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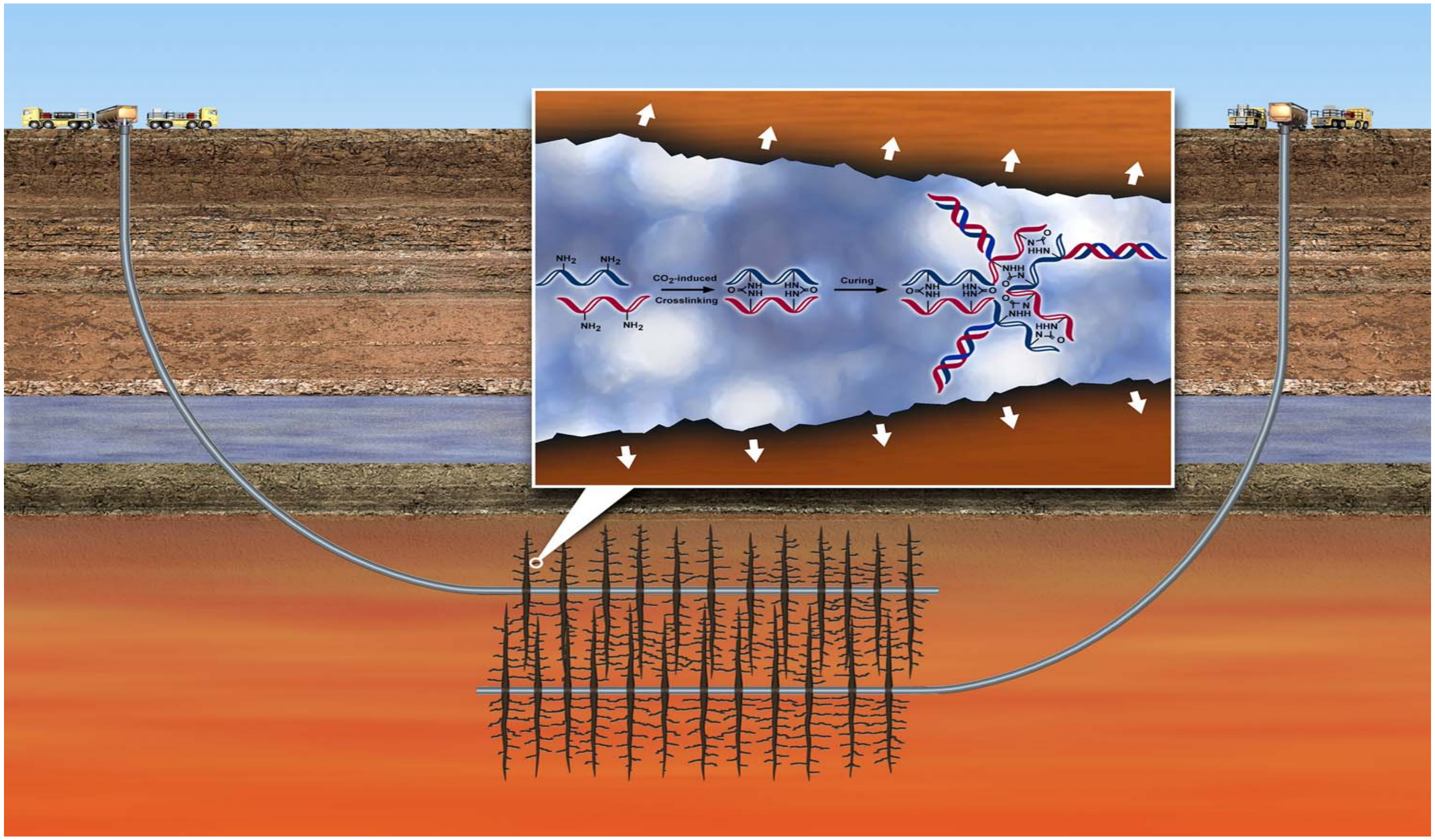

Reservoir Stimulation with Operational Monitoring for the Creation of EGS

Project Officer: Lauren Boyd
Total Project Funding: $1,203,350
November 14th, 2017

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Pacific Northwest National Laboratory

Track Name

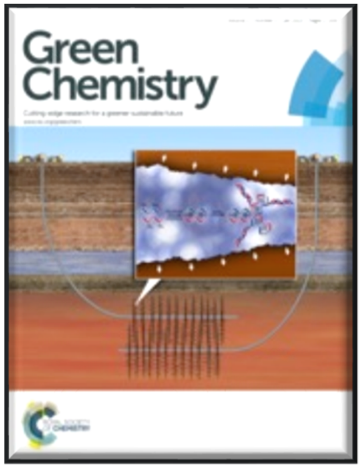
Relevance to Industry Needs and GTO Objectives

Challenges/Barriers project is trying to address

- Inability to cost-effectively create high-permeability reservoirs from impermeable igneous rock at depth and high T (150 C – 350 C)
- Low-water or water-less alternatives, critical due to the volumes of water and wastewater that must be treated and disposed of
- Reservoir stimulation represents approximately 45% ($4.9 million) of a typical well budget, which averaged $11 million in 2016.
- EGS field projects have not sustained production at rates greater than half of what is needed for economic viability.

