Modeling of reactive flow and transport in the presence of a complex phase transition phenomena

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CO₂ sequestration

CO₂ plumes can migrate for long distance and trapped by:

- Structural trapping
- Residual trapping
- Dissolution trapping
- Mineralization
Example: Johansen formation

Model description:
- 100 x 100 x 11
- 84,600 active blocks
- Layer 6-10 - pay zone
- 5000 years of simulation
- 1 injector, constant rate
- 50 years of injection
- totally 453 Kt CO₂
- Different trapping mechanisms
Residual and dissolution trapping

Layer 6

Layer 8

Layer 10

$p$

$S_g$

$x_g$
Effect of enhanced dissolution
How important is scale resolution?
Modeling of CO$_2$ sequestration

- Brine composition controls
  - CO$_2$ dissolution
  - Phase properties
  - Precipitation and dissolution of solids
- Required an accurate coupling of phase behavior with precipitation/dissolution reactive dynamics
- Spatial scale resolution is important

Rigorous modeling framework is required!
Governing equations

\[
\frac{\partial}{\partial t} \left( \phi \sum_{p=1}^{n_p} x_{cp} \rho_p S_p \right) + \nabla \sum_{p=1}^{n_p} (x_{cp} \rho_p U_p + s_p J_{cp}) + \sum_{p=1}^{n_p} x_{cp} \rho_p q_p = \sum_{k=1}^{n_e} \nu_{ck} r_k
\]  

(1)

**Symbols:**
- $U_p$ – convective flux
- $\phi$ – porosity
- $S_p$ – phase saturation
- $x_{cp}$ – phase concentration
- $\rho_p$ – phase density
- $J_{cp}$ – diffusive flux
- $\nu_{ck}$ – stoichiometry coefficients
- $r_k$ – reaction mass rate
Thermodynamic equilibrium

\[ F_{cp} = f_{c1}(p, T, x_1) - f_{cp}(p, T, x_p) = 0 \]  \hspace{1cm} (2)
\[ c = 1, \ldots, n_c, \quad p = 2, \ldots, n_p \]

\[ K_{sp,i}(p, T, x) - Q_{sp}(x) = 0 \]  \hspace{1cm} (3)

- Natural variables formulation:
  - Nonlinear unknowns: \( p, T, S_p, x_{cp} \) \([n_c n_p + 1]\)
  - Solve conservation equations \(+ (2) + (3)\) fully coupled

- Molar variables formulation:
  - Nonlinear unknowns: \( p, T, z_c \) \([n_c + 1]\)
  - Solve \((2) + (3) + F_{c1} = z_c - \sum p v_p x_{cp} = 0\) on each iteration
  - Find derivatives using inverse theorem: \( \frac{dx}{dz} = \frac{dF}{dz} \left( \frac{dF}{dx} \right)^{-1} \)
Rearrangement of equations

Conservation of flowing & precipitated species:

\[ \frac{\partial a}{\partial t} + l + q = Vr \]

Annihilation matrix (depends on precipitating solids):

\[ \mathbf{E}[n_e \times n_c], n_e < n_c : \mathbf{E} \times \mathbf{V} = 0 \]

Modified conservation equations:

\[ \frac{\partial \mathbf{Ea}}{\partial t} + \mathbf{El} + \mathbf{Eq} = 0. \]
Nonlinear formulations with reactions

\( n_c \)- components, \( n_p \)- phases, \( n_k \)- kinetic and \( n_q \)- equilibrium reactions

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_c ) component balance ( n_c ) ( n_p ) ( n_k ) ( n_q )</td>
<td>( a_e + l_e + q_e = 0 ) ( a_c + l_c + q_c = V_r_c ) ( n_k ) kinetic reaction ( a_c + l_c + q_c = V_r_c )</td>
<td>( p ) ( S_p ) ( x_{cp} ) ( [n_e+n_k - n_p] )</td>
<td>( p ) ( z_c ) ( [n_e+n_k - 1] )</td>
<td>( p ) ( z_e ) ( [n_e+n_k - 1] )</td>
</tr>
<tr>
<td>Phase equilibrium &amp; constraints</td>
<td>Phase equilibrium &amp; constraints</td>
<td>Component-to-element constrain</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( \alpha_j \) \( \beta \) \( x_{cp} \) \( \nu_p \) \( z_c \)
Extension of natural formulation

Secondary equations in natural formulation:

\[ f_1(p, T, x_1) - f_p(p, T, x_p) = 0 \quad \text{Thermodynamic equilibrium} \]

\[ K_{sp,i}(p, T, x) - Q_{sp}(x) = 0 \quad \text{Chemical equilibrium} \]

