AREA 2: Novel Materials for Robust Repair of Leaky Wellbores in CO_2 Storage Formations

Project Number DE-FE0009299

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U.S. Department of Energy

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Developing the Technologies and
Infrastructure for CCS

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Presentation Outline

- Motivation and relevance to Program
- Project goals
- Technical status
- Accomplishments
- Summary
- Future plans

Benefit to the Program

- Program goals being addressed
  - Develop and validate technologies to ensure 99% storage permanence
- Project benefits statement
  - Existing wellbores with inadequate or compromised zonal isolation can allow leakage of brine or CO_2 from the storage formation into shallow fresh-water resources or to surface. This project will test a novel pH-triggered polymer gelant which improves existing technologies in two ways: (i) placement of the gelant is straightforward, even into narrow gaps which allow leakage but will not admit a cement slurry, and (ii) the gelant is converted to gel only after contacting the cement and earth formations that contain the leakage path. The benefit to the storage community would be a new technology that would work best where current technology has the greatest difficulty.

Project Overview: Goals and Objectives (1)

- Overall objective: determine performance of pH-triggered polymer gelant as sealant for leakage paths along a wellbore
- Project goals
  – determine optimal gelant composition
  – test capability of optimal formulation in fractured cement cores to withstand pressure gradient applied with acidic brine and CO_2
  – develop models
    - reactive transport of acidic gelant through fracture in alkaline cement
    - Rheology, i.e. viscosity of gelant, yield stress of gel.
  – develop plan for deploying material in field.
- Relevance to Program Goals
  – Novel material to stop hard-to-fix leaks helps achieve 99% storage permanence

Project Overview: Goals and Objectives (2)

- Overall objective: determine performance of pH-triggered polymer gelant as sealant for leakage paths along a wellbore
- Success criteria
  - Capability of pH-triggered gels to stop brine leaks at constant pressure gradient
  - Validated model of acid-consuming reactions and their rates
  - Validated model of gelant/gel rheology including at elevated temperature
  - Capability of gel to stop leaks of bulk phase CO_2 at constant pressure gradient

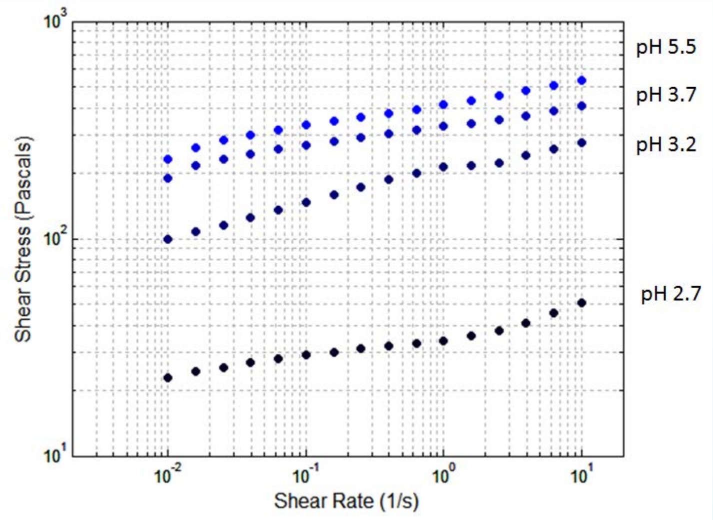
Technical Status

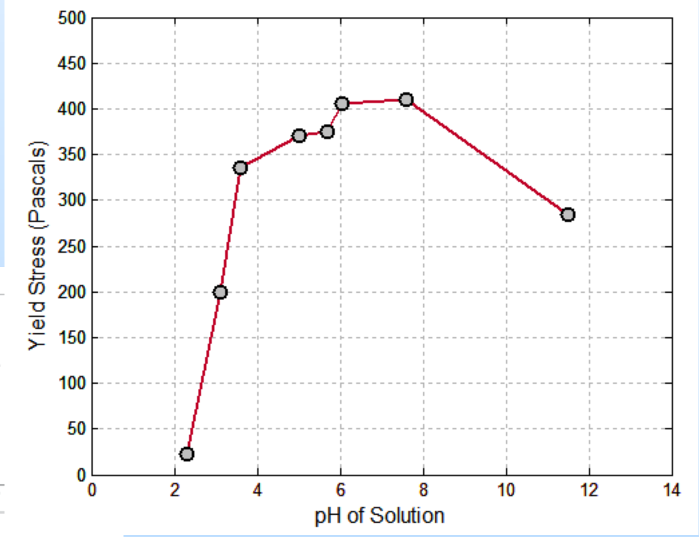
- Gelant and gel rheology measurement and modeling (Mohammad Shafiei)
  - *Quantification of non-Newtonian viscosity of gelant, and yield stress of gel, in terms of pH, polymer concentration, shear rate, salinity, Ca^{++} concentration, and temperature*
- Gelant placement in cement fracture experiments (James Patterson/ Jostine Ho)
  - *Characterization of (i) pressure gradient and effluent pH change during gelant injection, and (ii) pressure build-up after shut-in (due to yield stress of gel), in terms of fracture gap and length, injection rate, salinity, polymer concentration, and temperature*
- Gelant placement reactive transport modeling (Jostine Ho/ Prof. Matt Balhoff's modeling team)
  - *2-D modeling of gelant transport and gel layer formation in model fracture*
  - *3-D modeling of gelant transport and the competing formation of gel layer and Ca-polymer layer in "real" fracture*