Project Objectives

- To cost-effectively enhance permeability of geothermal reservoirs and increase energy production rates by
  1. Making stimulation processes less water- and energy- intensive
  2. Rendering stimulation process more environmentally friendly (non-toxic, recyclable component)
  3. Reducing regulation and permitting costs
- All contributing to reduction of the LCOE on geothermal power generation

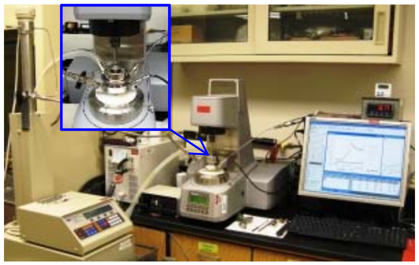


Project Supports the following GTO Goal(s)

- Accelerating a commercial pathway to and securing the future of Enhanced Geothermal Systems
- Improving processes of identifying, accessing, and developing geothermal resources
- Overcoming deployment barriers
- Collaborating on solutions to subsurface energy challenges

Summary of 4y-project plan

- ***FY13:***
  1. Capability development
  2. Proof of concept: demonstrate StimuFrac's volume expansion at EGS-representative Ts
  3. Proof of concept: demonstrate that the volume expansion can induce fractures
- ***FY14:***
  1. Study what triggers the volume expansion
  2. Demonstrate StimuFrac application flexibility in a range of Ps, and Ts
- ***FY15:***
  1. Study pH influence on StimuFrac's performance
  2. Evaluate CO_2 source alternatives
- ***FY16:***
  1. Determine mechanical properties of StimuFrac (fluid's compressibility and generated overpressures)
  2. Can StimuFrac propagate fractures over long distances?



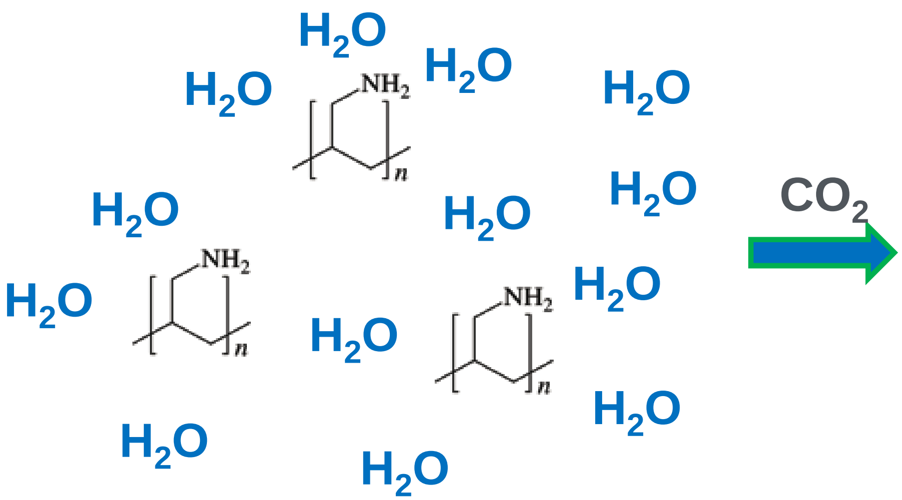
HP/HT multi-fluid rheometer

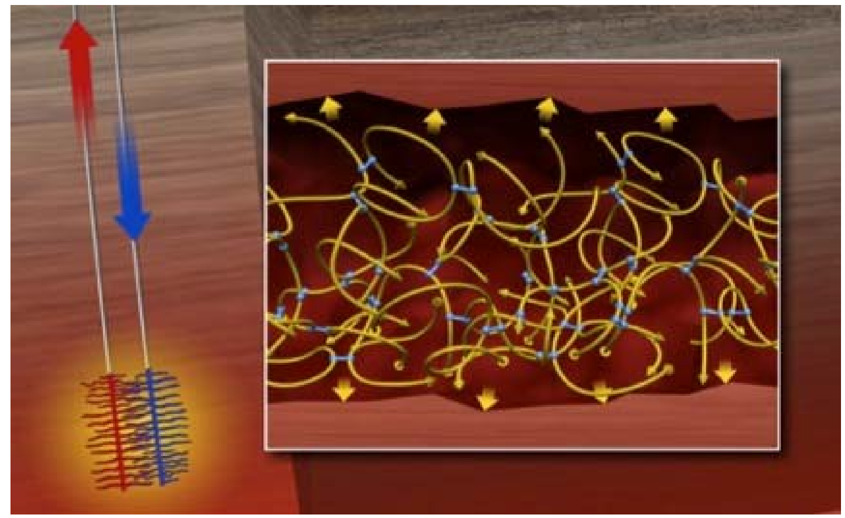
Tasks performed

1. Screening different polymers and EGS Ps/Ts for volume expansion with CO_2 using high-P view vessel (FY13)
2. Perform lab-scale stimulation experiments at an EGS-representative P/T (FY13).
3. Study chemical speciation of polymers with CO_2 using HP/HT MAS-NMR (FY14)
4. Perform viscosity studies as function of CO_2 pressure at EGS temperatures (FY14)
5. Perform lab-scale stimulation with in-operando acoustic monitoring at two different EGS Ps/Ts (FY14)
6. Perform volume expansion and viscosity studies as a function of pH (FY15)
7. Perform lab-scale stimulation at different EGS-representative pHs (4, 7, and 10) (FY15)
8. Evaluate sodium bicarbonate as an alternative source of CO_2: volume expansion exps. (FY15)
9. Determination of compressibility of StimuFrac (FY16)
10. Measure overpressures generated by StimuFrac and propose a fracturing mechanism (FY16)
11. Study CO_2 transport in sand-packed columns filled with StimuFrac solutions (FY16)

HP/HT MAS-NMR capability

StimuFrac Technology



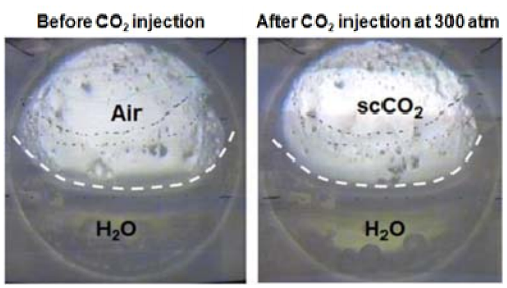


- A stimuli-responsive fracturing fluid that can mediate a chemically-activated expansion in confined environments
- Provides a controllable increase of hydraulic stress to aid in fracturing processes, i.e., it expands where we want it to expand
- Provides *in situ* control of the rheological properties of the fracturing fluid
- Corrosion inhibitor and biocide
- Nontoxic and inexpensive

