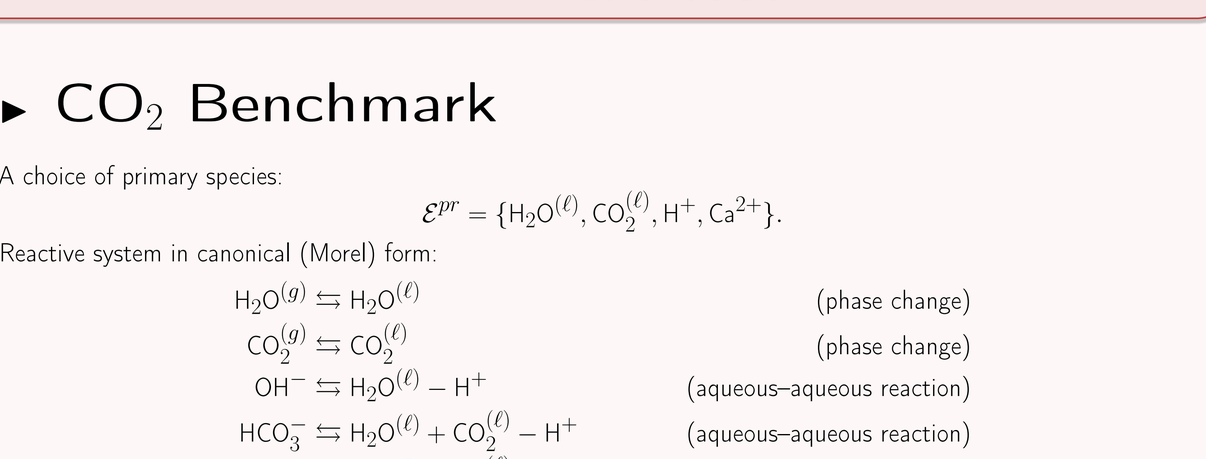

Figure: Numerical results for the carbon dioxide injection test case at times $t = 1$ day (column 1), $t = 500$ days (column 2), and $t = 1000$ days (column 3). The first row shows the gas saturation (1 = gas only, 0 = no gas), the second row presents the concentration of CO_2 in the gaseous phase, and the third row displays the water vapor concentration.

▸ Hydrogen Storage

A choice of primary species:

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

We add Na^+ to ensure electro-neutrality.
Reactive system in canonical (Morel) form:

$$\begin{aligned}
H_2S^g &\leftrightarrows H_2S^\ell && \text{(phase change)}\\
H_2^g &\leftrightarrows H_2^\ell && \text{(phase change)}\\
SO_4^{2-} &\leftrightarrows H_2S^\ell - 4H_2^\ell + 4H_2O - 2H^+ && \text{(aqueous–aqueous reaction)}\\
HS^- &\leftrightarrows H_2S^\ell - H^+ && \text{(aqueous–aqueous reaction)}\\
OH^- &\leftrightarrows H_2O - H^+ && \text{(aqueous–aqueous reaction)}
\end{aligned}$$

Thus,

$$E := \begin{array}{c} \begin{pmatrix} H_2S^\ell & H_2^\ell & H_2O & H^+ & SO_4^{2-} & HS^- & OH^- & H_2S^g & H_2^g \\ 1 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & -4 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 4 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -2 & -1 & -1 & 0 & 0 \end{pmatrix} \\ \end{array} \begin{array}{c} H_2S^\ell \\ H_2^\ell \\ H_2O \\ H^+ \end{array}$$

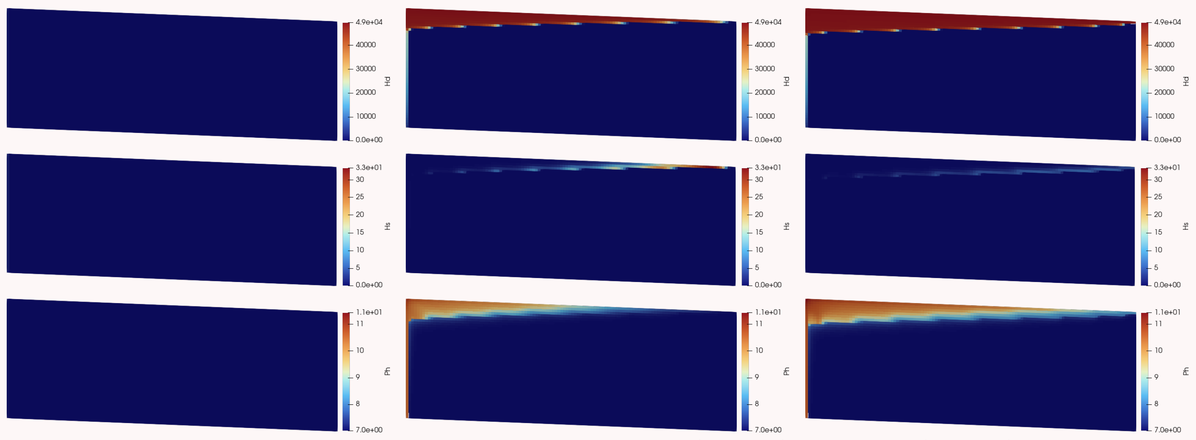

Figure: Numerical results for the hydrogen injection test case at times $t = 1$ day (column 1), $t = 500$ days (column 2), and $t = 1000$ days (column 3). The first row shows the H_2^g concentration, the second row presents the concentration of H_2S^g, and the third row displays the pH.

Bibliography

[1] Etienne Ahusborde et al. "A Benchmark Study on Reactive Two-Phase Flow in Porous Media: Part II - Results and Discussion". en. In: *Computational Geosciences* 28.3 (June 2024), pp. 395–412. DOI: 10.1007/s10596-024-10269-y.

[2] Keith H. Coats. "An Equation of State Compositional Model". en. In: *Society of Petroleum Engineers Journal* 20.05 (Oct. 1980), pp. 363–376. DOI: 10.2118/8284-PA.

[3] Robert Eymard et al. "Vertex-Centred Discretization of Multiphase Compositional Darcy Flows on General Meshes". en. In: *Computational Geosciences* 16.4 (Sept. 2012), pp. 987–1005. DOI: 10.1007/s10596-012-9299-x.

[4] Yaqing Fan, Louis J. Durlofsky, and Hamdi A. Tchelepi. "A Fully-Coupled Flow-Reactive-Transport Formulation Based on Element Conservation, with Application to CO2 Storage Simulations". en. In: *Advances in Water Resources* 42 (June 2012), pp. 47–61. DOI: 10.1016/j.advwatres.2012.03.012.

[5] Allan M. M. Leal et al. "An Overview of Computational Methods for Chemical Equilibrium and Kinetic Calculations for Geochemical and Reactive Transport Modeling". In: (May 2017). Medium: application/pdf. DOI: 10.3929/ETHZ-B-000191292.