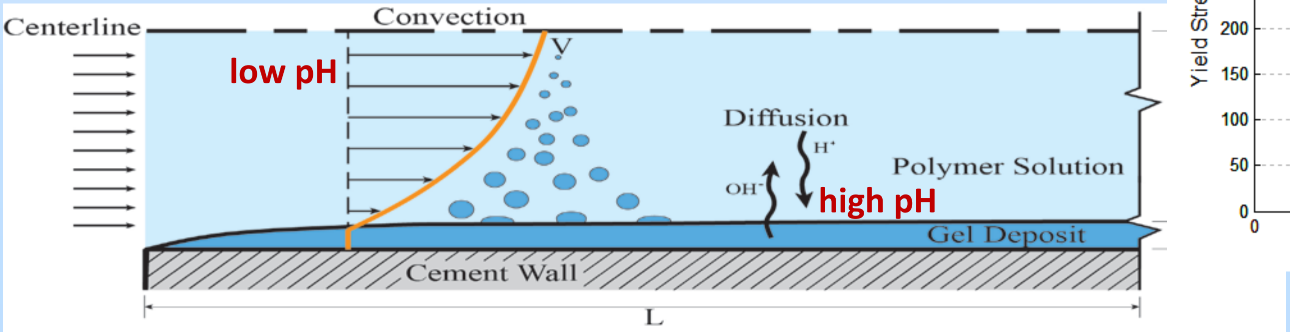
Sealing Cement Fracture using pH Triggered Polymer Gel

Original process concept:

- Injection of solid polymer microgel dispersion in low pH condition
- Diffusion of OH^- out of cement to form a thin gel layer on cement surface, which drastically reduces further “leaching out” of OH^- and allows rapid propagation of the low-viscosity solid microgel in the fracture
- Subsequent shut-in allows formation of gel with high yield-stress throughout the fracture, blocking any leakage flow





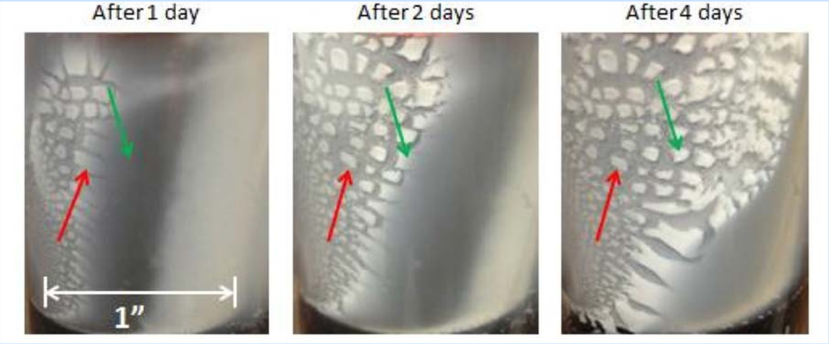


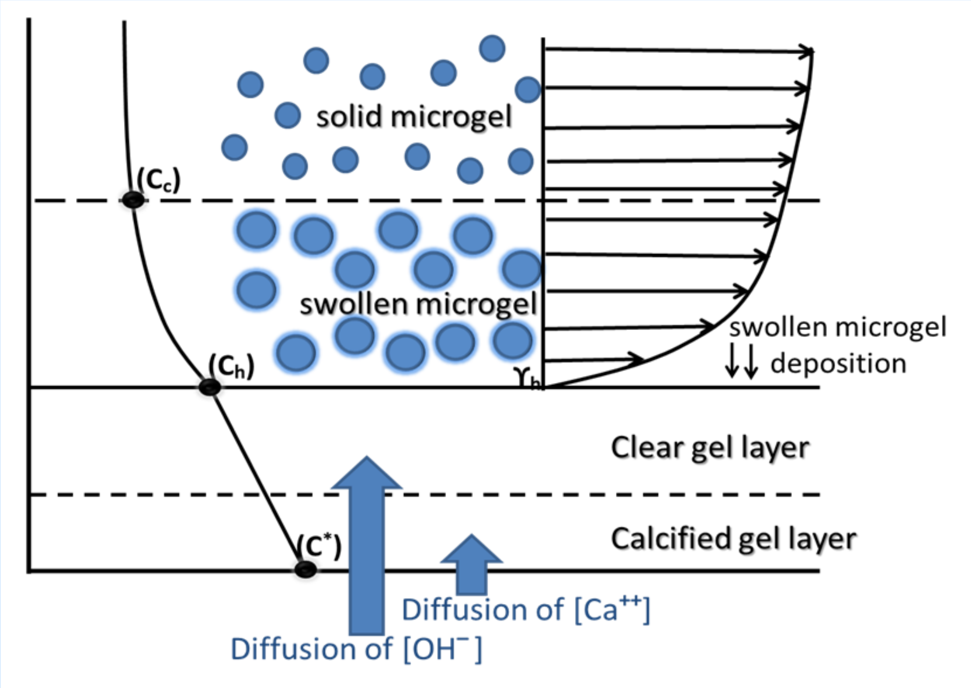
Sealing Cement Fracture using pH Triggered Polymer Gel

Modified process to remedy complication:

- In addition to OH^-, Ca^{++} ion also diffuses out from cement, which causes the contraction of swollen gel network. Water expelled from the contracted gel sometimes forms water channel
- Before polymer gelant injection, the fracture is pre-flushed with a small bank of chelating agent, such as EDTA or Na phosphate, to remove Ca^{++} from a thin layer of cement
- Subsequent polymer gelant injection allows formation of a layer of the yield-stress gel on the fracture surface, preventing the formation of the (Ca-polymer)

