Targeted Mineral Carbonation to Enhance Wellbore Integrity

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University of Virginia

Flo Liang, Jeff Fitts and Catherine Peters
Princeton
the concept

Ma et al. 2013
underlying principle

a. $T > T_C$
MSiO$_3$ contained
Buoyancy flow

b. $T < T_C$
MSiO$_3$ released
Buoyancy flow

c. $T < T_C$
MCO$_3$ precipitated
Pores blocked, no flow
reaction kinetics vs. depth
early results

shale grains

shale grains + CO$_2$ + CaSiO$_3$

Tao, et al. (2016), Env. Eng. Sci., 10/16
benefit to the program

- Program goals
  - >99% storage permanence
  - predict storage capacity to +/-30%
  - improve storage efficiency.

- Project benefits: This project will produce new materials and a novel method to seal leakage pathways that transect the primary caprock seal and are associated with active injection, extraction or monitoring wells (e.g., wellbore casing and cement, and proximal caprock matrix)
project overview:
goals and objectives

- Project management and planning
- Coated silicate development, characterization and interaction in porous media
  - Fluid mixing and buoyancy experiments at formation T/P to optimize material properties
  - Evaluate the performance of coated mineral silicates in packed columns
  - Targeted carbonation in porous media flow
  - Targeted Carbonation of fractured wellbore-zone materials
- Imaging quantification of carbonation in pore networks and fractures
  - 3D imaging of targeted carbonation in porous media
  - 3D Imaging of targeted carbonation in fractured wellbore-zone materials
- Modeling Targeted Carbonation
  - Multiphase fluid mixing and flow modeling
  - Pore network/fracture reactive transport modeling
  - Forward modeling of mitigated wellbore integrity
### nanoparticle core

<table>
<thead>
<tr>
<th>mineral</th>
<th>reaction</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>basaltic glass</td>
<td>$\text{MgSiO}_3 + \text{CO}_2 = \text{MgCO}_3 + \text{SiO}_2$</td>
<td>80.0</td>
</tr>
<tr>
<td>olivine</td>
<td>$\text{MgSiO}_4 + 2\text{CO}_2 = 2\text{MgCO}_3 + 2\text{SiO}_2$</td>
<td>76.2</td>
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<tr>
<td>serpentine</td>
<td>$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 = 3\text{MgCO}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O}$</td>
<td>70.1</td>
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<tr>
<td>albite</td>
<td>$2\text{NaAlSi}_2\text{O}_8 + \text{CO}_2 = \text{Na}_2\text{CO}_3 + 6\text{SiO}_2 + \text{Al}_2\text{O}_3$</td>
<td>65.0</td>
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<tr>
<td>wollastonite</td>
<td>$\text{CaSiO}_3 + \text{CO}_2 = \text{CaCO}_3 + \text{SiO}_2$</td>
<td>54.7</td>
</tr>
<tr>
<td>talc</td>
<td>$\text{Mg}_3\text{Si}<em>4\text{O}</em>{10}(\text{OH})_2 + 3\text{CO}_2 = 3\text{MgCO}_3 + 4\text{SiO}_2 + \text{H}_2\text{O}$</td>
<td>51.4</td>
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<tr>
<td>anorthite</td>
<td>$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{CO}_2 = \text{CaCO}_3 + 2\text{SiO}_2 + \text{Al}_2\text{O}_3$</td>
<td>48.4</td>
</tr>
</tbody>
</table>
pseudowollastonite v wollastonite

diffusion limited results - kinetics and transport
Diffusion
complex reaction pathway

Unreacted Pseudowollastonite

Calcium Carbonate

O-Si-Ca-C Phase
raman scans of column

calcite

CSH
effects on permeability
1D geochemical modeling approach

Reactions

\[
\text{CaSiO}_3(\text{s}) + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{SiO}_2(\text{aq}) + \text{H}_2\text{O}
\]

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3(\text{s})
\]

\[
\text{SiO}_2(\text{aq}) \leftrightarrow \text{SiO}_2(\text{am})
\]

Transport

\[
\frac{\partial (C\phi)}{\partial t} = D \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial x} \phi \right)
\]

C = concentration
\phi = porosity
D = diffusion coefficient
CaCO$_3$ and SiO$_2$(am) precipitation concentrate near the opening of the glass bead column, leading to significant porosity decrease by 45 hrs of reaction.
• CO₂ diffuses into the column, lowering pH.

• The pH increases as CaSiO₃ dissolves.

• The pH throughout the column is largely controlled by CaSiO₃ dissolution.