<table>
<thead>
<tr>
<th>Phase\Component</th>
<th>H2O</th>
<th>CO2</th>
<th>Ca2+</th>
<th>CO3-</th>
<th>CaCO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Brine</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>2. Gas</td>
<td>x</td>
<td>x</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3. Solid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>x</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Status</th>
<th>Number of equations</th>
<th>Type of equations (constraints)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. 12 (conservation)</td>
<td>Eq. 6 (thermodynamic)</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>4</td>
</tr>
</tbody>
</table>
Variable substitution

Active variables depending on status:

<table>
<thead>
<tr>
<th>Status</th>
<th>$n_p$</th>
<th>$p$</th>
<th>$S_1$</th>
<th>$x_{21}$</th>
<th>$x_{31}$</th>
<th>$x_{41}$</th>
<th>$x_{22}$</th>
<th>$c_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>x</td>
<td>-</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>x</td>
<td>-</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
<td>x</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Annihilation matrix:

Status 1&2

$$E = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}$$

Status 3&4

$$E = \begin{bmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 1 \\
0 & 0 & 0 & 1 & 1
\end{bmatrix}$$
## GFLASH: A Cubic EOS Library

<table>
<thead>
<tr>
<th>Capability</th>
<th>Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation of State (EOS)</td>
<td>Soave-Redlich-Kwong(SRK) + volume translation</td>
</tr>
<tr>
<td></td>
<td>Peng-Robinson (PR) + volume translation</td>
</tr>
<tr>
<td></td>
<td>Predictive SRK (PSRK)</td>
</tr>
<tr>
<td></td>
<td>electrolyte Predictive SRK (ePSRK)</td>
</tr>
<tr>
<td></td>
<td>multi-Scale Gibbs-Helmholtz Constrained (GHC)</td>
</tr>
<tr>
<td>Fluid Phases Allowed</td>
<td>liquid, vapor, supercritical fluid; up to four</td>
</tr>
<tr>
<td>Aqueous Electrolytes</td>
<td>H⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, OH⁻, Cl⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻ plus others</td>
</tr>
<tr>
<td>Solid Molecular Salts</td>
<td>CaCO₃, MgCO₃, NaCl, KCl, CaSO₄, and others; any number of precipitates</td>
</tr>
<tr>
<td>Other Phases</td>
<td>hexagonal ice, gas hydrates</td>
</tr>
</tbody>
</table>
Gibbs-Helmholtz Constrained EOS

A radically new and predictive approach to cubic EOS

\[ p = \frac{RT}{V-b} - \frac{a(T, p)}{[V(V+b)]} \]

Three Simple Ideas

- estimate \( b \) from solid or glassy molar volume (\( b = 1/\rho^s \))
- use Gibbs-Helmholtz equation to constrain \( a(T, p) \)
- use Monte Carlo simulation to evaluate \( U^D \)

\[
a(T, p) = \left[ \frac{a(T_c, p_c)}{T_c} + \frac{bU^D}{(T_c\ln2)} + 2bR\ln T_c/\ln2 \right] T
\]

\[ - bU^D/\ln2 - [2bR/\ln2] T \ln T \]

A. Lucia et al. (2012)
Salt Deposition

Key Steps

- Equilibrium solubility products ($K_{sp}$)
  
  $K_{sp}$ computed from Gibbs free energy of formation, $\Delta G_{f}^{0}$, data adjusted for temperature and pressure using heat of formation $\Delta H_{f}^{0}$, data

- Ion solubility products ($Q_{sp}$)
  
  $Q_{sp}$ calculated directly from ion concentrations

- Testing for Deposition
  
  $Q_{sp} < K_{sp} \rightarrow$ under-saturated, no precipitation
  $Q_{sp} = K_{sp} \rightarrow$ saturated, no precipitation
  $Q_{sp} > K_{sp} \rightarrow$ super-saturated, precipitation

- Deposition test easily incorporated as constraints in reservoir model

A. Lucia et al. (2015)
CO$_2$-brine reactions

Carbonate reaction:

\[ \text{CO}_2 + 3\text{H}_2\text{O} \leftrightarrow 2\text{H}_3\text{O}^{+} + \text{CO}_3^{2-} \]

Precipitation/dissolution of minerals:

\[ \text{NaCl}(s) \leftrightarrow \text{Na}^{+}(aq) + \text{Cl}^{-}(aq) \]

\[ \text{Na}_2\text{CO}_3(s) \leftrightarrow 2\text{Na}^{+}(aq) + \text{CO}_3^{2-}(aq) \]

\[ \text{CaCl}_2(s) \leftrightarrow \text{Ca}^{2+}(aq) + \text{Cl}^{-}(aq) \]

\[ \text{CaCO}_3(s) \leftrightarrow \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \]
Case 1: precipitation/dissolution

CO2 injection in 2D homogeneous reservoir (50x50)