Contraction of swollen gel network by Ca^{++} ion

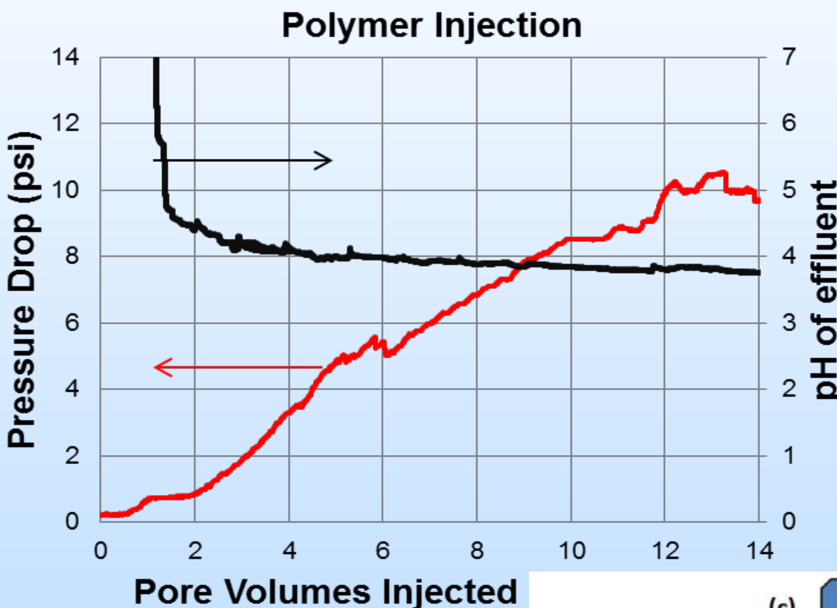


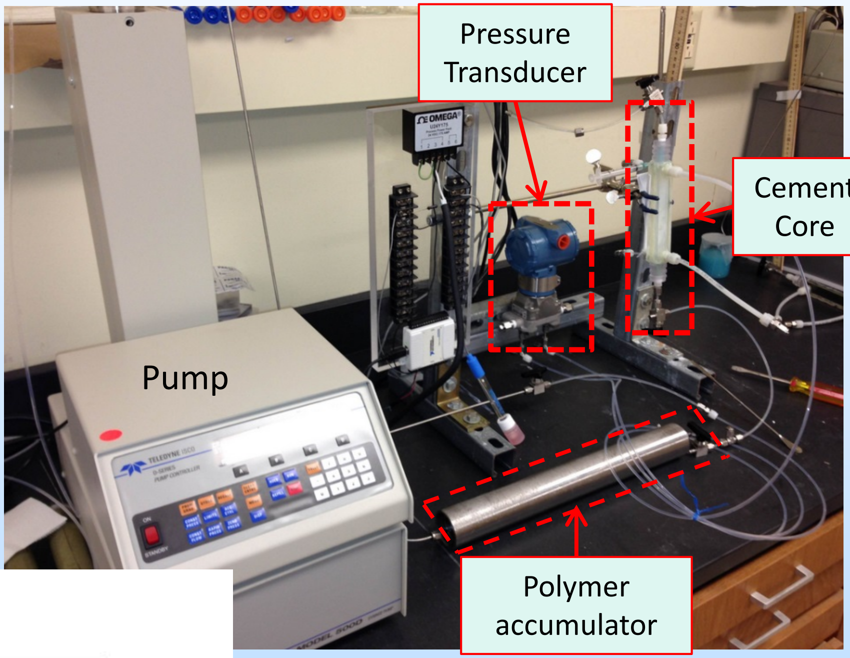


Injecting pH Triggered Polymer Gelant through Fractured Cement

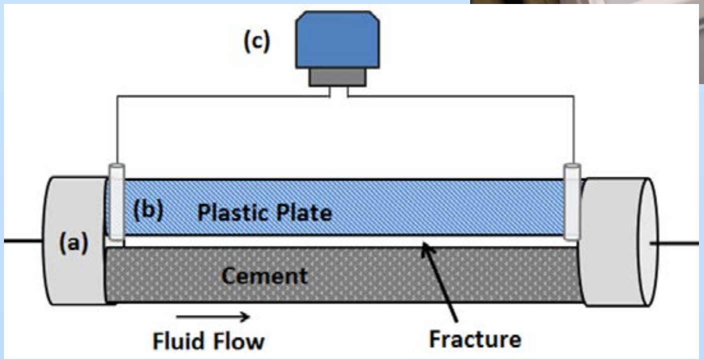
Key performance measures:

- Placing low viscosity reactive polymer into the entire length of narrow leakage paths, so that flow blocking gel is formed after shut in
- Ability of gelled polymer to withstand brine/ CO_2 imposed pressure gradient





