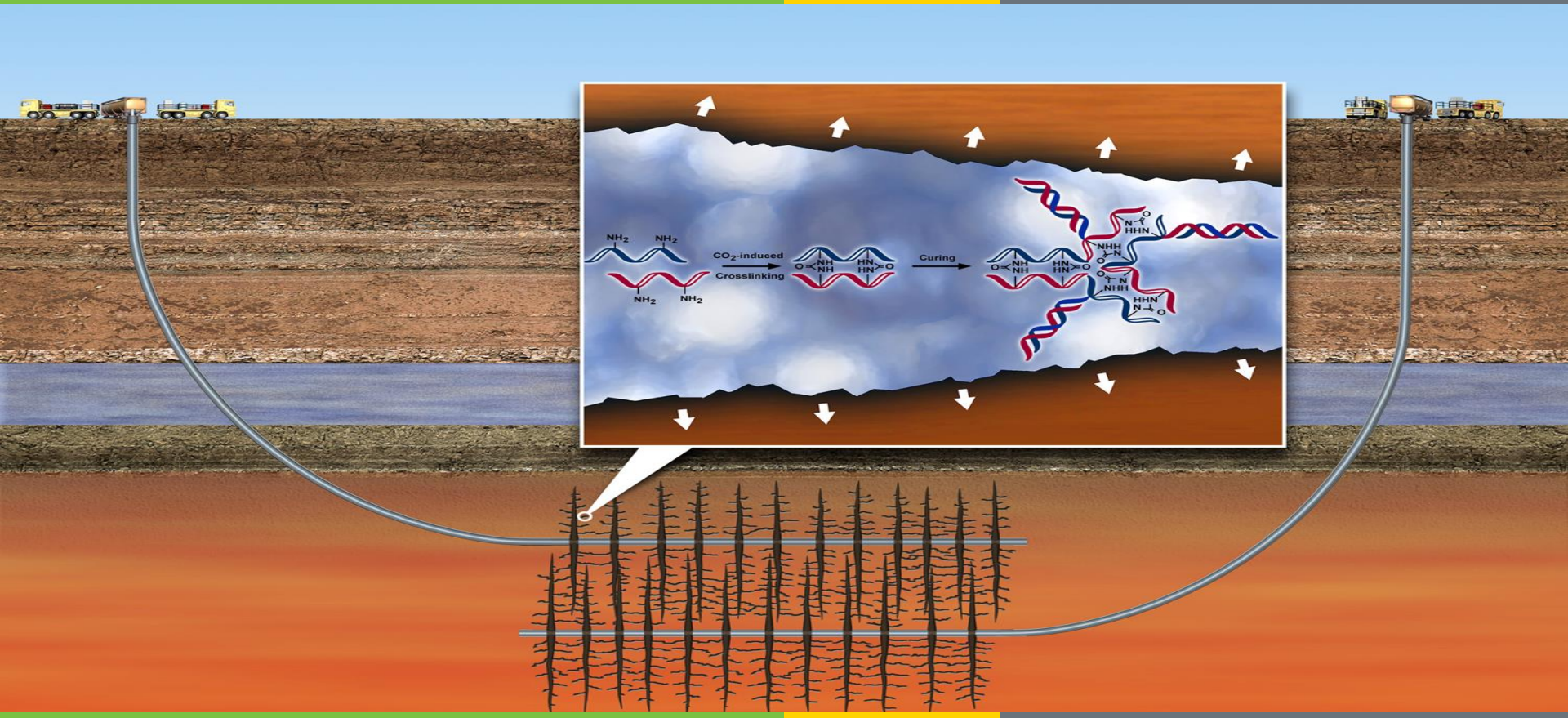


Reservoir Stimulation Optimization with Operational Monitoring for Creations of EGS

Project Officer: Lauren Boyd

Total Project Funding: $785,000

May 11th, 2015

Carlos A. Fernandez

Pacific Northwest National Laboratory

Track Name

Relevance/Impact of Research

Project Objectives

- **To cost-effectively enhance permeability of geothermal reservoirs and increase energy production rates**
- Advance characterization/monitoring methods at the lab-scale (fluid chemistry, stimulation, etc.)

Project supports three GTO goals:

- **Develop the ability to create EGS reservoirs with the technical characteristics required for economic viability**
- Develop improved tools for the characterization and modeling of the subsurface at EGS project sites: *via applying in-operando monitoring and ex-situ characterization and computational modeling tools to optimize stimulation processes at the lab scale*
- Demonstrate ability to accurately describe the physical characteristics of created EGS reservoirs: *via throughout characterization of lab scale reservoir rock samples before and after stimulation*

