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Well – Reservoir – Cap rock INTERFACE

Modeling Cement CO$_2$-Alteration Mechanisms

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> Introduction
  • Objectives

> Modeling Approach
  • Considered Scenario
  • Modeling tool
  • Geometry and Gridding

> Results – Discussion
  • Illustration Parisian Basin
  • Cement Alteration Mechanisms

> Conclusions
  • Limitations and Perspectives
INTERFACE CO$_2$-Mechanisms - Objectives

> **Modeling** Geochemical interactions due to CO$_2$ injection at the Well-Reservoir-Caprock INTERFACE

- Characterization of reactions pathways
- Identification of new resulting minerals
- Chemical stability of cement-caprock interface
- Consequences in Porosity Evolution of the 3 zones
Injection Well cement alteration due to *acid brine only*
   - CO₂ Injection downhole $\Rightarrow$ Reservoir Brine acidification

Diffusion only of HCO₃⁻ and H⁺ (from CO₂aq), *no flow, no gas phase*
   - Cement degradation due to brine contact
   - Cement leaching due to caprock contact

Code Used: **ToughReact**
   - (finite volumes)

1m*2m-scale *axisymmetric* model
   - 2753 cells
   - $\Delta R = \Delta Z = 2$ mm at the interface
   - $\Delta t = 9$ sec for kinetic convergence reasons
Illustration: Parisian Basin context

*Initial state, equilibrated water at \( t=0 \) and at the 2 Limit Conditions border-Cells (\( LC_\infty \))*

<table>
<thead>
<tr>
<th>In-Situ Minerals</th>
<th>Formula</th>
<th>Composition (% Vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>( \text{CaCO}_3 )</td>
<td>Dogger 77.5% Callovo-Oxfordian clays 14.0%</td>
</tr>
<tr>
<td>Dolomite</td>
<td>( \text{CaMg(CO}_3\text{)}_2 )</td>
<td>Dogger 10.2% Callovo-Oxfordian clays 11.0%</td>
</tr>
<tr>
<td>Illite-Mg</td>
<td>( K_{0.85}\text{Mg}<em>{0.25}\text{Al}</em>{2.35}\text{Si}<em>{3.4}\text{O}</em>{10}(\text{OH})_2 )</td>
<td>Dogger 0.1% Callovo-Oxfordian clays 42.3%</td>
</tr>
<tr>
<td>Quartz</td>
<td>( \text{SiO}_2 )</td>
<td>Dogger - Callovo-Oxfordian clays 24.0%</td>
</tr>
<tr>
<td>Mg-Montmorillonite-Na</td>
<td>( \text{Na}<em>{0.33}\text{Mg}</em>{3}\text{Al}<em>{4.33}\text{Si}</em>{3.67}\text{O}_{10}(\text{OH})_2 )</td>
<td>Dogger 5.8% Callovo-Oxfordian clays 6.0%</td>
</tr>
<tr>
<td>Siderite</td>
<td>( \text{FeCO}_3 )</td>
<td>Dogger 4.1% Callovo-Oxfordian clays -</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2 )</td>
<td>Dogger 2.0% Callovo-Oxfordian clays -</td>
</tr>
<tr>
<td>Magnesite</td>
<td>( \text{MgCO}_3 )</td>
<td>Dogger 0.3% Callovo-Oxfordian clays -</td>
</tr>
<tr>
<td>Pyrite</td>
<td>( \text{FeS}_2 )</td>
<td>Dogger - Callovo-Oxfordian clays 1.0%</td>
</tr>
<tr>
<td>Chamosite</td>
<td>( \text{Fe}_5\text{Al}(\text{AlSi}<em>3)\text{O}</em>{10}(\text{OH})_8 )</td>
<td>Dogger - Callovo-Oxfordian clays 1.0%</td>
</tr>
<tr>
<td>Celestite</td>
<td>( \text{SrSO}_4 )</td>
<td>Dogger - Callovo-Oxfordian clays 0.7%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Class_G Cement</th>
<th>Formula</th>
<th>Composition (% Vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSH_1.6</td>
<td>( \text{Ca}<em>{1.8}\text{SiO}</em>{3.6}:2.58\text{H}_2\text{O} )</td>
<td>Dogger 38.1%</td>
</tr>
<tr>
<td>Portlandite</td>
<td>( \text{Ca(OH)}_2 )</td>
<td>Dogger 26.1%</td>
</tr>
<tr>
<td>Ettringite</td>
<td>( \text{Ca}_6\text{Al}_2(\text{SO}_4)<em>3(\text{OH})</em>{12}:26\text{H}_2\text{O} )</td>
<td>Dogger 13.8%</td>
</tr>
<tr>
<td>Katoite_SI1</td>
<td>( \text{Ca}_3\text{Al}_2\text{SiO}_4(\text{OH})_8 )</td>
<td>Dogger 10.5%</td>
</tr>
<tr>
<td>C3FH6</td>
<td>( \text{Ca}_3\text{Fe}<em>2(\text{OH})</em>{12} )</td>
<td>Dogger 5.5%</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>( \text{Mg}_4\text{Al}_2\text{O}_7:10\text{H}_2\text{O} )</td>
<td>Dogger 5.4%</td>
</tr>
<tr>
<td>Calcite</td>
<td>( \text{CaCO}_3 )</td>
<td>Dogger 0.6%</td>
</tr>
</tbody>
</table>