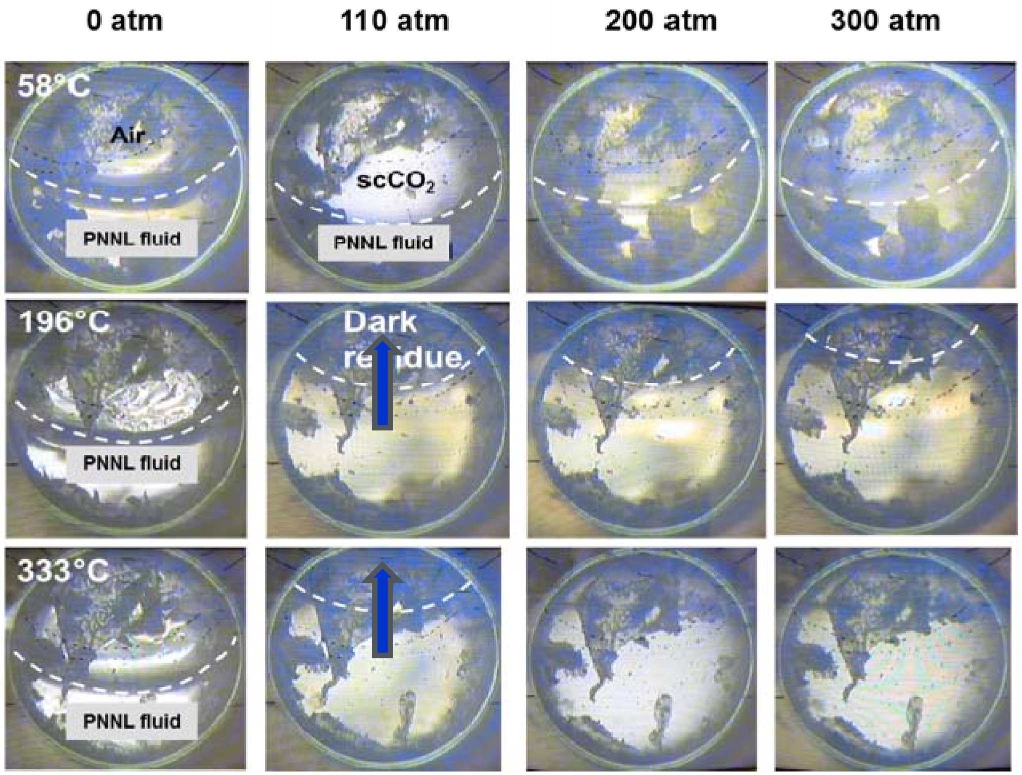
All milestones met on time and budget

Remarkable Volume Expansion at EGS Ps/Ts

- Volume expansions of **up to 150%** at a range of reservoir P & T conditions (196–402 ºC and 130–300 atm).
- 1 wt% aqueous polymer
- Aqueous polymer stable up to 400 ºC
- Vol. expansion also occurs at pH=7 and pH=10



Control experiment

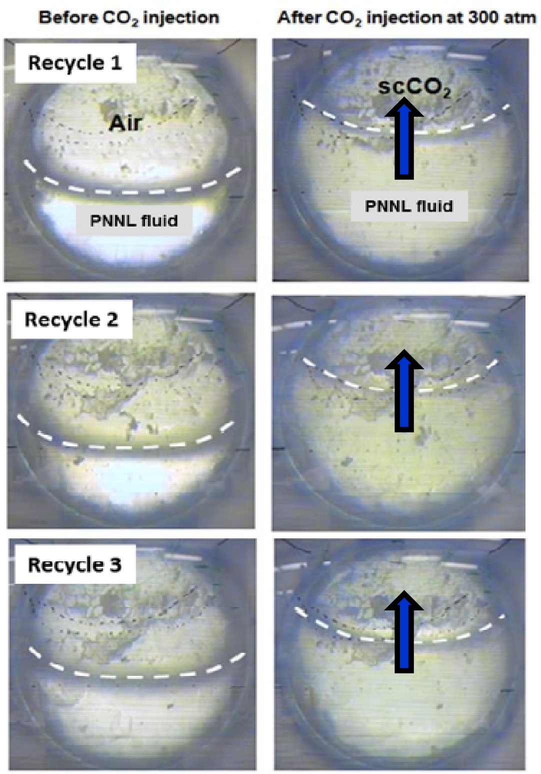


FY13 M3 met: achieve greater than 10% volume increase at EGS-representative Ps/Ts
FY15 M2-A met: demonstrate volume expansion at pH=7 and/or PH=10 at temperatures and pressures relevant to EGS.

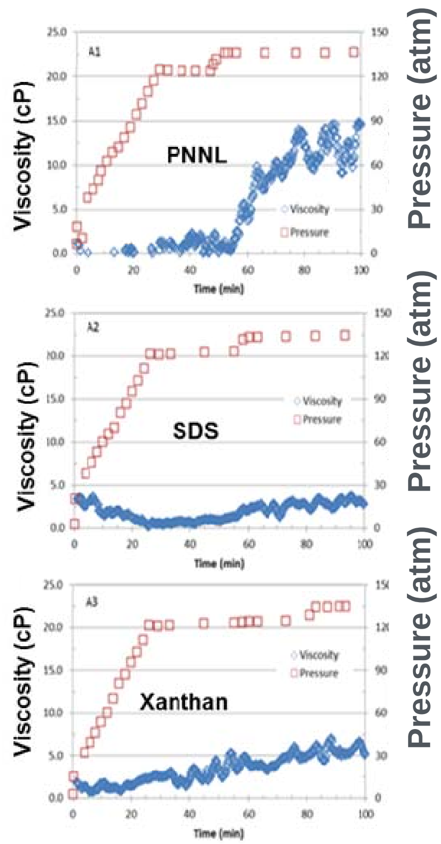
Expansion also demonstrated by thermal decomposition of sodium carbonate