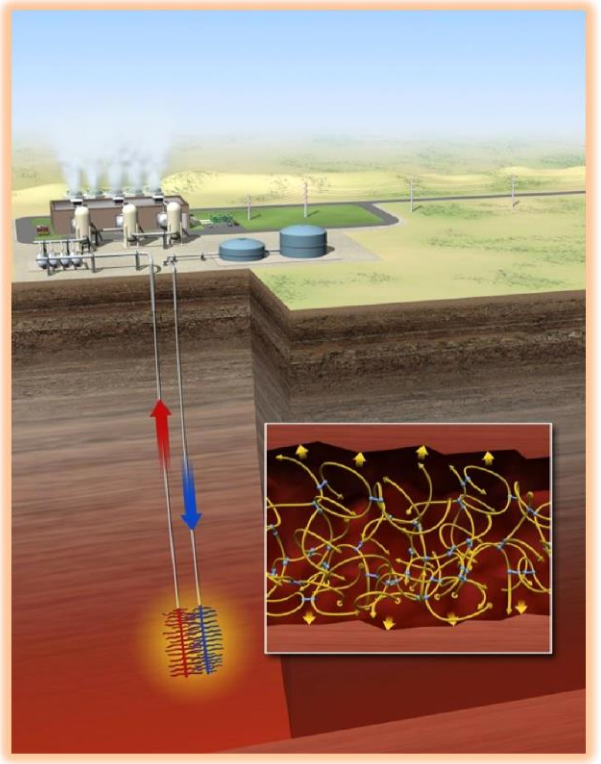
Relevance/Impact of Research

Project Innovation

Stimuli-responsive, rheoreversible fracturing fluids that introduces additional mechanical stress in confined environments at EGS temperatures (150-400 ºC)

Project Impact

- **It could reduce costs** in terms of number of stimulation stages, pumping costs and infrastructure
- It could **significantly reduce water usage** during stimulation
- **Will reduce environmental concerns**:
  - high thermal stability of fluid component (polymer)
  - non-toxic
  - can reduce concentration and number of chemical additives (polymer solution is biocide, corrosion inhibitor, with adjustable rheology)
  - potentially recyclable



