Chemical Reaction Modeling in CO₂ Storage Simulation

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Outline

• Reactive transport modeling
• Overall-composition variable formulation
• Problem of water disappearance
• Porosity change modeling
• Simulation case results
• Future work
Reactive Transport Modeling in GPRS

- GPRS implementation (Fan, 2010): Applied to in-situ oil-shale upgrading and CO₂ sequestration in saline aquifers

- AD-GPRS developments:
  - Natural variable formulation
  - Deposition modeling
  - Overall-composition variable formulation
  - Modeling porosity change

Model Description

Diagram showing aqueous species, gas, rock, minerals, convection, CO₂, H₂O, phase equilibrium, chemical equilibrium, and kinetics.
Chemical Reaction in AD-GPRS

Fluid Species
\[
\frac{\partial M_i}{\partial t} + \nabla \cdot (\rho_j X_{ij} u_j) + q_{i,\text{well}} = \sum_{l=1}^{n_R} v_{i,l} r_l
\]

Minerals
\[
\frac{\partial M_j}{\partial t} = \sum_{l=1}^{n_R} v_{j,l} r_l
\]

\[
\frac{\partial M}{\partial t} + \nabla F + q_{\text{well}} = \mathbf{F}
\]

Phase equilibrium and phase constraints remain unchanged

Chemical Reaction Treatment

\( \mathbf{E} \): Equilibrium Rate Annihilation Matrix (ERA matrix)

\[
\mathbf{E} = \begin{pmatrix}
    a_{1,1} & \cdots & a_{1,n_s} \\
    \vdots & \ddots & \vdots \\
    a_{n_e,1} & \cdots & a_{n_e,n_s}
\end{pmatrix}^{\text{Elements}}
\]

\[
\mathbf{V} = \begin{pmatrix}
    v_{1,1} & \cdots & v_{1,n_r} \\
    \vdots & \ddots & \vdots \\
    v_{n_s,1} & \cdots & v_{n_s,n_r}
\end{pmatrix}^{\text{Species}}
\]

\[
\mathbf{E} \mathbf{V} = 0
\]

\[
\frac{\partial \mathbf{E} \mathbf{M}}{\partial t} + \nabla (\mathbf{F} \mathbf{E}) + \mathbf{E} q_{\text{well}} = \mathbf{E} \mathbf{F} \mathbf{r} = 0
\]

Element Balance

Fan et al., Advances in Water Resources, 2012
Species to Element Balance

\[ n_c = n_e + n_{rk} + n_{req} \]

\[ \frac{\partial M}{\partial t} + \nabla \cdot F + q_{well} = Vr \]

Overall-Composition Variable Formulation

\[ v_p = \frac{S_p \rho_p}{\sum_j S_j \rho_j} \]

\[ \rho_T = \sum_{j=1}^{n_p} S_j \rho_j = \left( \sum_{j=1}^{n_p} \frac{v_j}{\rho_j} \right)^{-1} \]

\[ z_c = \frac{\sum_j S_j \rho_j x_{cj}}{\sum_j S_j \rho_j} = \sum_{j=1}^{n_p} v_j x_{cj} \]

\[ S_p = v_p \rho_T / \rho_p \]
Overall-Composition Variable Formulation, FIM

In Each Newton iteration

1. Globally solve for primary variables \( x_p = \{P, T, z\} \)
   - Mass conservation equations

2. Solve local constraints for each individual block to update secondary unknowns \( x_s = \{x_{cp}, \nu_p\} \)
   - Phase equilibrium
   - Phase constraints

3. Update
   \[
   \frac{\partial x_s}{\partial x_p} = - \left( \frac{\partial R_s}{\partial x_s} \right)^{-1} \frac{\partial R_s}{\partial x_p}
   \]