Potentially Recyclable

Due to rheoreversibility



Viscosity Increase at Reservoir P/T

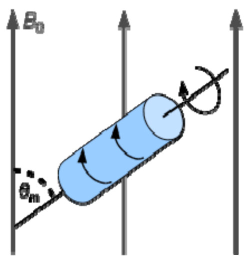


- **15X** viscosity increases at 2000psi & 190 ºC
- Shear-thinning properties of critical importance to support pumping into the reservoir
- 1 wt% aqueous polymer
- Viscosity increase was also demonstrated at higher P/T and higher pHs

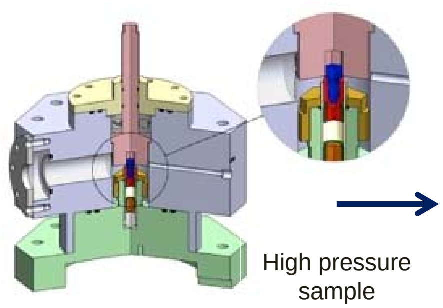
FY13 M2 met: Demonstrate less than 15% decay of the reactor polymer compounds at EGS temperatures and pressures
FY13 M4 met: Demonstrate capability to switch from liquid to gel multiple times.
FY14 M1 met: Demonstrate viscosity increase at low and mid-range pressures (130bar) and temperatures (190C)
FY15 M1 met: Demonstrate viscosity increase at mid and high range P and T conditions (up to 350 atm and 300 ºC)
FY15 M2-B met: Demonstrate increase in viscosity at pH=7 and/or pH=10 at T/P relevant to EGS

StimuFrac Chemistry: Speciation with CO_2

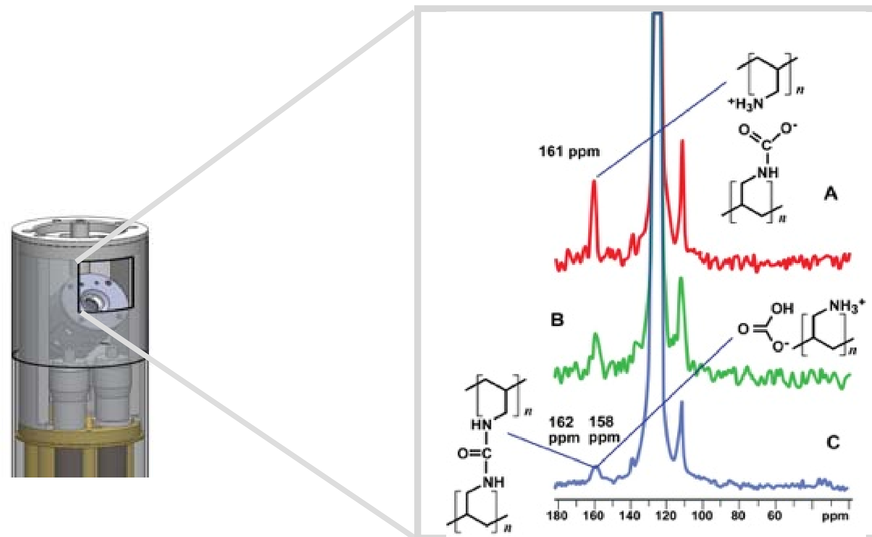
- State-of-the-art in situ high P/T ^{13}C MAS-NMR



Sample MAS NMR probe



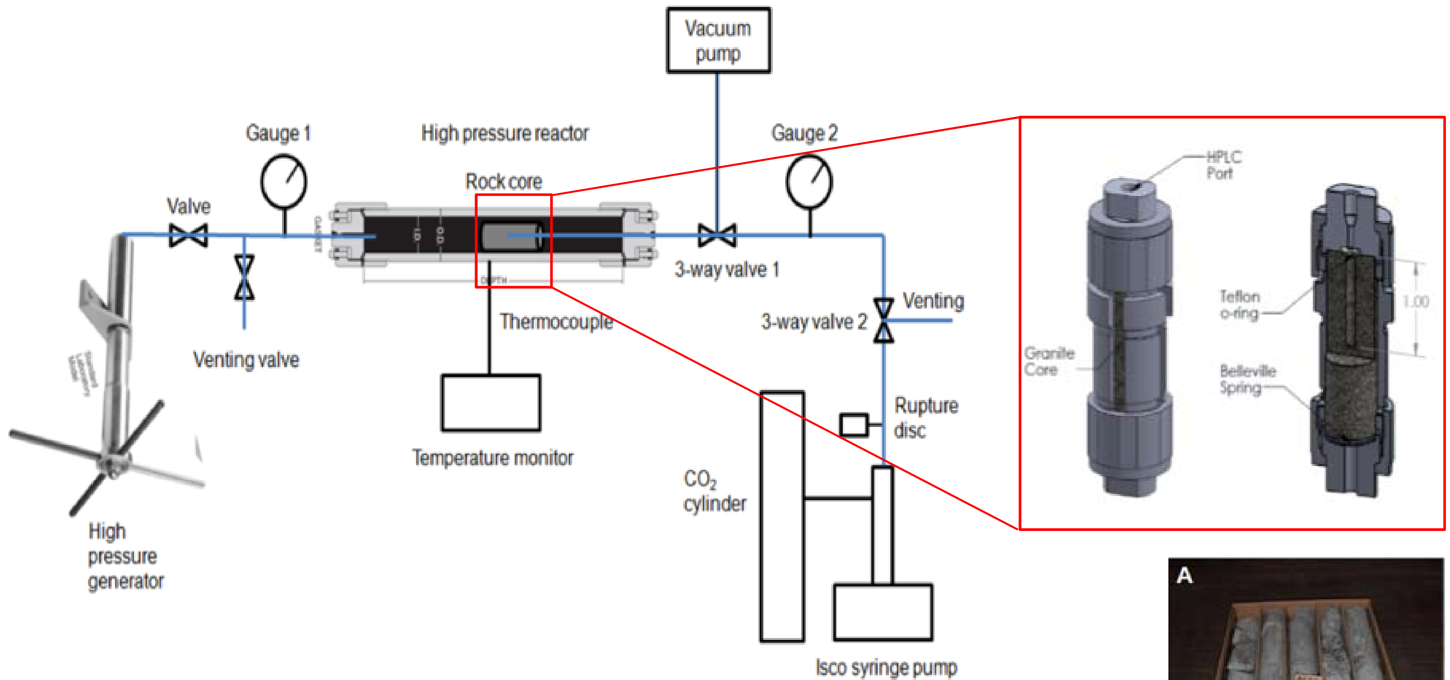
High pressure sample loading/ reaction chamber