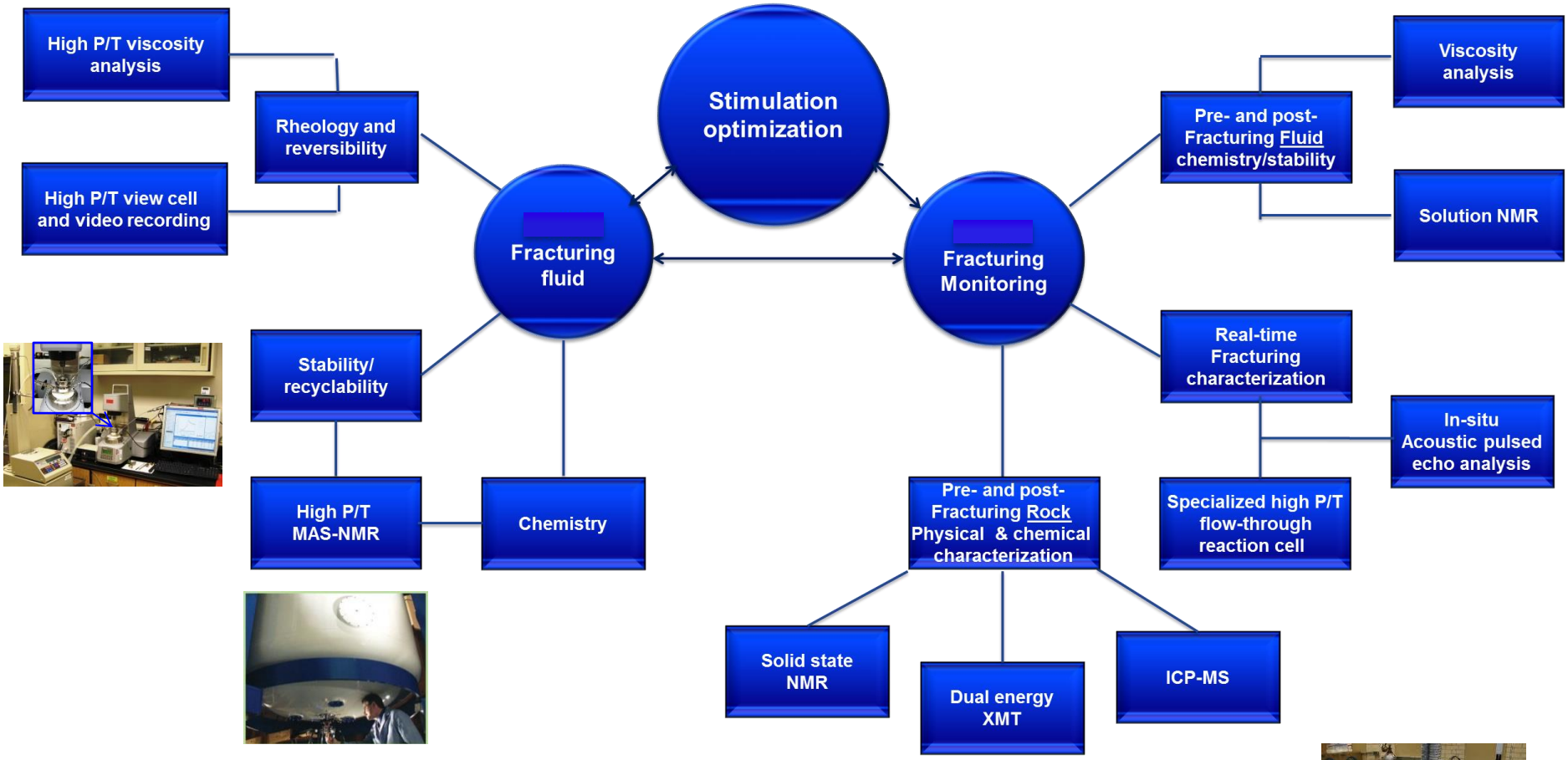
Scientific/Technical Approach

- **To design novel stimuli-responsive fracturing fluids:**
  - That undergo volume expansions that can create/propagate fracture networks
  - Where the expansion can be triggered using a renewable resource
  - Where the fluid component is inexpensive, non-toxic, thermally stable and potentially recyclable
  - That can be implemented in most, if not all, EGS reservoirs in the USA

- **Design and build/modify a set of tools for evaluation/optimization of the fracturing fluids performance including:**
  - Understanding and controlling/optimizing the chemistry responsible for the volume expansion
  - Studying fluids rheological properties and their variation with P, T, pH and shear rate
  - Performing lab-scale stimulation and in-operando monitoring experiments simulating EGS conditions (realistic ranges of confining P/T/pH and seismic monitoring)
  - Performing ex-situ 3D microtomography and computational fluid dynamics modeling

Ultimately fill all the knowledge gaps on this novel fracturing fluid towards licensing this technology

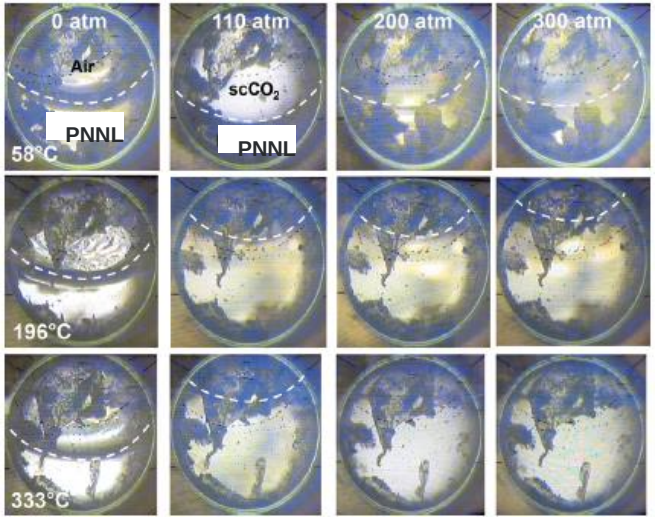
Scientific/Technical Approach

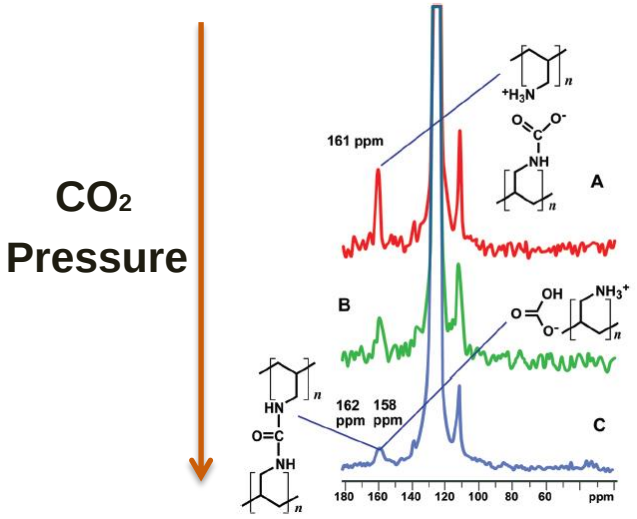


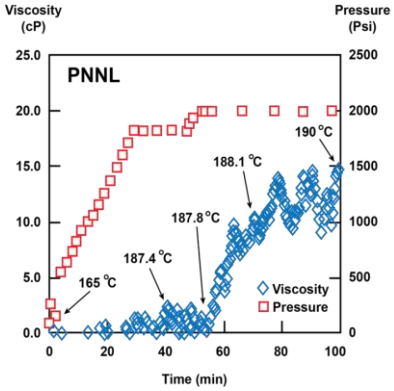
- **Advance hydraulic fracturing fluids**
- **Advance characterization/validation capability**
- **Ultimately, optimize stimulation to increase energy production rates**

Accomplishments, Results and Progress

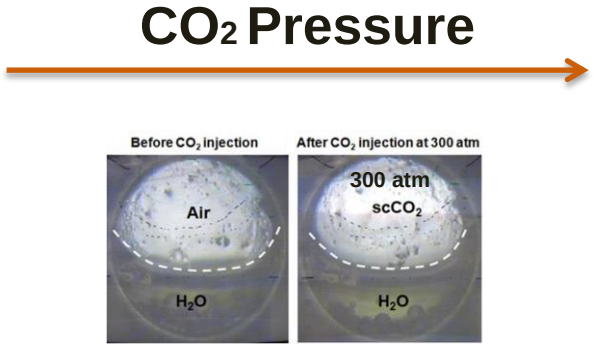
- Introduced a environmentally amenable fracturing fluid technology with volume expansions **up to 2.5 times** the original volume
- Demonstrated rheoreversible behavior
- Polymer **thermally stable (up to 400 °C)**
- Designed and **built a number of characterization and in-situ monitoring tools** for studying fracturing fluids





