Experiment-Based Model for the Chemical Interactions between Geothermal Rocks, Supercritical Carbon Dioxide and Water

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Project Officer: Ava M. Coy
Total Project Funding: $3,000,000
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This presentation does not contain any proprietary confidential, or otherwise restricted information.
Relevance/Impact of Research

Project objectives

1) Determine **what** chemical interactions occur between relevant minerals and water-CO$_2$ fluids

2) Understand **how** the chemical interactions affect transition to and performance of a CO$_2$-EGS

Purpose of the project

- Better assessment of risks associated with an EGS reservoir development using CO$_2$ as a working fluid;
  - Magnitude of the rock-fluid interactions
  - Location of the geochemical changes
  - Breadth of the interface zone
  - Characterize zone permeability & contact area

- More accurate quantification of the power generation capacity, and prediction of the geothermal production lifetime
Relevance/Impact of Research

Technical challenges

• Starting materials composition different than expected
• Highly accurate experimental data required for a geochemical model
• Parallel experimentation complicated by diverse dissolution kinetics
• Reactive surface area is changing during the rock-fluid interaction
• Re-mineralization that may occur during an experiment would affect subsequent mineral behavior
• Difficulty in parameterizing complex interactions in the modeling software

Issues being addressed

• Improve data accuracy and build experimental complexity into the models
• Understand the surface area effect and adopt it into rock-fluid interaction model
• Specific issues related to behavior of rocks from the Cranfield CO$_2$ injection site
Scientific/Technical Approach

Technical approach

1) Build a multi-channel batch system and generate mineral solubility data (2011/12)
2) Upgrade the system by adding a circulation flow-through channel (mid 2012)
3) Simulate the injection-production cycle to advance the CO$_2$-EGS model (finishing)
4) Conduct SEM analysis on pre- and after-reaction mineral samples and compare the changes in textures and mineralogy (ongoing)
5) Experiment using rocks from actual CO$_2$ injection site at Cranfield, MS (ongoing)
6) Create the experiment-based model (ongoing)
Accomplishments, Results and Progress

1) Generated a solubility map for relevant minerals under various CO$_2$-water & PT conditions
2) Added a flow-through channel and synchronized it with all five batch reactors built earlier
3) Determined effects of the particle size and surface area of minerals on dissolution kinetics
4) Improved ion detection sensitivity to identify conditions for dissolution of low-solubility minerals
5) Evaluated changes in mineral textures due to mineral dissolution / precipitation by SEM
6) Obtained kinetic parameters from the batch experiment data for key geothermal minerals
7) Discovered unexpected behavior of some minerals in CO$_2$-water at high temperature
8) Assessed complexity of a real rock sample through behavior of its individual components
9) Performed reactive transport modeling of changes in geological conditions of an EGS
10) Turned experimental findings on rock-fluid interactions into a model of real CO$_2$ injection site

<table>
<thead>
<tr>
<th>Original Planned Milestone/Technical Accomplishment</th>
<th>Actual Milestone/Technical Accomplishment</th>
<th>Date Completed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add and validate flow-through channel</td>
<td>Works in-sync with five other reactors</td>
<td>6/30/2012</td>
</tr>
<tr>
<td>Develop rock characterization workflow</td>
<td>Included new particle sizing methodology</td>
<td>7/31/2012</td>
</tr>
<tr>
<td>Perform experiments with water-CO$_2$ fluids circulation through a rock bed</td>
<td>Included a real rock sample from the existing CO$_2$ sequestration site (Cranfield)</td>
<td>to be completed 4/31/2013</td>
</tr>
<tr>
<td>Develop an experiment-based model of an EGS transition from water to CO$_2$</td>
<td>Initial reactive transport modeling already performed and adopted to a real setting</td>
<td>to be completed 7/31/2013</td>
</tr>
</tbody>
</table>
Experimental system upgrade

New continuous flow / circulation channel operates together with the five batch reactors, sharing the feeding and analytical parts of the complete system.
Two Cranfield rock samples obtained as a courtesy of Prof. Susan Hovorka and Dr. Jiemin Lu from the University of Texas at Austin

Cranfield Sample #1 - more carbonates

Cranfield Sample #2 - more chlorite

Chlorite & Illite: very little known, presumably of very low solubility
Calcite & Dolomite: well known as highly soluble in water-CO₂
Kaolinite: quickly disintegrates into 100 nm nanoparticles
Quartz: practically insoluble

Effect of mineral granularity on dissolution

Mineral Dissolution Profiles

Particle size bins
- ▲ 25-63 µm
- ■ 63-150 µm

Surface area measurement
BET method (argon absorption)

Particle size distribution
Multi-angle light scattering

Dissolution Conditions
PARC rock-fluid system
Fluid: CO₂-saturated water
Temperature: 150 °C
Pressure: 1,200 psi

Particle Size Distributions

Labradorite
BET surface area: 0.230 m²/g

Mg²⁺
still no equilibrium!

Chlorite

Mg²⁺

Illite
disintegrated particles?!