FY13 M1 met: Capability development for rheological, chemical, and stimulation studies
FY14 M2 met: Understand CO2-polymer speciation mechanisms at low P and T conditions

C. A. Fernandez et al *Green Chemistry*, **2015**,17, 2799-2812

Lab-Scale Stimulation System



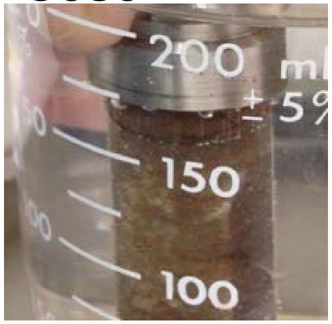
Worked with geophysicists on experiment design

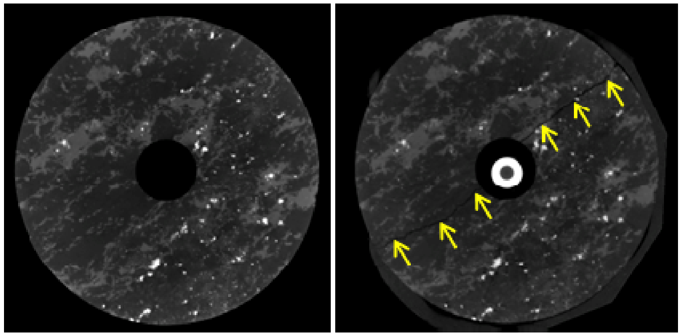
FY13 M1 met: Capability development for rheological, chemical, and stimulation studies

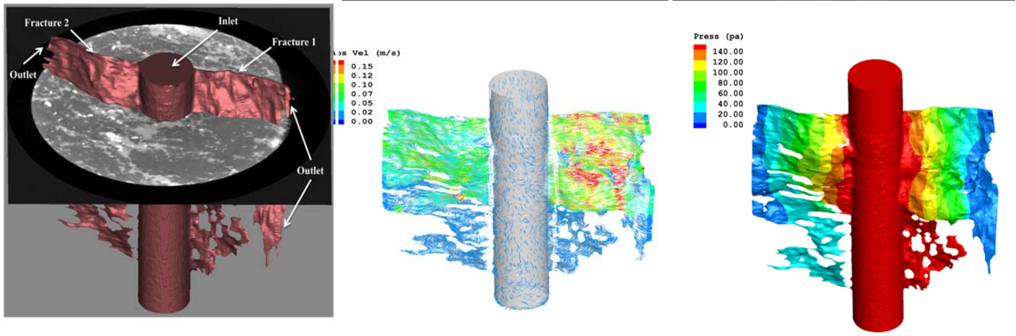
Rock cores obtained from the Coso Geothermal site located in the eastern portion of central California, and the Newberry Geothermal site located near Bend, Oregon.

Stimulation studies

Coso







Average Bulk Permeability: Before: <1μD ; After: 440 mD

Note: compare to H_2O/CO_2 average permeability: 32 μD

Confining P/T conditions:
300 ºC and 5000 psi

Measured average effective pressure:

- **PAA/CO_2: 12 atm (190 psi)**
- H_2O/CO_2: 37atm (550psi). **3X higher**

Similar results shown at pH=7 and pH=10 with Coso samples

Go/No-go passed: Demonstrate the ability to increase overall sample permeability by at least 10% at pH = 7 and pH =10 compared to current technology