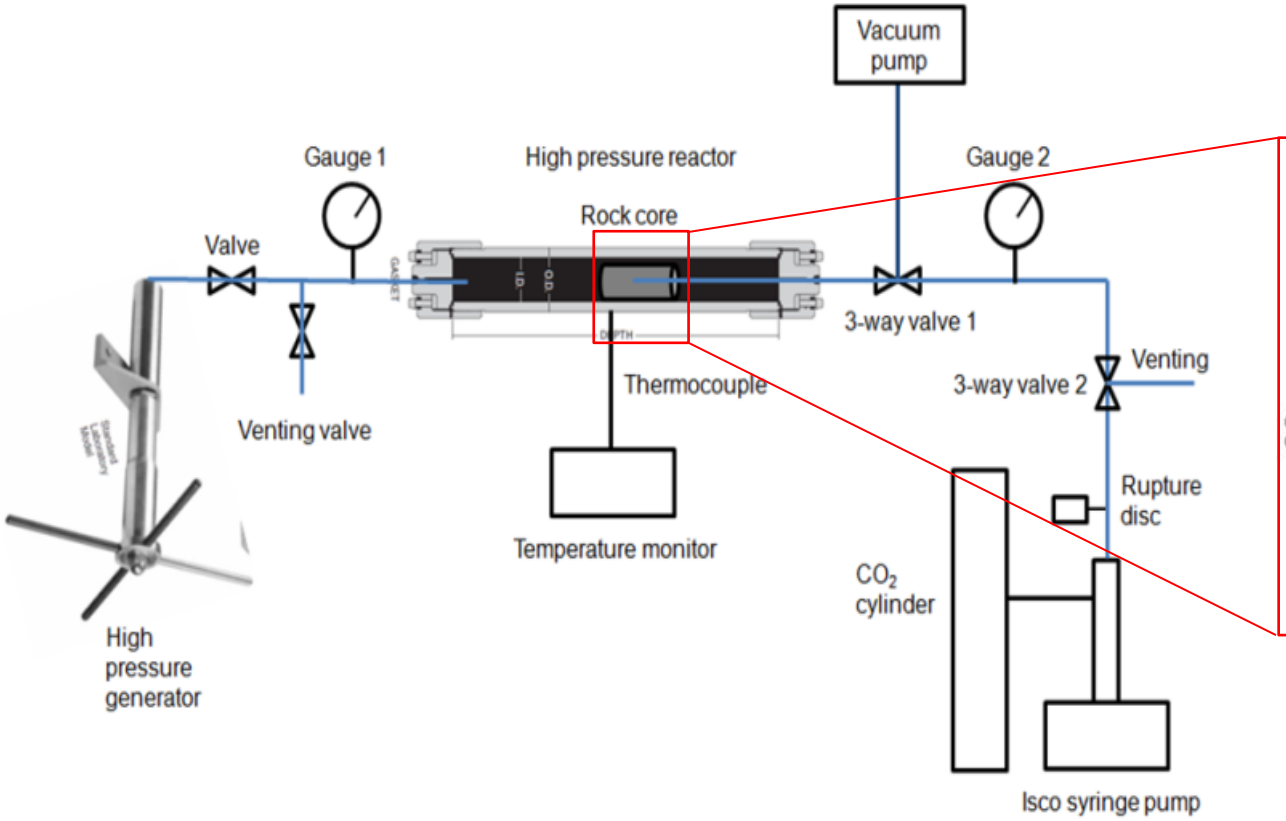


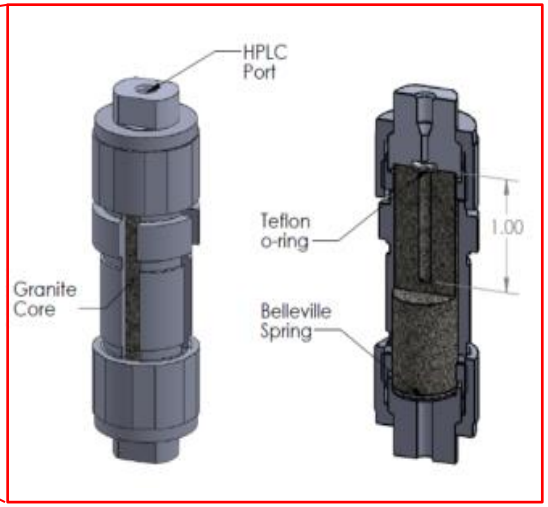
CO2 Pressure



Control experiment

Accomplishments, Results and Progress





Working with geophysicists on experiment design

Right: 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.