"Half-fracture" with plastic plate for visual observation of gelling dynamics



Fracture generation using Brazilian test

Injecting pH Triggered Polymer Gelant through Fractured Cement

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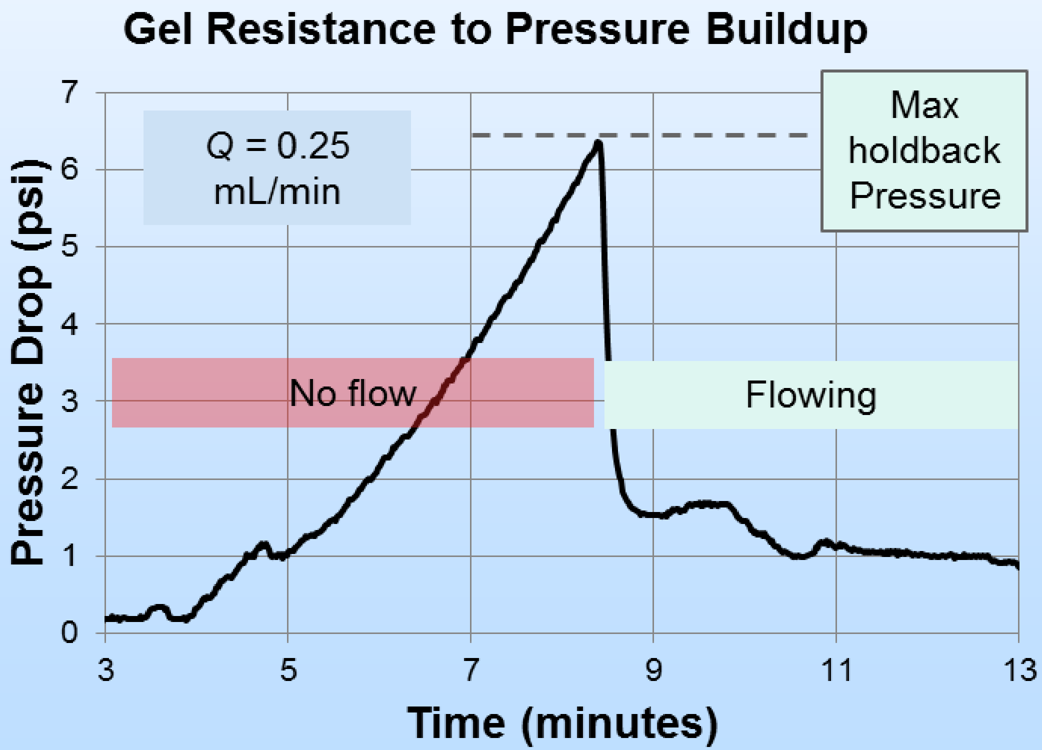


Core 6FP-29

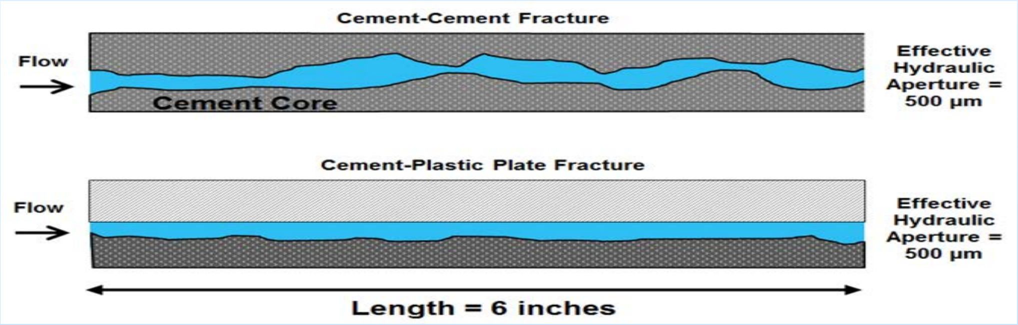
2 wt% Carbopol 934

Placed under 2.6 psi/ft pressure holdback since June 12, 2014

6'' Cement Fracture Core Experiments

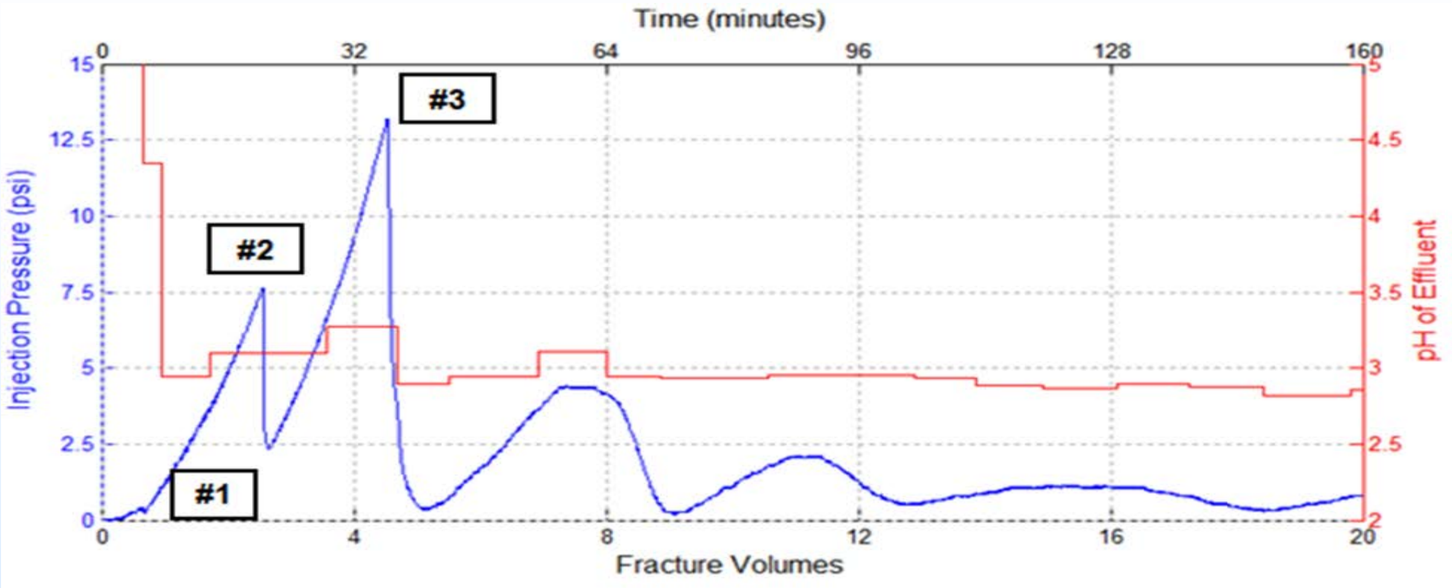
Core	Surface Type	Aperture (mm)	Polymer Wt%	Res Time (min)	Hold Back 2.5 psi/ft
6FP-1	B	0.744	3	32	Broke Through
6FP-2	B	0.388	3	32	14 days
6FP-3	B	0.613	3	16	13 days
6FP-4	S	0.511	3	16	Broke Through
6FP-5	B	0.712	3	16	-
6FP-6	B	0.542	3	16	-
6FP-11	S	0.399	3	1	28 days
6FP-13	S	0.399	3	1	Broke Through
6FP-15	S	0.358	0.5	1	Broke Through
6FP-24	S	0.157/0.168	3	8	> 4 months
6FP-26	S	0.270/0.314	3	8	1 month
6FP-29	S	0.1624	2 wt % Polymer 0.2 wt% Laponite	0.67	8 weeks