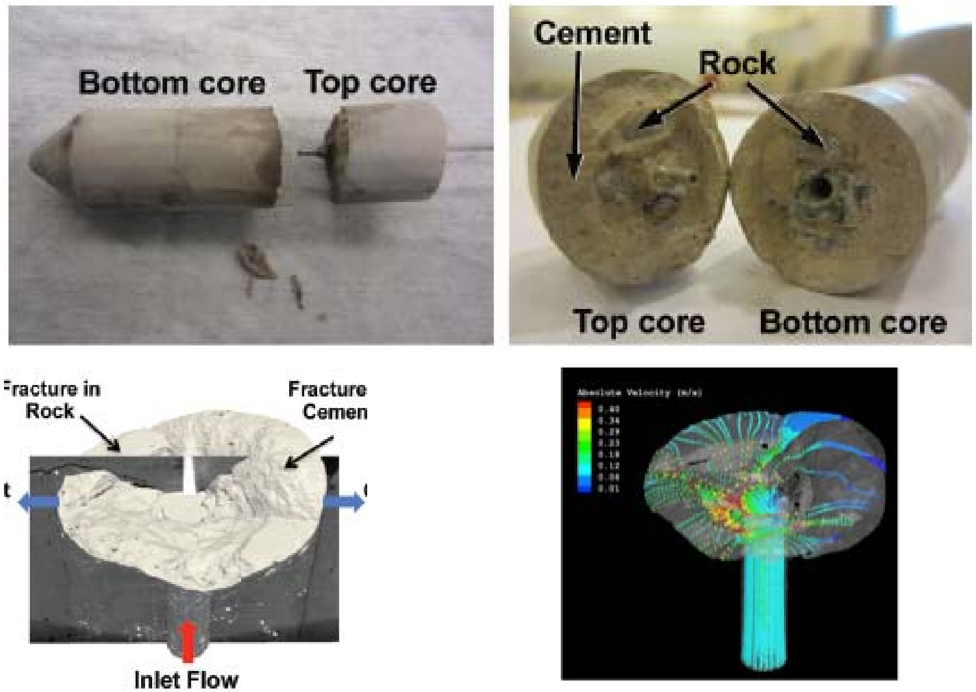
FY14 M3 met: Demonstrate at least 10% fracture propagation increase at a second pH condition (pH=7) as compared to current technology
FY14 M4 met: Demonstrate at least 10 % increase in fracture propagation on samples from two different reservoirs at low and mid-range P and T conditions as compared to current technology
FY15 M3 met: Demonstrate at least 10% fracture propagation increase at a third pH condition (pH=10) as compared to current technology

Newberry:

H_2O/CO_2 showed only 10% higher effective P than PAA/CO_2, similar permeabilities

Stimulation studies

Coso



Average Bulk Permeability: Before: <1μD ; After: 92 mD

Note: compare to H_2O/CO_2 average permeability: 20 μD

Confining P/T conditions:
210 ºC and 3000 psi

Measured average effective pressure:

- **PAA/CO_2 = 6atm (90 psi)**
- H_2O/CO_2 = 50atm (730psi). **8X higher**

Newberry:

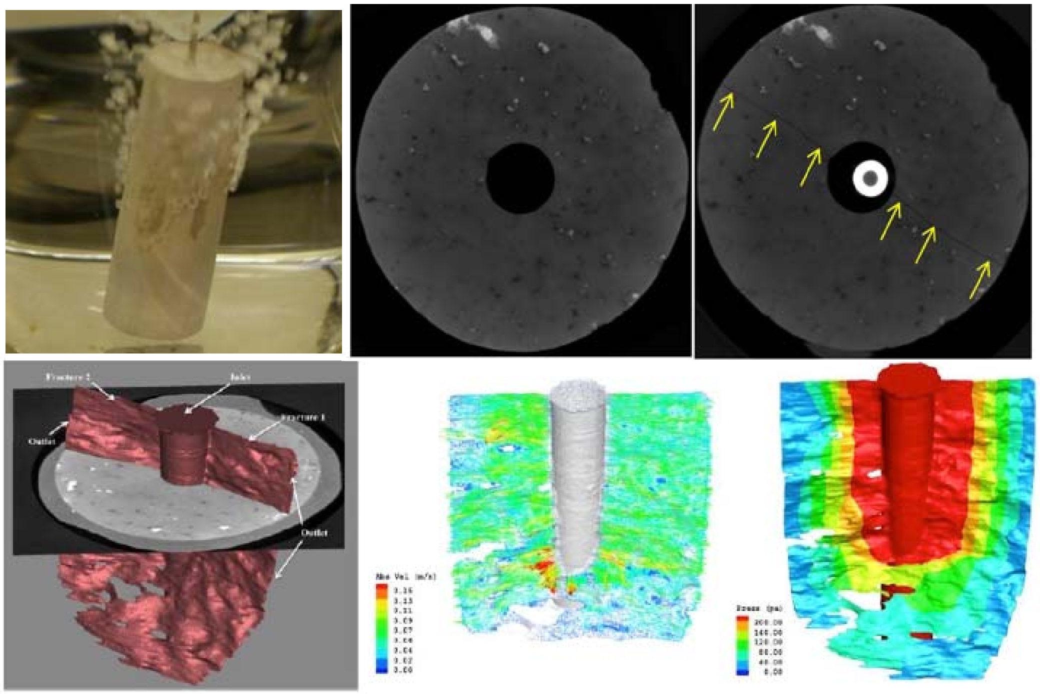
No available data

FY14 M4 met: Demonstrate at least 10 % increase in fracture propagation on samples from two different reservoirs at low and mid-range P and T conditions as compared to current technology

C. A. Fernandez et al *Green Chemistry*, **2015**,17, 2799-2812

Stimulation studies

Newberry



Average Bulk Permeability: Before: <1μD ; After: 2.8 mD

Note: compare to H_2O/CO_2 average permeability: 9 μD

Confining P/T conditions:
150 ºC and 3700 psi

Measured average effective pressure:

- **PAA/CO_2: 125 atm (1840 psi)**
- H_2O/CO_2: >118 atm (>1735psi)

Coso:

PAA/CO_2 showed similar effective P and permeability values to H_2O/CO_2

FY14 M4 met: Demonstrate at least 10 % increase in fracture propagation on samples from two different reservoirs at low and mid-range P and T conditions as compared to current technology
FY15 M4 met: a per-review publication and a patent application