Accomplishments, Results and Progress

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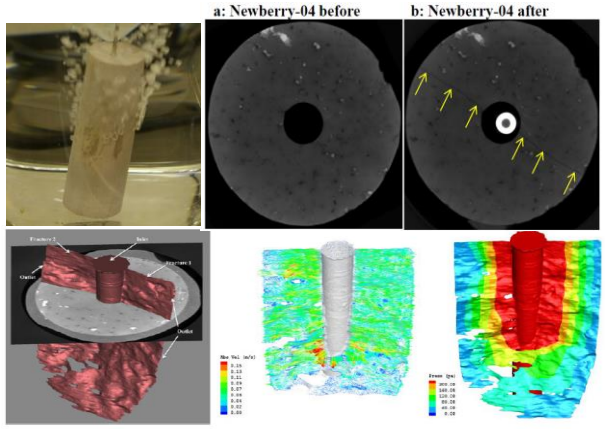
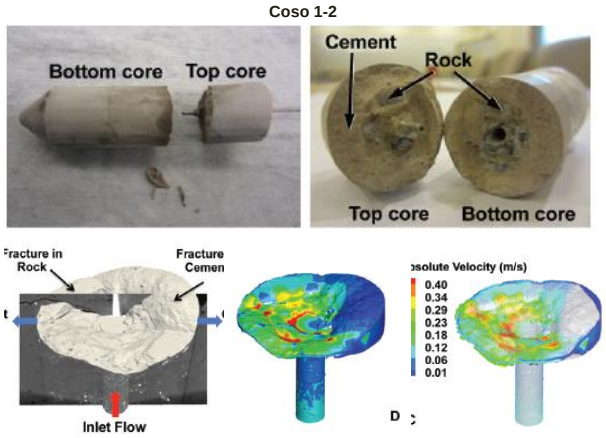
Confining P/T conditions:
150 ºC and 3500 psi



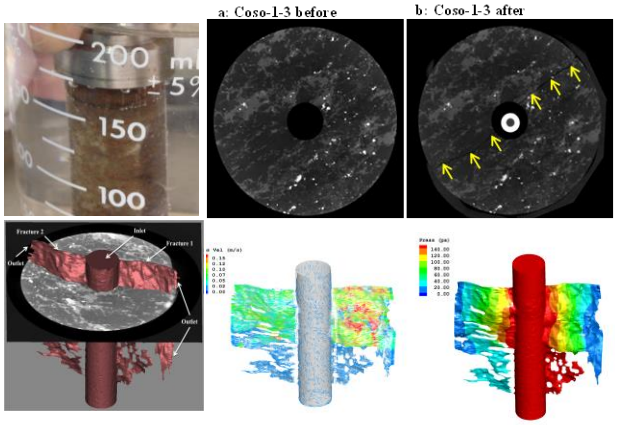
Bulk Permeability: Before: <1μD
After: **383 mD**

Confining P/T conditions:
200 ºC and 3500 psi



Bulk Permeability: Before: < 1μD
After: **496 mD**

Confining P/T conditions:
300 ºC and 5000 psi

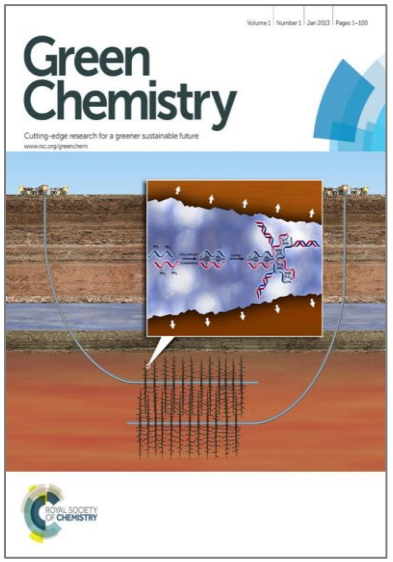


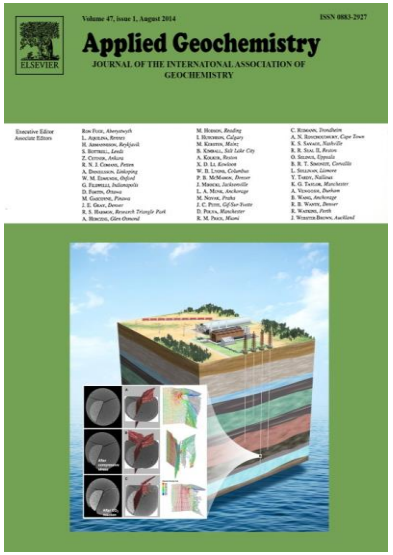
Bulk Permeability. Before: < 1μD
After: **251 mD**

- **PNNL Fluids significantly enhance permeability from μD to hundreds of mD in highly impermeable igneous rock.**
- **The effective pressure** required for stimulation was **significantly lower (up to two orders of magnitude)** as compared to current technology
- Demonstrated reproducible creation of fracture networks in the **entire range of EGS P/T conditions**