Measured Ion Concentration, ppm

Reaction Time, hours

Particle Size, µm

% Volume
Labradorite
- Sieved into particle size range 63-150 µm
- Exposure to 120/150 °C water-CO₂ for up to 240 hours
- Particle size distribution by MALS
- Particle imaging by SEM

1) no / minor exposure
2) moderate exposure
3) major exposure
Compositional changes during dissolution

**Illite**
- Sieved into particle size range 63-150 µm
- Complex chemical composition expected \((K,H_3O)(Al,Mg,Fe)_{2}(Si,Al)_{4}O_{10}[(OH)_{2},(H_2O)]\)
- 240 hr exposure to 120/150 °C water-CO$_2$
- Spot elemental analysis by EDS
- Particle imaging by SEM

1) **No exposure:**
   - typical K-Mg-Fe aluminosilicate

2) **Moderate exposure:**
   - from the column back
   - mineral reconstitution(?)
   - no trace of carbon(ates)

3) **Major exposure:**
   - from the column front
   - some remineralization(?)

... this work continues
Mineral solubility response to temperature

**Illite**

\[ (K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10} \]

\[ [(OH)_2(H_2O)], 63-150 \mu m \]

**Chlorite**

\[ Mg,Fe,Ni,Mn,Al/(AlSi_3) \]

\[ O_{10}(OH)_9, 63-150 \mu m \]

**Reactor system setting:**
- Continuous flow channel in circulation mode at 3 mL/min, with 600 mL fluid reservoir and 20 mL mineral column.
- Set temperature: 90, 120, 150 up to 180 °C in 12 hr steps.
- Set total reservoir pressure: 1,200 psi maintained by helium.

**Dissolved mineral response:**
- Total ion peak area as detected by on-line ion chromatography.

**Fluids and Pressures:**
- 500 mL water pressurized up to 1,200 psi helium with various partial pressures of CO₂ for illite and chlorite:
  - 0 psi CO₂
  - 62 psi CO₂
  - 88 psi CO₂
  - 600 psi CO₂
  - 1200 psi CO₂

**Surprises at 150-180 °C**
1. drop in illite solubility
2. accelerated dissolution of chlorite, no equilibrium

... Cranfield sample evaluation still ongoing
Initial model of 20-yr transition to CO$_2$-EGS

Simulation of temperature changes over 20 years of recycled CO$_2$ injection in a Cranfield-like reservoir

Animation: move your cursor above and click the “play” button
The starting mineralogical composition in volume fraction is based on literature data (Lu et al, *J. Greenhouse Ctrl.*, in press):

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>0.794</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.118</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.031</td>
</tr>
<tr>
<td>Illite</td>
<td>0.013</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.011</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.004</td>
</tr>
<tr>
<td>Albite</td>
<td>0.002</td>
</tr>
<tr>
<td>Non-reactive</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Simulation of mineral composition changes in a Cranfield-like reservoir over 20 years of recycled CO₂ injection.

Animation: move your cursor above and click the “play” button.
Future Directions

- Key activities to project completion in July 2013:
  - Finish the ongoing experiments (chlorite equilibrium and Cranfield sample)
  - Hand over the experimental data to LBNL (raw and reduced up to date)
  - Further characterize pre-/post-experiment samples (Cranfield, chlorite, illite)
  - Adopt the experimental findings into the reactive transport modeling effort
  - Refine existing geochemical models further (reactive surface area evolution)
  - Create a new CO$_2$-EGS model around the Cranfield reservoir setting

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<tr>
<th>Milestone or Go/No-Go</th>
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<td>Complete the project</td>
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The kinetics can mislead the thermodynamic measurements as slowing down may often look like reaching an equilibrium.

Trace level components may easily overshadow the effect of major ones, requiring separation-based detection to deconvolve.

Even the simplest physical / chemical interactions can become overwhelmingly complex if changes affect the process itself.

Accuracy of rock-fluid interaction data is the critical factor for realistic modeling of a geothermal reservoir in transition.

Modeling can hardly capture complexity of multicomponent dynamic rock-fluid interactions without an experimental input.
The initial delay due to program Novation from original awardee to PARC

The financial information corresponds to the 2/28/2013 status:

Timeline:

<table>
<thead>
<tr>
<th>Planned Start Date</th>
<th>Planned End Date</th>
<th>Actual Start Date</th>
<th>Current End Date</th>
</tr>
</thead>
</table>

Budget:

<table>
<thead>
<tr>
<th>Federal Share</th>
<th>Cost Share</th>
<th>Planned Expenses to Date</th>
<th>Actual Expenses to Date</th>
<th>Value of Work Completed to Date</th>
<th>Funding needed to Complete Work</th>
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</thead>
<tbody>
<tr>
<td>$3,000,000</td>
<td>$1,004,705</td>
<td>$3,000,000</td>
<td>$2,704,782</td>
<td>$3,433,390</td>
<td>$295,218</td>
</tr>
</tbody>
</table>

Everything proceeds according to the plan updated at Novation:
- PARC prepares for completing the experimental work
- Modeling activities at PARC accelerate
- The workload and corresponding funding is to shift towards LBNL
- Interacting with industry leaders and still looking for opportunities

We expect to complete the whole project in time and within the budget