Targeted Mineral Carbonation to Enhance Wellbore Integrity

DE-FE0026582

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U.S. Department of Energy
National Energy Technology Laboratory
Mastering the Subsurface Through Technology, Innovation and Collaboration:
Carbon Storage and Oil and Natural Gas Technologies Review Meeting
August 16-18, 2016
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)
motivation
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
motivation and underlying chemistry

(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
motivation and underlying chemistry

Ma et al. 2013
motivation and underlying chemistry

$\text{MSiO}_3(s) + \text{CO}_2(l,sc) \rightarrow \text{MCO}_3(s) + \text{SiO}_2(s)$

where $M = \text{Ca}, \text{Mg}$

adapted from http://www.co2crc.com.au
### 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>
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<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>
</tr>
<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>
</tr>
<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>$\text{Mg}_3\text{Si}_4\text{O}_10(\text{OH})_2 + 3\text{CO}_2 = 3\text{MgCO}_3 + 4\text{SiO}_2 + \text{H}_2\text{O}$</td>
<td>51.4</td>
</tr>
<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>
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</table>
nanoparticle core
The resultant product was centrifuged, washed with water several times. It was dissolved in 200 mL of Tris-HCl (10 mM, pH 8.5). Then, 2 g of Fertilizer (PCMCF).

This technology is facile and effective in controlling the release kinetics of the entrapped nutrients. Such thermo-responsive release properties, and such thermo-induced switches in soft materials (i.e., NIPAm on the Pdop layer) have excellent thermoresponsive release of a coated fertilizer. The Pdop layer was deposited on the salty core, providing copper, potassium, and phosphorus. Subsequently, the SI-ATRP was employed to graft Pdop onto the coated fertilizer (PPCMCF).

We developed a Si-ATRP to graft dopamine hydrochloride (Aldrich) onto the coated fertilizer. These coated fertilizers with a supported initiator were denoted as PCMCF. A 100 mL round-bottomed flask containing PCMCF (2.0 g), CHCl₃ (20.0 mL), TEA (2.0 mL), the CuBr (1.0 g) and CuBr (50.2 mg, 0.36 mmol) was sealed with a rubber stopper and evacuated and degassed by a freeze-pump-thaw cycle 3 times, and injected to the Schlenk line. The mixture was reacted for 23 h at room temperature to produce the supported initiator. After washing and drying overnight under vacuum, PPCMCF was obtained by centrifugation, washing, and drying. These supported initiators were studied systematically in water. The results revealed that the release behavior of elements from the coated fertilizer is in accordance with the reported procedure.

Table:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>LCST (°C)</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>gNIPAAm</td>
<td><img src="image" alt="Structure" /></td>
<td>32</td>
<td>[Hugo Almeida, Maria Amat et al. (2012)]</td>
</tr>
<tr>
<td>PNVCL</td>
<td><img src="image" alt="Structure" /></td>
<td>33-39</td>
<td>[Carolina Alarcon et al. (2005)]</td>
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<td>PEG-b-PNVCL</td>
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<td>[Ji Liu et al. (2014)]</td>
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<td>[Hugo Almeida, Maria Amat et al. (2012)]</td>
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<td>PDMAEMA</td>
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<td>[Kang Moo Huh, et al. (2000)]</td>
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<td>Poly[N(L-...)poly(acrylamide)]</td>
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<td>[Hugo Almeida, Maria Amat et al. (2012)]</td>
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<tr>
<td>PEO/PPO</td>
<td><img src="image" alt="Structure" /></td>
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<td>[Z. Ma, X. Jia et al (2013)]</td>
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<td>[Madlen Cohen Stuart et al. (2010)]</td>
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<td>[Zhibing Hu et al. (2010)]</td>
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</tbody>
</table>

Ma et al. 2013

Preparation of Pdop-Coated Multi-element Compound Fertilizer (MCF). The synthesis of the double copper potassium fertilizer was carried out by adding the copper sulfate solution (0.1 M) to the pyrophosphate trihydrate, a mul-
experimental setup
mercury intrusion porosimetry
precipitate relationship to flow

\[ \text{CaSiO}_3 + \text{CO}_2 = \text{CaCO}_3 + \text{SiO}_2 \]
synchrotron xCT images of columns

2D grey scale

segmented 2D slice

3D volume colors depict connectivity
synchrotron xCT images of columns

2D grey scale slice collected above the Xe k-edge

below the Xe k-edge

the subtracted image
synchrotron xCT images of columns

15.5 MPa, 95°C, Wollastonite:Shale = 20:80, flow rate = 0.1 ml/min

before reaction

SiO$_3$ particles visible

after reaction

SiO$_3$ particles mostly dissolved creating new pores, some of matrix cemented
pore network modeling

$\text{CaSiO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}^{2+} + \text{SiO}_2 + \text{CaCO}_3$
pore network modeling

pore network modeling

- **Flow field**
  \[ \sum_{j}^{N_i} Q_{ij} = \sum_{j}^{N_i} G_{ij} \frac{p_i - p_j}{L_{ij}} = 0 \]
  
  the subscripts i and ij denote the pore body and pore throat
  
  \( Q_{ij} \) [L3/T] is the volumetric flow rate of water from pore body i to j
  
  \( G_{ij} \) [L5T/M] is the pore throat conductivity
  
  \( p \) [M/LT2] is the water pressure at pore body
  
  \( N_i \) is the number of pore throats connected to pore body i,
  
  \( L_{ij} \) [L] is the pore throat length

- **Species**
  \[ V_i^0 (1 - \varepsilon_{ij}^c) \frac{dC_i^m}{dt} = -C_i^m \sum_{j}^{N_i} max(Q_{ij}, 0) - \sum_{j}^{N_i} min(Q_{ij}, 0) - \sum_{j}^{N_i} (D_{ij}^w A_{ij}^w) \frac{C_i^m - C_{ij}^m}{L_{ij}/2} + V_i^0 R_i^m \]
  