Water Disappearance

- Some species exist only in the aqueous phase
- Such species must be tracked upon full disappearance of water
- Natural variable formulation suffers from near-singular/singular Jacobian at very low to zero water saturations
- Special treatment developed for natural variables, not needed for overall-composition variables
**Deposition Term for Aqueous Species**

\[
\frac{\partial M_i^F}{\partial t} + \nabla \cdot (\rho_w X_{iw} u_w) + q_{i,\text{well}} = \sum_{l=1}^{n_R} v_{il} r_l - r_i^D
\]

\[
\frac{\partial M_i^D}{\partial t} = r_i^D
\]

\[
r_i^D = c_i k_D \phi S_w \left(1 - \frac{I}{I_{\text{max}}} \right)
\]

**Definitions:**
- \(I\) : Ionic Strength
- \(c_i\) : molar fraction in deposited phase
- **F** : Fluid
- **D** : Deposited

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**Generalized Treatment of Solid Species**

\[
\frac{\partial M}{\partial t} + \nabla F + q_{\text{well}} = V r \\
M_c = \sum_{p}^{n_p} V_p \rho_p x_{cp}
\]

\[
V_p = \begin{cases} 
\phi_f S_p & 1 \leq p \leq n_p_{\text{fluid}} \\
\phi_{rs} S_p & n_p_{\text{fluid}} < p \leq n_p_{\text{fluid}} + n_p_{\text{solid}} 
\end{cases}
\]

- Fluid and reactive solid phase saturations defined wrt the corresponding porosity
- Time dependent porosity values
- Enhanced convergence

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Case 1

- 12 species: 9 aqueous species and 3 minerals
- 6 elements
- 6 reactions
  - 3 equilibrium reactions (homogeneous, aqueous)
  - 3 kinetic reactions (heterogeneous, mineral dissolution and precipitation)
- 2D, 100 grid blocks, injection and production wells at two corners, injecting pure CO$_2$ for 1 year

Pressure Profile, 200 days
Water Saturation Profile, 365 days

Case 2

- 12 species: 9 aqueous species and 3 minerals
- 6 elements
- 6 reactions
  - 3 equilibrium reactions (homogeneous, aqueous)
  - 3 kinetic reactions (heterogeneous, mineral dissolution and precipitation)
- 1D, 10 grid blocks, injection and production wells at the two ends, Injecting pure CO₂ for 290 days
High values of $k_0$ result in lack of convergence with natural variables.
Numerical Results

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Time Steps</th>
<th>Newton Iterations</th>
<th>Linear Solves</th>
<th>EoS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural ($k_D=10^{-4}$)</td>
<td>523</td>
<td>835</td>
<td>835</td>
<td>1182</td>
</tr>
<tr>
<td>Natural ($k_D=6\times10^{-3}$)</td>
<td>1226</td>
<td>3744</td>
<td>3744</td>
<td>1194</td>
</tr>
<tr>
<td>Overall-composition</td>
<td>553</td>
<td>1906</td>
<td>1906</td>
<td>50399</td>
</tr>
</tbody>
</table>

Case 4

- Same reaction system as before
- 1.5 km x 1.5 km x 8 m
- 15×15×4 (900) grid blocks
- Heterogeneous permeability field
- Injecting pure CO₂ for 49 years
- Employing overall-composition formulation
Case 4, Water Saturation Profile

After 49 years of injection

After 550 years

Case 4, Injection Well Block

Water disappearance/reappearance

Dissolved Mass of Ion1

Dissolved Mass of Ion2
Conclusions

- Implemented both natural and new overall-composition formulations in AD-GPRS
- Verified consistent solutions in cases with no aqueous-phase disappearance
- Illustrated behavior of overall-composition formulation for cases with aqueous phase disappearance
- Applied to 3D heterogeneous example

Future Work

- Investigate robustness, nonlinear behavior, and time stepping behavior of the overall-composition formulation; address the EOS cost
- Model realistic heterogeneous geological formations with more comprehensive reaction systems
- Apply sequential iteration for reaction modeling
- Model effects of geochemistry on formation properties
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