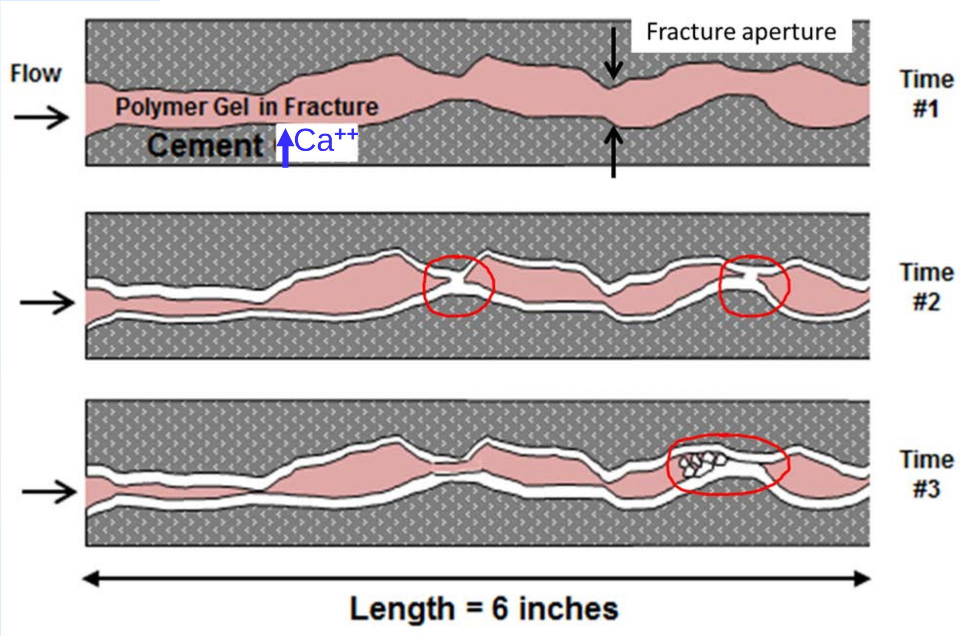
S *= Sawed Fracture Surface*
B *= Brazilian Fracture Surface*
B/B *= Cement-Cement Tensile Fracture*



- Cement-cement tensile fractures (B/B) always exhibited cyclic injection pressure build-up and breakthrough. No other core types exhibited such behavior
- Fractures with smooth surfaces (S) formed uniform gel layer with much less Ca-polymer patch formation
- Competing formation of gel layer and Ca-polymer layer was a strong function of injection rate

Gelant Transport in Cement-Cement Tensile Fracture





- Competing formation of gel layer and Ca-polymer layer needs to be modeled accurately to ensure long-distance transport of gelant

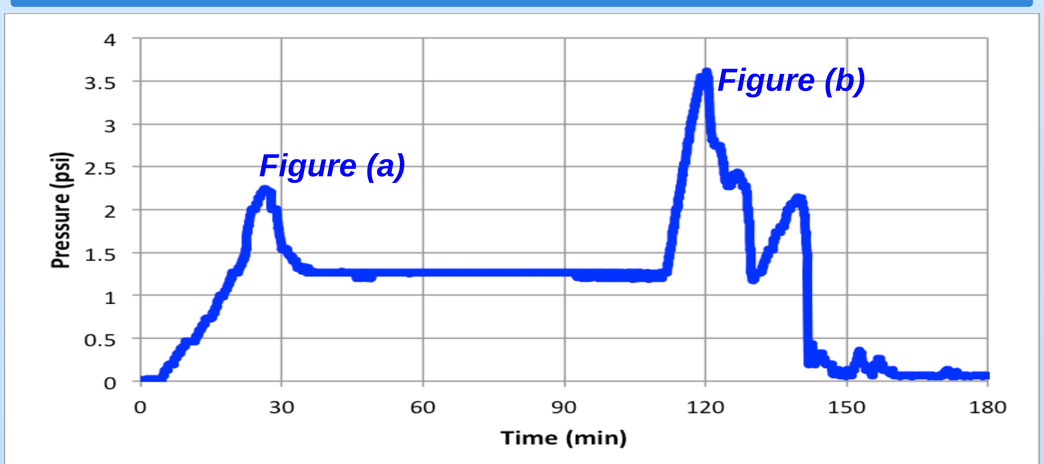
Successful Transport of Gelant with Chelating Agent Pre-flush