  \( V_i^0 \) \( \varepsilon_{ij}^c \) \( C_i^m \) \( N_i \) \( j \) \( max \) \( min \) \( Q_{ij} \) \( L_{ij} \)
  m denotes the species
  C is the species mass/molar concentration
  \( \varepsilon \) is the calcite volume fraction
  \( V_i^0 \) \( \varepsilon_{ij}^c \) \( C_i^m \) \( N_i \) \( j \)
  \( Vo \) [L3] is the volume of pore body in the absence of calcite
  \( D_{ij}^w \) \( A_{ij}^w \) are the species dispersivity in water phase
  \( Aw \) and \( Af \) \( ij \) \( ij \) \( ij \)
  \( Vo \) \( C_i^m \) \( C_{ij}^m \) \( L_{ij} \)
  \( R_i^m \)
  k1 , k2 , and k3 are the reaction rate constants
  a is the species activity
  \( K_{sp} \) is the solubility of product of calcite
  np is an empirical parameter
  Sc is the available specific area for calcite precipitation in a pore element

- **Solid phase volume fractions**
  \[ V_i^0 \rho_s \frac{d\varepsilon_{ij}^s}{dt} = V_i^0 R_{i/ij}^s \]
  
  \( V_i^0 \rho_s \) \( d\varepsilon_{ij}^s \) \( dt \) \( V_i^0 R_{i/ij}^s \)
  Sc is the available specific area for calcite precipitation in a pore element

- **Calcite precipitation/dissolution**
  \[ r_{prec/diss} = \beta (k_1 a^{H^+} + k_2 a^{H_2CO_3} + K_3^a) \left( 1 - \frac{a^{Ca^{2+}} a^{CO_3^{2-}}}{K_{sp}} \right)^n p \]
  
  k1 , k2 , and k3 are the reaction rate constants
  a is the species activity
  \( K_{sp} \) is the solubility of product of calcite
  np is an empirical parameter
  Sc is the available specific area for calcite precipitation in a pore element

- **Source/sink**
  \[ R_s = -r_{prec/diss} M^s \]
  
  Ms is the molecular weight of solid phase
preliminary results
accomplishments to date

– Synthesized wollastonite nanoparticles (10s of nm to μm)
– Synthesized coatings with a LCST of 25°C
– Measured permeability change in packed columns reacted with uncoated wollastonite
– Obtained xCT images of columns at APS
– Processed data using segmentation analysis to measure connectivity of pores
– Imaged cores using μCT at UVa
– Used SEM and EDS to begin exploring connections between flow and precipitation
– Developed pore network modeling framework
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 $P_{CO_2}$ environment. These reactions would leverage the favorable kinetic conditions of the deep subsurface. Our focus on developing temperature sensitive coatings is to control the location (depth) where these reactions occur. Ongoing experiments are showing the temperature sensitivity of these functionalized nanoparticles. The carbonation of these silicates and precipitation of the carbonates is dependent on both $CO_2$ concentration (as a reactant) and $H_2CO_3^*$ (as an acid). Models are being developed to help us optimize the conditions under which maximum carbonation will occur.
many thanks
Organization Chart
## Gantt Chart

### Schedule of Tasks and Milestones

<table>
<thead>
<tr>
<th>Task</th>
<th>Description</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>
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<tbody>
<tr>
<td>Task 1</td>
<td>Project management and planning</td>
<td>Clarens</td>
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<td>Task 2</td>
<td>Coated silicate development, characterization and interactions in porous media (Clarens)</td>
<td>Clarens</td>
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<td>SubTask 2.1</td>
<td>Fluid mixing and buoyancy experiments at formation</td>
<td>Clarens</td>
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<td>SubTask 2.2</td>
<td>T/P to optimize fluid properties</td>
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<td>Optimize Calcium source transport to targeted flow pathways</td>
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<td>Targeted carbonation in fractured wellbore-zone materials</td>
<td>Clarens</td>
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<td>Task 3</td>
<td>Imaging carbonation in pore networks and fractures</td>
<td>Fitts</td>
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<td>Subtask 3.1</td>
<td>3D imaging of targeted carbonation in porous media from SubTask 2.3</td>
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<tr>
<td>Subtask 3.2</td>
<td>3D imaging of targeted carbonation in fractured wellbore-zone materials from SubTask 2.4</td>
<td>Fitts</td>
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<td>Task 4</td>
<td>Modeling Targeted Carbonation</td>
<td>Clarens</td>
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<td>Subtask 4.1</td>
<td>Multimodal fluid mixing and flow modeling</td>
<td>Clarens</td>
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<td>Subtask 4.2</td>
<td>Pore network/fracture reactive transport modeling</td>
<td>Peters</td>
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<td>Subtask 4.3</td>
<td>Forward modeling of mitigated wellbore integrity</td>
<td>Clarens/Fitts</td>
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Bibliography


Appendix