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

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Objectives

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

Coats Formulation

- Primary species:
$$\mathcal{E}^{\text{pr}} = \{e_1^{\text{pr}}, \dots, e_M^{\text{pr}}\}.$$
- Secondary species:
$$\mathcal{E}^{\text{sec}} = \{e_1^{\text{sec}}, \dots, e_{N-M}^{\text{sec}}\},$$
such that
$$e^{\text{sec}} \leftrightarrows \sum_{e^{\text{pr}} \in \mathcal{E}^{\text{pr}}} E_{e^{\text{pr}},e^{\text{sec}}}\, e^{\text{pr}},$$
where
$$E := [E_{e^{\text{pr}},e}]_{e^{\text{pr}} \in \mathcal{E}^{\text{pr}}, e \in \mathcal{E}} \in \mathbb{R}^{\mathcal{E}^{\text{pr}} \times \mathcal{E}}.$$
- We set $\mathcal{E} := \mathcal{E}^{\text{pr}} \cup \mathcal{E}^{\text{sec}}$.
- To link a species $e \in \mathcal{E}$ to its phase $\beta \in \mathcal{P}$:
$$\alpha : e \in \mathcal{E} \mapsto \alpha(e) \in \mathcal{P}.$$

Symbol	Description	Unit
S^β	Saturation of phase β	$[-]$
η^β	Mobility of phase β	$[\text{Pa}^{-1} \cdot \text{s}^{-1}]$
ζ^β	Volumetric molar density of phase β	$[\text{mol} \cdot \text{m}^{-3}]$
ϕ	Volume fraction of fluid phases (porosity)	$[-]$
C_e	Mole fraction of chemical species e	$[-]$
n_e	Volumetric molar concentration	$[\text{mol} \cdot \text{m}^{-3}]$
ϕ^s	Volume fraction of reactive rock	$[-]$
$1 - \phi_T$	Volume fraction of non-reactive rock	$[-]$
$\mathbf{u}^\beta$	Velocity of phase β	$[\text{m} \cdot \text{s}^{-1}]$

Equations

- Primary Equations (Total molar conservation): for e^{pr} in $\mathcal{E}^{\text{pr}}$
$$\sum_{e \in \mathcal{E}} E_{e^{\text{pr}},e} \partial_t n_e + \sum_{e \in \mathcal{E}^{\text{f}}} E_{e^{\text{pr}},e}\, \text{div}\left(\zeta^{\alpha(e)} C_e \mathbf{u}^{\alpha(e)}\right) = 0.$$
- Secondary Equations:
  - Phase transition: Fugacity equality.
  - Chemical equilibrium: Law of mass action,
  - Kinetic reaction: Conservation equation with reaction rate T_e.
- Closure Equations:
  - Total volume conservation:
$$\underbrace{\phi}_{\text{fluid}} + \underbrace{\phi^{\text{s}} + 1 - \phi_{\text{T}}}_{\text{solid}} = 1,$$
  - Closure relations:
$$\sum_{\beta \in \mathcal{P}^{\text{f}}} S^\beta = 1, \quad \sum_{e \in \alpha^{-1}(\{\beta\})} C_e = 1, \ \forall \beta \in \mathcal{P}^{\text{f}} \text{ and } \phi^{\text{s}} = \sum_{m \in \mathcal{P}^{\text{s}}} \frac{n_m}{\zeta^m}.$$

Discretization

- Finite volume with TPFA and upwind scheme,
- $\mathcal{Q}_K = (\mathcal{Q}_K^{\text{f}}, \mathcal{Q}_K^{\text{s}})$: set of present fluid/solid phases in cell K,
- $\chi_K(e) := \mathbf{1}_{\mathcal{Q}_K}(\alpha(e))$.
- Additional concentration unknowns chosen based on the rank deficiency of the formula matrix restricted to the present species:
$$\widetilde{n}_{e,K}, \quad e \in \widetilde{\mathcal{E}}_{\mathcal{Q}_K},$$

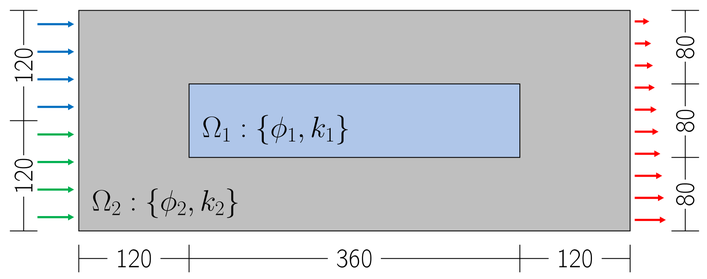
Discretized conservations of total primary species

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

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

- **Phase removal**
  - Fluid phase β: if $S^\beta < 0$.
  - Mineral phase m: if $n_m < 0$.
- **Phase appearance with liquid phase**
  - A mineral phase: if its solubility product exceeds equilibrium.
  - A gas phase: if
$$\widetilde{n}_e > 0$$
for any gas species e in $\widetilde{\mathcal{E}}_{\mathcal{Q}_K}$, or if
$$\sum_e \widetilde{C}_e > 1.$$
- **Without liquid phase**
  - A multiphase flash calculation is performed at fixed total composition.