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Injection</th>
<th>Undersaturated</th>
<th>Initial</th>
</tr>
</thead>
<tbody>
<tr>
<td>p, bars, bars</td>
<td>240</td>
<td>-</td>
<td>220</td>
</tr>
<tr>
<td>T, K</td>
<td>350</td>
<td>-</td>
<td>350</td>
</tr>
<tr>
<td>$C_{NaCl}$, kmol/m$^3$</td>
<td>0</td>
<td>1.2</td>
<td>.05</td>
</tr>
<tr>
<td>$z$(CO$_2$), mol %</td>
<td>97.9997</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>$z$(H$_2$O), mol %</td>
<td>2.0000</td>
<td>99.43</td>
<td>80.06</td>
</tr>
<tr>
<td>$z$(Na$^+$), mol %</td>
<td>0.0002</td>
<td>0.20</td>
<td>9.83</td>
</tr>
<tr>
<td>$z$(Ca$^{2+}$), mol %</td>
<td>0.0000</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>$z$(Cl$^-$), mol %</td>
<td>0.0000</td>
<td>0.28</td>
<td>9.99</td>
</tr>
<tr>
<td>$z$(CO$_3^{2-}$), mol %</td>
<td>0.0002</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Initial and injection conditions
Case 1: simulation results
Case 2: transient CTZ

Boundary conditions & properties are similar to Elenius et al. (2015)

Initial and injection conditions

<table>
<thead>
<tr>
<th>Composition</th>
<th>Upper part CTZ</th>
<th>Lower part CTZ</th>
<th>Below the plum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z(\text{CO}_2)$, mol %</td>
<td>34.7254</td>
<td>1.3676</td>
<td>0.00</td>
</tr>
<tr>
<td>$z(\text{H}_2\text{O})$, mol %</td>
<td>65.2746</td>
<td>98.6324</td>
<td>99.98</td>
</tr>
<tr>
<td>$z(\text{Na}^+)$, mol %</td>
<td>0.0</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>$z(\text{Ca}^{2+})$, mol %</td>
<td>0.0</td>
<td>0.0</td>
<td>0.01</td>
</tr>
<tr>
<td>$z(\text{Cl}^-)$, mol %</td>
<td>0.0</td>
<td>0.0</td>
<td>0.01</td>
</tr>
<tr>
<td>$z(\text{CO}_3^{2-})$, mol %</td>
<td>0.0</td>
<td>0.0</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Case 2: simulation results
Case 3a: stagnant CTZ (normal)

\[ x_g \]

\[ x_g^{nr} \]

\[ \varphi \]

\[ C_m \]
Case 3b: stagnant CTZ (magnified)
Case 3c: stagnant CTZ (with NaCl)
Conclusion

• Simulation framework for modeling of CO2 sequestration is developed based on ADGPRS/GFLASH combined software.

• Rigorous phase behavior of CO$_2$-brine system in the presence of
  – Capillary transient zone
  – Different ions in brine
  – Precipitation and dissolution of minerals

• The precipitation and dissolution of minerals can affect the dynamic of dissolution trapping
  – Strongly depends on thermodynamic conditions and composition of brine
Acknowledgements

• SUPRI-B consortium
• The Petroleum Institute of Abu Dhabi
• Sara Farshidi
• Maria Elenius
Evaluating $U^D$ Using MC

Key Ideas
● Use internal energy of departure, $U^D$, as natural bridge between
  
  molecular $\leftarrow U^D \rightarrow$ bulk phase

● Use *a priori* pure component NTP Monte Carlo simulations to evaluate $U^D$
  
  need only be done once
  
  $U^D$ vs. T & p placed in look-up tables
  
  only practical approach for flash & other applications

General applicability: *just put relevant forces in $U^D* function

  CO$_2$ has quadrupole
  H$_2$O typically SPC or TIP4P-Ew models
  electrostatic for ions in solution (NaCl + H$_2$O)
Density: ePSRK vs. GHC

- **Density**: ePSRK vs. GHC
- **Experimental density (g/cm³)**
  - 0.80
  - 0.85
  - 0.90
  - 0.95
  - 1.00
  - 1.05
  - 1.10
- **Calculated density (g/cm³)**
  - 0.80
  - 0.85
  - 0.90
  - 0.95
  - 1.00
  - 1.05
  - 1.10
- **GHC** = filled symbols
- **ePSRK** = unfilled symbols
- **red** = NaCl
- **green** = KCl
- **black** = CaCl₂

**Graph Details**
- No. data points = 308
- Molality = [0.1 – 1 m]
- Temperature = [277 - 448 K]
- Pressure = [1 – 684 bar]
- AAD% error (ePSRK) = 4.53%
- AAD% error (GHC) = 1.05%
Convergence of onset time

Sensitivity of onset time of enhanced dissolution on vertical and horizontal resolution