• Differences in pH and CO₂ at the top vs. bottom of the column may lead to the formation of unaccounted solids in the model.
Differences exist in the density of the material filling the pore space at the top and bottom of the column.
xCT images of columns

Pre-reaction

Post-reaction
pore connectivity decrease

Pre-reaction

Post-reaction
pore network modeling
PDMAEMA polymer coating

- LCST: vary from 14 to 50°C in pure water (46°C in pH 7 buffer)
- Coating: surface-initiated atom transfer radical polymerization (SI-ATRP) on the surface of wollastonite nanoparticles
- pH responsive: phase transition and solving/collapsing under low pH condition.
fracture test-rig
accomplishments to date

- Discovered secondary mineral phase precipitates in the pseudowollastonite/CO$_2$ system
- Actively working to characterize the properties of these precipitates
- Observed dramatic permeability reductions when these minerals form and there could be synergies with CaCO$_3$
- Are characterizing these permeability reductions based on xCT analysis of pore structure
- Synthesized coatings with a LCST of 40$^\circ$C
- Developed 1D model of column dynamics to help understand the reaction kinetics and transport dynamics in our system
- Built an experimental test-rig to evaluate the performance of these cements in fractures
Lessons learned

- Psuedowollastonite reactivity very different than wollastonite
- The ability to precipitate something other than a carbonate appears to impart important properties from the standpoint of permeability reduction
- We have still not fully characterized the mechanism by which these precipitates form, but we are getting close
- Some CO₂ appears to be necessary but not too much
- Organic coating appear to work to limit reactivity, though not perfectly
- The resulting cements are effective at joining a fractured surface
synergy opportunities

– w/ other PIs in this program:
  – Experience with nanoparticles use in fractures and porous media
    – Functionalization
    – Transport
    – Modeling
– w/ other PIs in Basalt storage area:
  – Reaction of carbonates in high $P_{CO_2}$ environments where the interplay between dissolution and precipitation needs to be controlled
– Mineral silicates can be used to cement porous media and reduce its permeability when delivered as nanoparticles and exposed to a high $P_{\text{CO}_2}$ environment

– The unanticipated formation of silicate hydrates, driven by the presence of low partial pressures of CO$_2$, could be an important step to producing stable cements

– Significant drops in permeability have been observed and these precipitates are very resistant to re-dissolution in the presence of CO$_2$.

– Temperature sensitive coatings appear to be able to help us selectively deploy these materials at the desired depths
many thanks
Organization Chart

Project PI/PD
A. Clarens (UVa)

Project co-PI
J. Fitts (Princeton)
C. Peters (Princeton)

Imaging and quantification
Fitts

Coated Silicate Development and Testing
Clarens

Modeling
Fitts, Peters, and Clarens

Synthesis and characterization
Task 2.1
Clarens

Transport in tall column
Task 2.2
Clarens

Transport in short column
Task 2.3
Clarens

Transport in fractured media
Task 2.4
Fitts

3D Imaging in porous media
Task 3.1
Fitts

3D Imaging in fractured media
Task 3.2
Fitts

Multiphase flow modeling
Task 4.1
Clarens

Pore-network transport reactive modeling
Task 4.2
Fitts

Forward modeling of enhanced wellbore integrity
Task 4.3
Fitts
### SCHEDULE of TASKS and MILESTONES

<table>
<thead>
<tr>
<th>Task 1 – Project management and planning</th>
<th>PI</th>
<th>BP1 Jan 2016 to Dec 2016</th>
<th>BP2 Jan 2017 to Dec 2017</th>
<th>BP3 Jan 2018 to Dec 2018</th>
</tr>
</thead>
</table>

- **Task 1** – Project management and planning
  - PI: Clarens
  - Schedule:
    - Y1Q1: J F M A M J J A S O N D
    - Y2Q1: J F M A M J J A S O N D
    - Y3Q1: J F M A M J J A S O N D
    - Y4Q1: J F M A M J J A S O N D

### Task 2 – Coated silicate development, characterization and interactions in porous media (CLARENS)
- Subtask 2.1: Fluid mixing and buoyancy experiments at forward modeling
- Subtask 2.2: Optimize Calcium source transport to targeted flow pathways
- Subtask 2.3: Targeted carbonation in porous media flow experiments using materials optimized in SubTask 2.1
- Subtask 2.4: Targeted carbonation in fractured wellbore-zone materials

- PI: Clarens
- Schedule:
  - Y1Q1: J F M A M J J A S O N D
  - Y2Q1: J F M A M J J A S O N D
  - Y3Q1: J F M A M J J A S O N D
  - Y4Q1: J F M A M J J A S O N D

### Task 3 – Imaging carbonation in pore networks and fractures
- Subtask 3.1: 3D Imaging of targeted carbonation in porous media from SubTask 2.3
- Subtask 3.2: 3D Imaging of targeted carbonation in fractured wellbore-zone materials from SubTask 2.4

- PI: Clarens
- Schedule:
  - Y1Q1: J F M A M J J A S O N D
  - Y2Q1: J F M A M J J A S O N D
  - Y3Q1: J F M A M J J A S O N D
  - Y4Q1: J F M A M J J A S O N D

### Task 4 – Modeling Targeted Carbonation
- Subtask 4.1: Multiphase fluid mixing and flow modeling
- Subtask 4.2: Pore network/fracture reactive transport modeling
- Subtask 4.3: Forward modeling of mitigated wellbore integrity

- PI: Clarens
- Schedule:
  - Y1Q1: J F M A M J J A S O N D
  - Y2Q1: J F M A M J J A S O N D
  - Y3Q1: J F M A M J J A S O N D
  - Y4Q1: J F M A M J J A S O N D
Bibliography