Accomplishments, Results and Progress

- **Four publications** including an editorial article, and two journal covers
- **Three IDRs** submitted and a **non-provisional patent application**
- **Seventeen presentations**.
- **Interviewed by Nature** magazine, **World Chemistry** magazine and **Chemical & Engineering News**
- **Eighteen Press Releases** on this technology
- Nominated for the 2015 **PECASE awards**
- Capabilities developed can also be applied for other proposal efforts including FORGE and two multi-lab AOPs submitted to the GTO
- Currently having conversations w/potential collaborators/stakeholders including:
  - **ETH Zurich**
  - **BP**
  - **GE**
  - **YPF (Argentina)**
  - **Chevron**
  - **Shell**
  - **AltaRock**
  - **Raft River**





Proof of concept / capability development

FY13 Original Planned Milestone/ Technical Accomplishment	Actual Milestone/ Technical Accomplishment	Date Completed
Laboratory equipment development and testing (Q1)	Completed	01/20/2013
Obtain and characterize rock samples from EGS sites (Q1)	Completed	01/20/2013
Monitoring system development and testing (Q2)	Completed	03/31/2013
Baseline hydraulic fracturing testing (Q2-Q3)	Completed	6/30/2013
Preliminary reactive-polymer fracturing testing (Q3)	Completed	6/30/2013
Preliminary monitoring-enabled optimal permeability enhancement testing (Q4)	Completed	09/15/2013
Annual Progress Report (Q4)	Completed	09/15/2013
SMART: Demonstrate less than 15% decay of the reactor polymer compounds at EGS temperatures and pressures of 300°C and 550 bar	Completed, no obvious polymer decomposition at temperatures as high as 400 C	09/15/2013
SMART: Achieve greater than 10% volume increase with gel formation at 300°C and 550 bar	Completed	09/15/2013
End of FY13 go/No-go: Demonstrate at least 10% volume expansion of fluid at EGS P/T	Completed, up to 150% volume expansion **(2.5 X original volume)**	09/15/2013

Demonstrated fluid flexibility with EGS P and T

FY14 Original Planned Milestone/ Technical Accomplishment	Actual Milestone/ Technical Accomplishment	Date Completed
Advance experimental setup to increase P/T fracturing conditions, but limited to 500 bar and 300C. (Q1)	Completed	12/15/2013
Demonstrate viscosity increase at low and mid-range pressures (limited to 130bar) and temperatures (limited to 190C). (Q2)	Completed	03/31/2014
Understand CO2-polymer speciation mechanisms at EGS P and T conditions to expand to hydrogels. (Q2)	Completed	03/31/2014
Demonstrate at least 10% fracture propagation increase at a 2nd pH as compared to current technology. (Q3)	Completed	6/30/2014
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. Limited to 500 bar and 300 C. (Q3)	Completed	6/30/2014
Report stress associated to volume expansion as a pressure value in atm (added on 05/14 by GTO). (Q4)	Partially completed, results not in agreement with fracturing experiments	09/15/2014
Publish a minimum of one peer reviewed journal article and complete the Annual Progress Report (Q4)	Completed, **two publications, one non-provisional patent**	09/15/2014
End of FY14 go/No-go: Demonstrate at least 10 % increase in fracture propagation (measured as overall permeability increase) on samples from two different reservoirs at low (200-250 bar, 150 C) and mid-range (450-500 bar, 250 C) P and T conditions as compared to current technology.	Completed. **Overall permeability on fractured samples increased by 4-5l orders of magnitude** (before < 1 μD; after: 50-490 mD) at **effective stress up to two orders of magnitude lower than control exps** .where no polymer was present.	09/15/2014

pH influence on fluid performance/ alternative CO_2 source

FY15 Milestone or Go/No-Go	Status & Expected Completion Date
1. Demonstrate viscosity increase at mid and high range P and T conditions (<350 atm; <300ºC). (Q1)	Completed.12/14/2015
2. A. Demonstrate volume expansion at pH=7 and/or PH=10 at P/T relevant to EGS (Q2) 2. B. Demonstrate increase in viscosity at pH=7 and/or pH=10 at P/T relevant to EGS (Q2)	Completed. 03/20/2015 Partially done, alignment issues with high P/T viscosity vessel. 03/31/2015
3. Demonstrate at least 10% fracture propagation increase at a different pH (compared to current technology) (Q3)	On track (estimated by 06/30/2015)
4. Show volume expansion using sodium bicarbonate as a CO_2 source alternative at EGS P/T (Q3)	On track (estimated by 06/30/2015)
5. Construction of a high P/T packed bed for diffusion tests (Q4)	Not started
6. Results dissemination in conferences and a per-review publication. Annual report. (Q4)	**Submitted two more papers and presented at AGU, AIChe, WGC, GEoProc, BNL workshop**
FY15 go/No-go: Demonstrate the ability to increase overall sample permeability by at least 10% at pH=7 and/or pH=10 compared to current technology	