Gelant Injection Procedure for Core 6FP-31

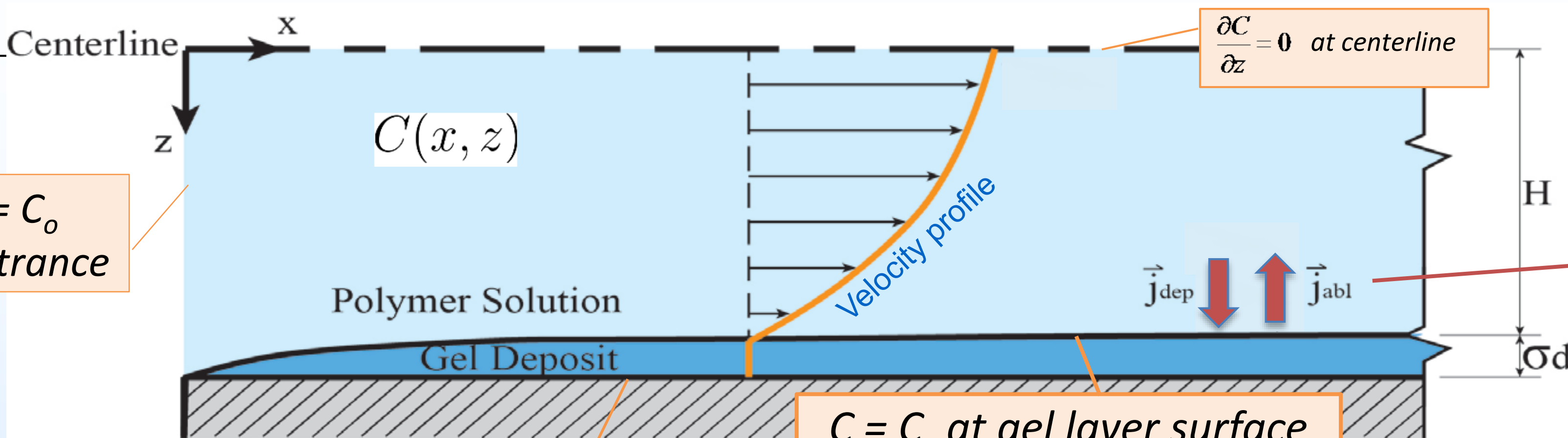
- Pre-treated with *EDTA tetrasodium salt* (activity at 40%) as a chelating agent for 24 hours
- DI water flush before polymer injection to clear out the EDTA in the fracture to prevent rapid gelling of the polymer solution

Core	Fracture Type	Aperture	Injected Solution	Injection Rate	Volume Injected	Flow Initiation Pressure Test
6FP-31	Cement-Plastic Sawed	0.2153 mm	2 wt% Carbopol 934	1.00 mL/min	96 FV	7.2 psi/ft

Flow Initiation (Dynamic) Pressure Test



2-D gelant transport modeling in model fracture



C = C_o at entrance

C = C_c at gel layer surface

C = C_w at cement surface

Proton transport

$$Pe\frac{\partial C}{\partial x} = \frac{\partial^2 C}{\partial z^2}\text{, where } Pe = \frac{\langle V \rangle d^2}{DL}$$

C: dimensionless proton concentration
C_o: initial polymer proton concentration, C_o = 1
C_w: cement wall proton concentration, C_w << 1
D: diffusivity of H^+ in water

Gel layer thickness

- ***Particle diffusion*** *deposition rate:*

$$j_{dep} = D_{gel}\frac{(C_p - C_{gel})}{H}$$

- ***Shear Removal*** *ablation rate:* $j_{abl} = A\tau_w$

j_{dep} >> j_{abl} for gel growth

Deposit thickness:

$$\sigma_d = f(j_{dep}, j_{abl}, t)$$

C_p: microgel concentration in polymer solution, C_{gel}: swollen gel concentration, D_{gel}: swollen gel diffusivity, A: ablation rate constant, τ_w: wall shear stress at z = H