▸ CO_2 Benchmark



→ Gas stream (pure $CO_2^{(g)}$): Q_{gas} [m^3/day]
→ Water stream (pure $H_2O^{(\ell)}$): Q_{wat} [m^3/day]
→ Outflow (hydrostatic pressure): p_{out} [bar]

Chemical System

- Primary species:
$$\mathcal{E}^{\text{pr}} = \{H_2O^{(\ell)}, CO_2^{(\ell)}, H^+, Ca^{2+}\},$$
- Secondary species:
$$\mathcal{E}^{\text{sec}} = \{HCO_3^-, OH^-, CO_3^{2-}, H_2O^{(g)}, CO_2^{(g)}, CaCO_3\}.$$
- Six reactions:
$$HCO_3^- \leftrightarrows H_2O^{(\ell)} + CO_2^{(\ell)} - H^+, \quad \text{(equilibrium aq-aq)}$$
$$OH^- \leftrightarrows H_2O^{(\ell)} - H^+, \quad \text{(equilibrium aq-aq)}$$
$$CO_3^{2-} \leftrightarrows H_2O^{(\ell)} + CO_2^{(\ell)} - 2H^+, \quad \text{(equilibrium aq-aq)}$$
$$H_2O^{(g)} \leftrightarrows H_2O^{(\ell)}, \quad \text{(phase change)}$$
$$CO_2^{(g)} \leftrightarrows CO_2^{(\ell)}, \quad \text{(phase change)}$$
$$CaCO_3 \leftrightarrows Ca^{2+} + H_2O^{(\ell)} + CO_2^{(\ell)} - 2H^+, \quad \text{(kinetic min-aq)}$$
- Phases:
$$\mathcal{P} = \{\ell, g, m_{CaCO_3}\}.$$
- Formula matrix:
$$\begin{array}{c} \\ H_2O^{(\ell)} \\ CO_2^{(\ell)} \\ H^+ \\ Ca^{2+} \end{array} \begin{array}{c} \begin{array}{cccc|cccccc} H_2O^{(\ell)} & CO_2^{(\ell)} & H^+ & Ca^{2+} & HCO_3^- & OH^- & CO_3^{2-} & H_2O^{(g)} & CO_2^{(g)} & CaCO_3 \end{array} \\ \left(\begin{array}{cccc|cccccc} 1 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & 1 \\ 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 & -1 & -1 & -2 & 0 & 0 & -2 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \end{array}\right) \end{array}.$$

Additional Unknowns ($\mathcal{Q}_K{}^{\text{f}} = \{g\}$)

- If $\mathcal{Q}_K{}^{\text{s}} = \emptyset$, then
$$E_{\mathcal{Q}_K} := \begin{array}{c} \begin{array}{cc} H_2O^{(g)} & CO_2^{(g)} \end{array} \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \end{array} \begin{array}{c} H_2O^{(\ell)} \\ CO_2^{(\ell)} \\ H^+ \\ Ca^{2+} \end{array},$$
→ two additional unknowns: $\widetilde{n}_{H^+}$ and $\widetilde{n}_{Ca^{2+}}$.
- If $\mathcal{Q}_K{}^{\text{s}} = \{m_{CaCO_3}\}$, then
$$E_{\mathcal{Q}_K} := \begin{array}{c} \begin{array}{ccc} H_2O^{(g)} & CO_2^{(g)} & CaCO_3 \end{array} \\ \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 0 & 0 & -2 \\ 0 & 0 & 1 \end{pmatrix} \end{array} \begin{array}{c} H_2O^{(\ell)} \\ CO_2^{(\ell)} \\ H^+ \\ Ca^{2+} \end{array},$$
→ one additional unknown: $\widetilde{n}_{H^+}$ (or $\widetilde{n}_{Ca^{2+}}$).
- To sum up:
$$\widetilde{\mathcal{E}}_{\mathcal{Q}_K} = \begin{cases} \{H^+, Ca^{2+}\} & \text{if } \mathcal{Q}_K{}^{\text{s}} = \emptyset \text{ and } \mathcal{Q}_K{}^{\text{f}} = \{g\}, \\ \{H^+\} & \text{if } \mathcal{Q}_K{}^{\text{s}} = \{m_{CaCO_3}\} \text{ and } \mathcal{Q}_K{}^{\text{f}} = \{g\}. \end{cases}$$