180 bar, 75°C, Salt = 25g/kg_w

Initial State

Clayay Cap Rock
\( \Phi = 14.4\% \)
\( \text{pH} = 7 \)

Class G Cement
\( \Phi = 28\% \)
\( \text{pH} = 11 \)

Dogger Reservoir
\( \Phi = 20\% \)
\( \text{pH} = 5 \)

Injection of Supercritical CO\(_2\)
Results: triple point cement alteration

- **Results:**
  - **Volume Fraction:**
    - **Time (d):** 0 to 50
  - **pH:** 4 to 12

- **Chemical Formulations:**
  - **Katoite:** Si_1 Ca_3 Al_2 SiO_4 (OH)_8
  - **Amorphous Silica:** SiO_2·0.5 H_2 O
  - **Ferrihydrite:** Fe(OH)_3
  - **CSH:** Ca_1.6 SiO_3.6·2.58 H_2 O, Ca_1.2 SiO_3.2·2.06 H_2 O, Ca_0.8 SiO_2·1.54 H_2 O
  - **Calcite:** CaCO_3
  - **Portlandite:** Ca(OH)_2
  - **Anhydrite:** CaSO_4
  - **Ettringite:** Ca_6 Al_2 (SO_4)_3 (OH)_{12·26} H_2 O
  - **Hydrotalcite:** Mg_4 Al_2 O_7·10 H_2 O
  - **Magnesite:** MgCO_3
  - **Ferrihydrite:** Fe(OH)_3
  - **C3FH6:** Ca_3 Fe_2 (OH)_{12}

- **Graphical Representation:**
  - **Graph:**
    - **Legend:**
      - Anhydrite
      - Ettringite
      - Boehmite
      - Strætlingite
      - KatoiteSi1
      - Hydrotalcite
      - Magnesite
      - Calcite
      - Portlandite
      - CSH_1.6
      - CSH_1.2
      - CSH_0.8
      - C3FH6
      - Ferrihydrite
  - **Key Points:**
    - **CSH-Decalcification**
    - **Calcite Increase Limited by HCO_3^- Diffusion**
    - **Anhydrite Increase Due to Neighbor Dissolution**
    - **Strætlingite Dissolves and Precipitates into CSH Gel and Boehmite**
    - **Al-Gel (Boehmite) AlO(OH)**

- **Additional Notes:**
  - **Increase Due to Neighbor Dissolution**
  - **Constant Calcite Increase Limited by HCO_3^- Diffusion**
  - **4 mm**
# Mechanisms Analysis - pH-Buffering and Volumes

## Simplified Reaction pathway:

- H⁺ and HCO₃⁻ Diffusion is the limiting factor for the global cement degradation process
- pH is buffered successively by different mineral phases
- New created phases should occupy more Volume (%), but
- Liberated ions also migrate outside the cement

<table>
<thead>
<tr>
<th>Element</th>
<th>pH</th>
<th>11 (initial)</th>
<th>10.7</th>
<th>10.5</th>
<th>10.4</th>
<th>10.3</th>
<th>10.2</th>
<th>9.7</th>
<th>9</th>
<th>7.7</th>
<th>5.5 (final)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Portlandite</td>
<td>Calcite (+11.71%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Si</td>
<td>CSH1.6</td>
<td>CSH1.2 (+2.41%)</td>
<td>CSH0.8 (+2.93%)</td>
<td>Silica_am, hydrated (+13.92%)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>C3FH6</td>
<td>Ferrihydrite (+16.19%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>Ettringite</td>
<td>(-66%)</td>
<td>Calcite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Katoite_Si1</td>
<td>Straetlingite (+93.27%)</td>
<td>Boehmite (+17.51%)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Mg</td>
<td>Hydrotalcite</td>
<td>Magnesite (+3.11%)</td>
<td></td>
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</tr>
</tbody>
</table>
System Evolution after 3 months (Ref Case)

Porosity collapses on cap rock side due to Calcite Precipitation

Calcite precipitation at the cement-clay interface due to Ca\textsuperscript{2+} migration

Calcite precipitation in the interface-destabilized cement

Portlandite dissolution in the interface-destabilized cement

Calcite CaCO\textsubscript{3}

Caprock

Acidified Reservoir
> **Determination of conceptual reaction pathway**

- Possibility to extract simplified scheme to use it in a Poro-Mechanical study (part of the Project)

> **Sensibility Analysis done on the cement tortuosity**

- Variation of the Damkholer Number (here diffusion/kinetics)

> **Limitations of the model:**

- Cement carbonation produces a lot of H\textsubscript{2}O (not considered in the mass/volume balance)

- Gas phase not considered (some experiments show a stronger effect of wet CO\textsubscript{2} than acidified brine)

- No heterogeneities