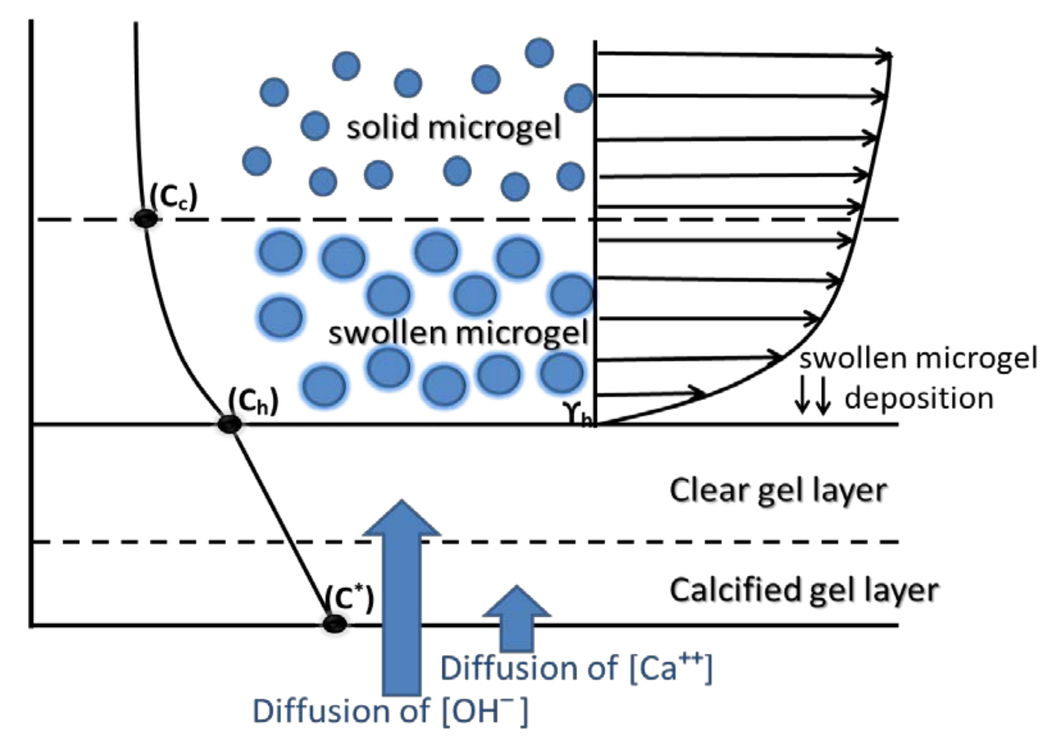
2-D modeling of competing formation of gel layer and Ca-polymer layer

- After the swollen gel layer formation (due to OH^- diffusion), the slow diffusion of Ca^{++} causes contraction of gel network with expulsion of water and formation of Ca-polymer layer
- Removal of Ca^{++} from the near-surface zone of cement, by the chelating agent pre-flush, allows a sufficient formation of swollen gel layer, delaying the Ca^{++} diffusion

Model Formulation

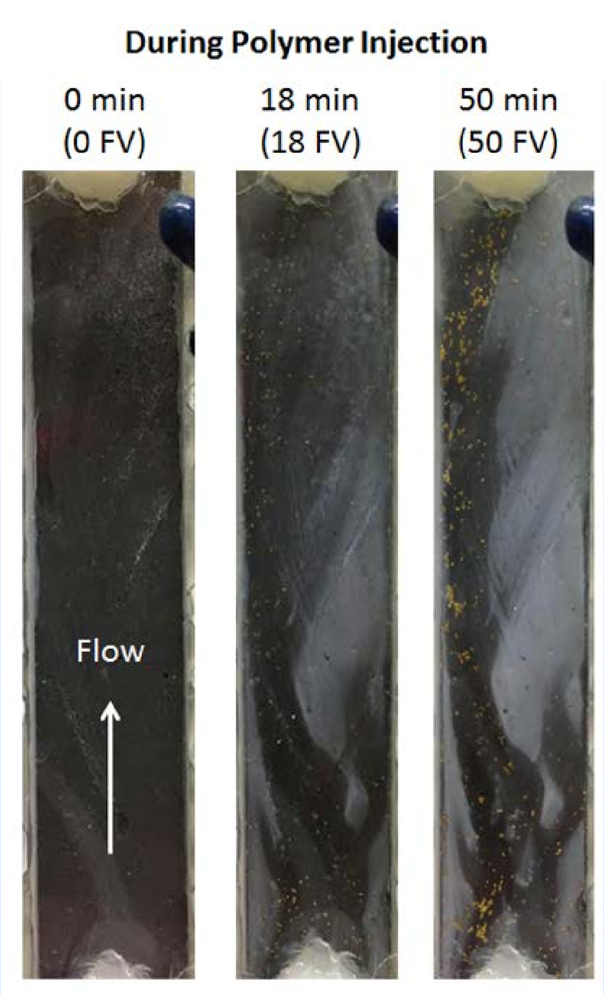
- Z-diffusion of OH^- and Ca^{++} through cement, Ca-polymer layer, and gel layer
- X-convection of gelant and swollen microgel
- Deposition of swollen microgel
- Reactions:

(1) Ca^{++} and polymer and
(2) Ca^{++} and chelating agent



3-D gelant transport modeling in “real” fracture

- Due to the areal variation of fracture gap width, the formation of gel layer and Ca-polymer layer is not uniform
- Formation of Ca-polymer layer from contraction of swollen gel sometimes generates a low-viscosity water channel



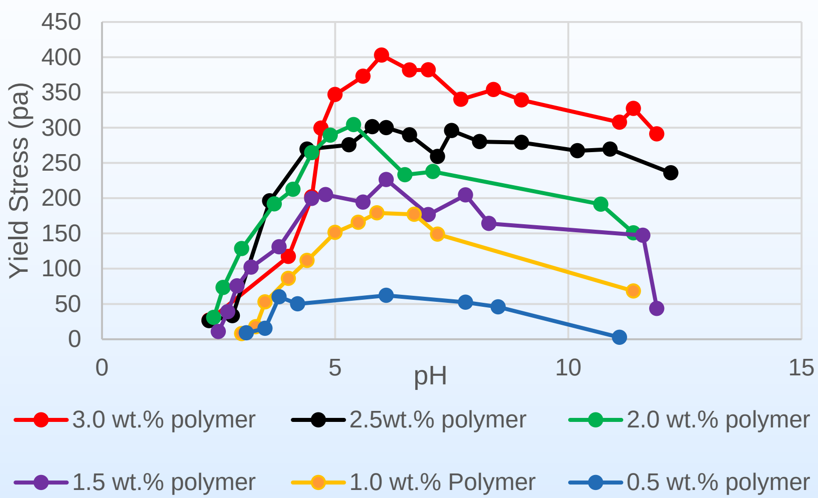
Implementation of Model Features in CFD Software