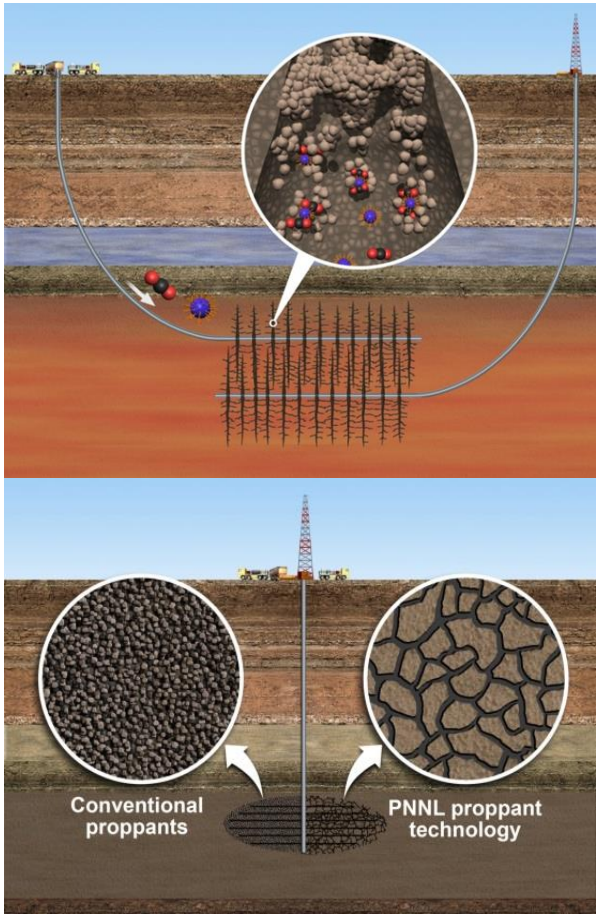
Technical Challenges

- **In-operando acoustic (emission) monitoring** had a number of issues, including the need to purchase a software update and the re-design/calibration of the sensors array.
  - Suggested solution: Software update and re-design/calibration of the sensors array will be part of the work plan for FY16.
  - Importance: Mapping fracture propagation as we perform lab-scale stimulation will greatly help to control/optimize fracturing fluid injection towards enhancing permeability and reducing stimulation cost.

- Although very challenging, we were able to measure **bulk overpressures** as a result of volume expansion. **Values obtained are significantly lower than the overpressures expected based on lab-scale stimulation experiments.**
  - Suggested solution: Developing a plan for FY16 to measure the overpressure ***in-situ*** in standard synthetic materials with well-known intrinsic properties, similar to rock properties.
  - Importance: Determining overpressures is critical to understand and optimize the mechanical stress introduced by the CO_2-triggered volume expansion of these fluids

Future Directions

- **Quantify/optimize overpressure** generated in confined environments (FY16)
- **Can sodium bicarbonate replace CO_2 injection**? How the permeability enhancement and effective stress compares? (FY16)
- **Determine CO_2 diffusion coefficients on viscous fluids and gels**. Data will feed a computational model to estimate diffusion coefficients in large scale fractures (hundred meters)
- **Recycling**: Quantify polymer mass recovered after lab-scale stimulation by simple depressurization at different EGS P/T conditions (FY16-FY17)
- **Foot-scale stimulation studies with seismic monitoring**, engaging in the process stakeholders towards licensing the technology (FY17)
- **Lightweight core/shell proppant technology** (FY16-FY17)



Proposed lightweight core/shell proppant technology

Ultimate goal: Make fracturing fluid technology ready for field deployment

Future Directions

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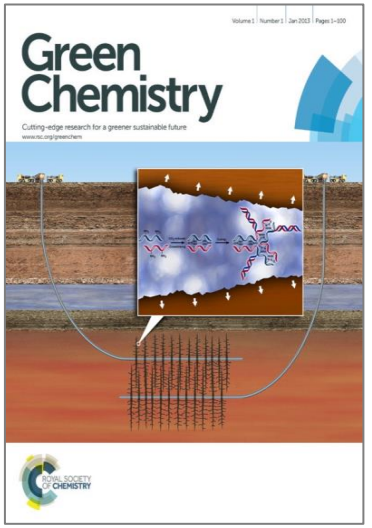
SMART Milestones or Go/No-Go	Status & Expected Completion Date
FY15 Go/No-go: Demonstrate the ability to increase overall sample permeability by at least 10% at pH=7 and/or pH=10 compared to current technology	On track
FY16: Report overpressure values at low, mid and high EGS temperatures	TBD
FY16: CO_2 diffusion coefficients at two P/T conditions in viscous fluids/hydrogels	TBD
FY16: Demonstrate sodium bicarbonate as a alternative for triggering volume expansion and reservoir stimulation at the lab scale.	TBD
FY17. Demonstrate a 50 % recovery of polymer mass after lab-scale stimulation	TBD
FY17: Demonstrate similar permeability enhancement by foot-scale reservoir stimulation	TBD
FY17: Introduce a lightweight core/shell proppant with similar or improved transport and packing properties to current technology w/o the need of introducing thickener chemicals	TBD

Summary Slide

Introduced a Stimuli-Responsive Fracturing Fluid which:

- **Significantly lowers the fracture initiation pressure** in highly impermeable rock as compared to conventional fluids (**up to two orders of magnitude lower**)
- **Increases permeability** in impermeable igneous rock by **4-5 orders of magnitude**
- Will **significantly reduce the volumes of water** required for stimulation
- Is a **considerably more environmentally friendly alternative** to standard methods
- Could **reduce costs** in terms of number of stimulation stages and pumping costs
- Is a **FLEXIBLE TECHNOLOGY:** It can be potentially used in nearly **ALL EGS** reservoirs in the US
- Can be **adapted for tight oil and gas recovery**
- **Has attracted interest on a number of potential stakeholders**



Developed/upgraded a number of capabilities

- **Laboratory-scale stimulation with in-operando monitoring**
- Multi-fluid high pressure (up to 15,000 psi) high temperature (up to 300 ºC) viscosity analysis
- **High P/T** MAS-NMR capability for **in-situ monitoring of fracturing fluids chemistry**

We have identified additional knowledge gaps and work required for field deployment

Additional Information: Press releases on this technology

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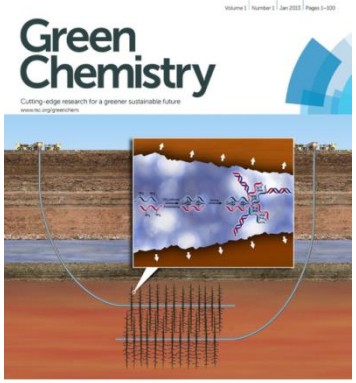
Volume 93 Issue 17 | p. 7 | News of The Week
Issue Date: April 27, 2015 | Web Date: April 23, 2015

Hydrogel Could Green Up Fracking

Sustainability: Expandable hydraulic fluid could cut water and chemical additives used in fracking, but journal editors debate its "greenness"

By Stephen K. Ritter

Department: Science & Technology | Collection: Sustainability, Green Chemistry
News Channels: Environmental SCENE, Materials SCENE
Keywords: fracking, hydraulic fracturing, hydrogel, polyallylamine



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Greener Fracking Tech Reduces Injection of Lots of Wasteful Fluid

Chemical expands underground, so drillers can use less fluid that turns into wastewater

chemistryworld

April 20, 2015 | By Laura Fisher and ChemistryWorld

Researchers in the US have created a chemically-responsive fluid to efficiently fracture rocks that could decrease the amount of energy required for fracking.

Current hydraulic fracturing methods are energy-intensive due to the need to pump, on average, 4 million gallons of water per reservoir, at very high pressures and flow rates deep into the ground. This water also

DOI: 10.1039/C5GC90020D (Editorial) *Green Chem.*, 2015, Advance Article

The subject of 'fracking' in *Green Chemistry*

Dear Readers,

On 2nd October 2014, we received a manuscript entitled "Stimuli-Responsive/Rheoreversible Hydraulic Fracturing Fluids as an Alternative to Support Geothermal and Fossil Energy Production" at the Cambridge office. Upon careful examination of its content, we had a very serious discussion at the Editorial Office on whether the paper would fall within the scope of *Green Chemistry* and should be sent out for review. In the end, we came to the conclusion that we wanted to have the scientific quality examined through the review process and to gather the opinions of those reviewers on whether the work was in keeping with the Principles of Green Chemistry. Three referees suggested acceptance with some revisions, and you can find the final result published in this issue (DOI: 10.1039/C4GC01917B).

chemistryworld

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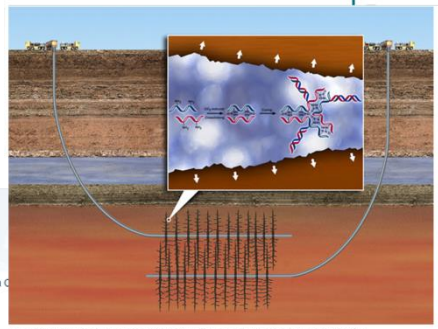
Making fracking greener

14 April 2015 Laura Fisher



News Center

U.S. DEPARTMENT OF ENERGY

Packing heat: New fluid makes untapped geothermal energy cleaner

Nontoxic solution could cut water use in half for enhanced geothermal systems

April 15, 2015 SHARE

Frances White, PNNL, (509) 375-6904

RICHLAND, Wash. – More American homes could be powered by the earth's natural underground heat with a new, nontoxic and potentially recyclable liquid that is expected to use half as much water as other fluids used to tap into otherwise unreachable geothermal hot spots.

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« Ionic liquid a perfect fit for rare earth recycling
Green Chemistry themed issue on Elemental Recovery and Sustainability now online »

Recent publication in Green Chemistry on fracking – Open Forum

By Alice Jensen, Development Editor.

Green Chemistry has recently published an article on the topic of fracking entitled 'Stimuli-responsive/rheoreversible hydraulic fracturing fluids as a greener alternative to support geothermal and fossil energy production'. This manuscript caused some debate at the Editorial Office in Cambridge due to the controversial nature of fracking and, more specifically, the validity of publishing an article on this topic in *Green Chemistry*.