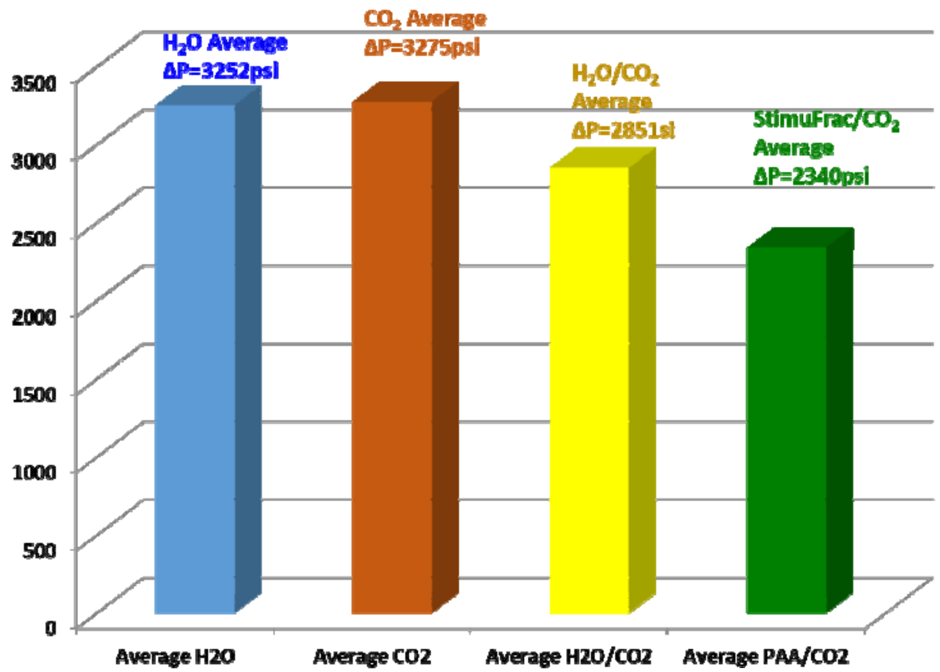
C. A Fernandez et al *Geothermics,* 2015, 58, 22
C. A. Fernandez et al *Corrigendum on Geothermics*

Determining Fracturing Mechanism

Fused silica sample

How to estimate the overpressure associated to volume expansion?

- Non-porous surrogate w/ mechanical properties similar to shale: **Fused silica**
- Predicted effective pressure for failure: 3400psi
- Lab-scale stimulation with different fluids (minimum 5 samples fractured per fluid)
- Confining P/T= 3000psi/200C



- **Conventional fluids such as water or CO_2 require ~40% (920psi) higher overpressures to fracture fused silica as compared to StimuFrac.**
- **Control H_2O/CO_2 requires 22% (510psi) higher overpressures than Stimufrac (PAA/CO_2).**

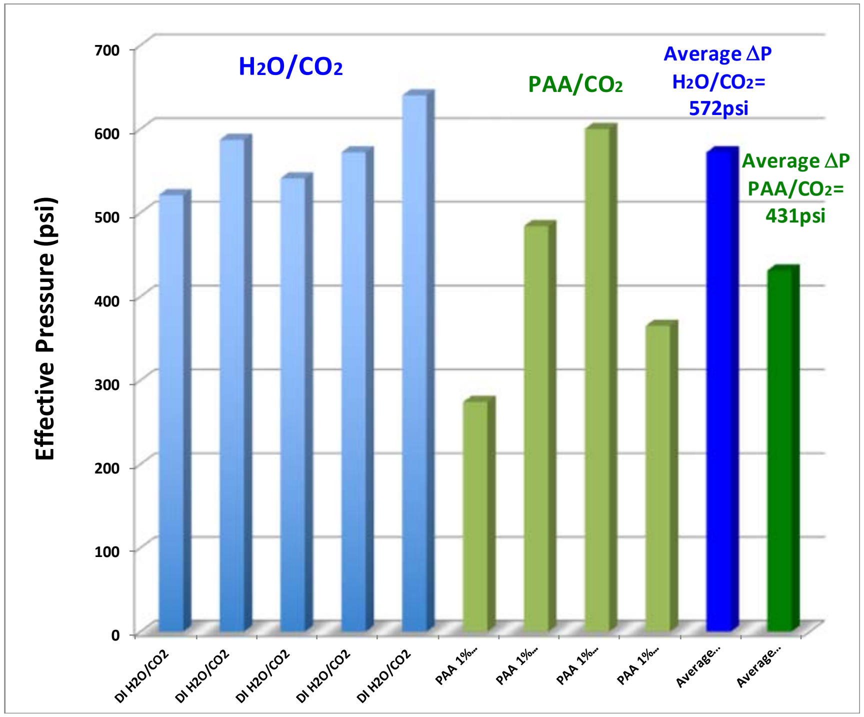
FY16 M1 met: A system and protocol in place to determine mechanical properties of PNNL fracturing fluids
FY16 M2 met: Compressibility factors and overpressures originated by the PNNL fluids at, minimum, one representative EGS P/T condition

Determining Fracturing Mechanism

EGS Coso
1623 feet (TVD, reservoir Coso CGC 18-27)

Is it just bulk overpressure?
What about phenomena occurring at the microscale?

- Porous surrogate w/ mechanical properties similar to shale? **N/A**
- Generated **9 igneous rock samples from a single core** (~1.1m^2/g, and 1.8nm. Porosity 1-2%)
- Stimulation with two fluids (minimum 4 samples tested per fluid)
- Confining P/T= 3000psi/200C

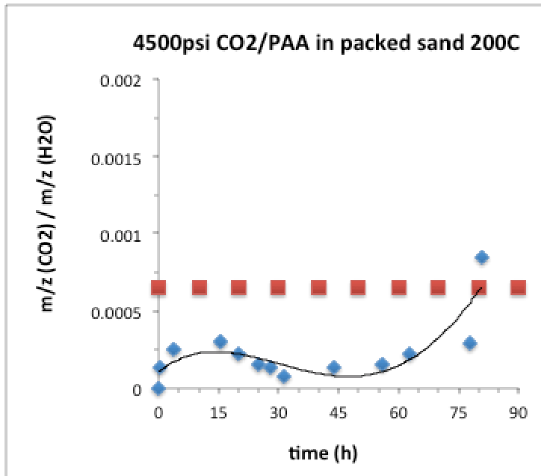


- **H_2O/CO_2 required 33% higher effective pressure as compared to StimuFrac (PAA/CO_2)**
- **Large variability in effective pressure for StimuFrac suggests a different fracturing mechanism to the control fluid (H_2O/CO_2). Pore invasion pressure?**