Numerical Results

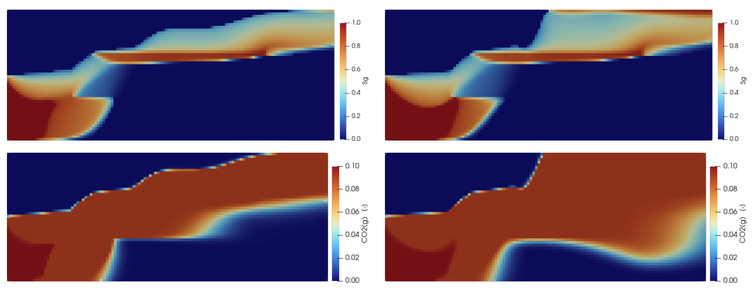
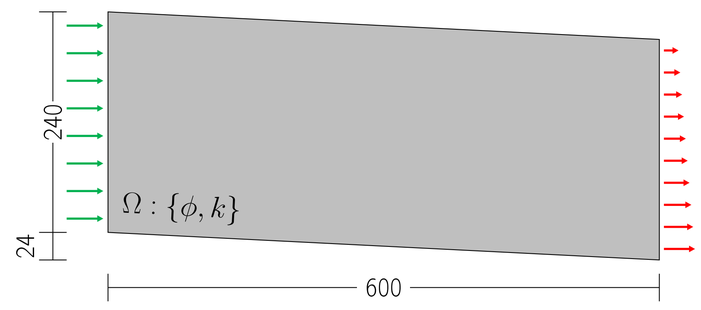


Figure: Numerical results for the carbon dioxide injection test case at times $t = 500$ days (column 1) and $t = 1000$ days (column 2). The first row shows the gas saturation (1 = gas only, 0 = no gas) and the second row presents the fraction of CO_2 in the gaseous phase.

▸ Hydrogen Storage



→ Gas stream (pure H_2^g): Q_{gas} [m^3/day]
→ Outflow (hydrostatic pressure): p_{out} [bar]

Chemical System

- Primary species:
$$\mathcal{E}^{\text{pr}} := \{H_2S^\ell, H_2^\ell, CO_2^{(\ell)}, H_2O, H^+, Ca^{2+}, Na^+\},$$
- Secondary species:
$$\mathcal{E}^{\text{sec}} = \{SO_4^{2-}, HS^-, OH^-, HCO_3^-, CO_3^{2-}, H_2S^g, H_2^g, CO_2^{(g)}, CaCO_3\}.$$
- Reactions:
$$SO_4^{2-} \leftrightarrows H_2S^\ell - 4H_2^\ell + 4H_2O - 2H^+, \quad \text{(kinetic aq-aq)}$$
$$HS^- \leftrightarrows H_2S^\ell - H^+, \quad \text{(equilibrium aq-aq)}$$
$$OH^- \leftrightarrows H_2O - H^+, \quad \text{(equilibrium aq-aq)}$$
$$HCO_3^- \leftrightarrows CO_2^{(\ell)} - H^+ + H_2O, \quad \text{(equilibrium aq-aq)}$$
$$CO_3^{2-} \leftrightarrows CO_2^{(\ell)} - 2H^+ + H_2O, \quad \text{(equilibrium aq-aq)}$$
$$H_2S^g \leftrightarrows H_2S^\ell, \quad \text{(phase change)}$$
$$H_2^g \leftrightarrows H_2^\ell, \quad \text{(phase change)}$$
$$CO_2^{(g)} \leftrightarrows CO_2^{(\ell)}, \quad \text{(phase change)}$$
$$CaCO_3 \leftrightarrows Ca^{2+} + CO_2^{(\ell)} - 2H^+ + H_2O, \quad \text{(equilibrium min-aq)}$$
- Phases:
$$\mathcal{P} = \{\ell, g, m_{CaCO_3}\}.$$
- Na^+ is added to ensure electro-neutrality.

Additional Unknowns

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

Numerical Results

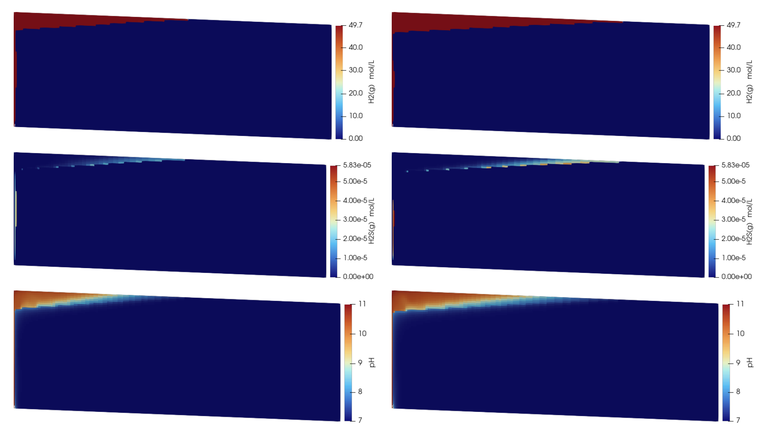


Figure: Numerical results for the hydrogen injection test case at times $t = 500$ days (column 1) and $t = 1000$ days (column 2). The first row shows the H_2^g molar concentration, the second row presents the molar concentration of H_2S^g, and the third row displays the pH.

Bibliography

[1] Etienne Ahusborde et al. "A Benchmark Study on Reactive Two-Phase Flow in Porous Media: Part II - Results and Discussion". In: Computational Geosciences 28.3 (June 2024), 395–412.

[2] Keith H. Coats. "An Equation of State Compositional Model". In: Society of Petroleum Engineers Journal 20.05 (Oct. 1980), 363–376.

[3] 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". In: Advances in Water Resources 42 (June 2012), 47–61.