FY16 M3 met: Identification/hypothesis of fracturing mechanism and better understanding of fracturing control

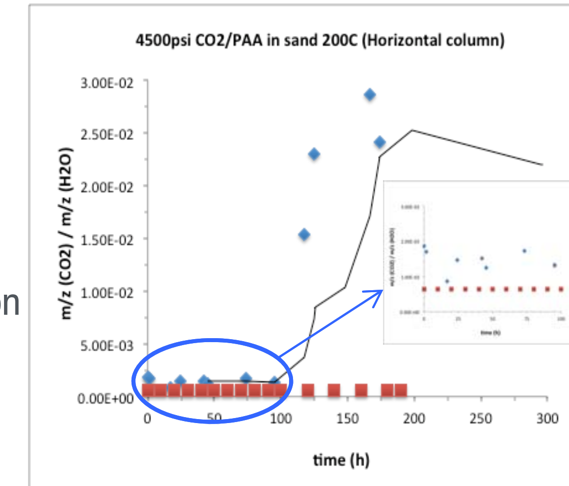
Determining CO_2 transport in aqueous PAA

- 16” Sand-packed column filled with water or StimuFrac fluid (PAA 1wt% in water).
- Vertical column: **mainly diffusion** (density of scCO2 at slightly lower than H2O density)
- Horizontal column: Diffusion and **convection.**



StimuFrac (PAA 1wt%): Diffusion only transport

CO_2 BKG concentration (red plot)



StimuFrac (PAA 1wt%): Diffusion + Convection

- Breakthrough time for diffusion and convection (right plot) is similar to breakthrough time obtained when diffusion only transport occur: **80-90h for PAA/CO_2.**
- **Solution(s): Co-injection of StimuFrac and CO_2 or using sodium bicarbonate as CO_2 source**

FY16 M4 met: CO2 diffusion and dispersion coefficients on, at least, one representative EGS P/T condition

Milestones/deliverables met on time & budget (no plan deviation). Cost: $ 1,203,350

Research Collaboration and Technology Transfer

- StimuFrac patent protected, US Patent # 9,447,315 B2
- Approached by several potential stake holders including:
  - **Major oil companies and field service companies**

Institute of Chemical Engineers (IChemE) Outstanding Achievement in Chemical and Process Engineering Award and Oil and Gas Award

Future Directions

- **Injection alternatives for StimuFrac**

  A. Co-injection of polymer solution and liquid CO_2 to maximize mixing

  B. Utilization of an alternative source of CO_2, sodium bicarbonate

- **Optimization/maximization of stress generated by StimuFrac**

  Variables: CO_2 concentration
  Polymer concentration
  Polymer molecular weight
  Polymer structural configuration (linear versus branched)

- **Recycling**: Quantify polymer mass recovered after lab-scale stimulation at different EGS P/T conditions
- **Foot (or meter)-scale stimulation** studies with seismic monitoring
- **Application in Unconventional oil/gas recovery?** Lower temperatures, higher pressures

Future Directions (Cont.)

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We project that use of Stimu-Frack could save as much as 125,000 barrels of water and as much as 125 tons of chemicals per well; field tests are required.

- **Overview of a candidate field test**
  - Well is 3,000 m deep with a 1,500 m long horizontal section
  - Analysis is based on tight oil plays where 200 tons of chemicals and 200,000 barrels of water (site and source: confidential)
  - Estimated savings: **$2.3M/well**
  - Field tests would examine reagent mixing, water cleanup and overall operation at scale.
  - Cost of the field test, say $250K, could be leveraged against federal funding if it were conducted under a CRADA-like arrangement.

	Conventional fracking	Stimu-Frack
Additive usage	200 ton	-
Polymer usage	-	113 ton
CO_2 usage	-	3087 ton
Chemical cost	$980K	$371K
Pump electric energy cost	$187K	$61K
Water usage	200K barrel	75K barrel
Water cost (incl. delivery)	$320K	$120K
Wastewater handling cost	$800K	$200K
Wastewater pool cost	$1.2M	$597K
Additional regulation cost	$254K	$20K
Total cost	$3.7M	$1.4M
Total cost saving	-	63%
Environment impact	High on potable water	Low on potable water

Summary

Stimu-Frack may confer financial, energy and environmental advantages over the use of conventional fluids.

Advantages over conventional fluids:

- ❑ Estimated **$2.3M in savings** per well (63% cost reduction)
- ❑ Creation of fracture networks with a **less energy intensive process** (effective pressures up to 3X lower than current technology)
- ❑ The amount of **water** required and waste water generated can be **dramatically decreased (by ~60%).**
- ❑ **Flexible Technology:** could be used in a range of reservoir P/T and pH conditions
- ❑ PNNL fracturing fluid is **more environmentally friendly (non-toxic and high T-stable polymer)**
- ❑ Rheoreversible properties make this fluid **potentially recyclable,** accelerating environmentally responsible and efficient domestic energy production**.**
- ❑ **Key process infrastructure for CO_2 delivery is available** (e.g. EOR). In addition, captured waste CO_2 from a power plant could also be used as a renewable resource

StimuFrac is gathering favorable reaction

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The fluid has attracted attention as a "green", less energy- and water-intensive alternative and could create an advantageous marketing position

- Green Chemistry Editor released an Editorial Note titled "The subject of 'fracking' in Green Chemistry" explaining the reasons for publishing PNNL's StimuFrac.
- In it he states "Fracking is a very controversial technique…" However, "all reviewers agreed that the authors of the study have carried out a sound and in depth study and presented data that might help to lower the impact of this particular aspect of the fracking industry."