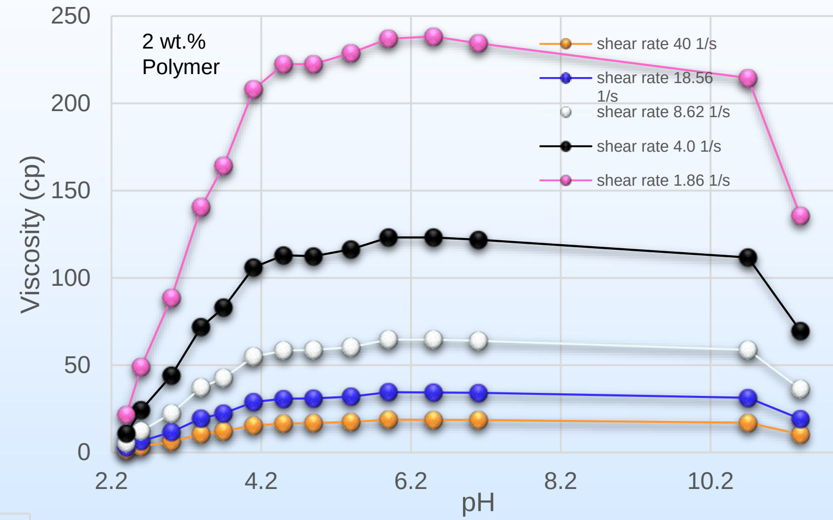
- Gelant and gel rheology
- Kinetics of deposition of swollen microgel
- Reactions:

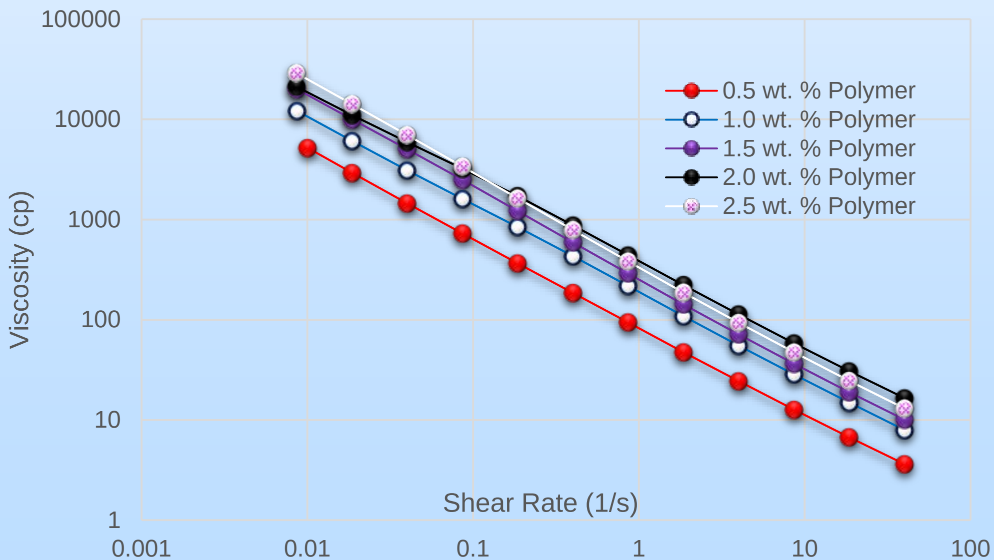
(1) Ca^{++} and polymer and
(2) Ca^{++} and chelating agent

Non-Newtonian viscosity and yield stress of gelant/gel for modeling

Polymer:Carbopol 934







Herschel-Bulkley model

$$\boldsymbol{\tau} = \boldsymbol{\tau_y} + \mathbf{k}\dot{\boldsymbol{\gamma}}^{\mathbf{n}}$$

where $\boldsymbol{\tau}$ and $\boldsymbol{\tau_y}$ are shear stress and yield stress respectively, **k**, **n** are the fluid consistency and fluid behavior indices respectively and $\dot{\boldsymbol{\gamma}}$ is the shear rate.

Accomplishments

- Developed apparatus for visual inspection of gelant placement process, gel transition and occasional development of breakdown pathway
- Found cause for the breakdown pathway development, and developed a remedy of injecting a small bank of chelating agent pre-flush before gelant injection
- Developed mathematical model for gelant placement
- Evaluated rheology (non-Newtonian viscosity of gelant & yield stress of gel) for family of gelants for wide range of conditions
- Addition of a small amount of nano-clay found to help maintain gel's yield stress at conditions gel de-swelling would occur otherwise

Summary

– Key Findings
  - Carbopol family of pH-triggered polymer gelants has rheology useful for stopping leaks along wellbore/rock interface
  - Breakdown pathway development is due to the contraction of gel network resulting from association of Ca^{++} with polymer's COO^{-}
  - Chelating agent pre-flush allows the gelant propagation through fracture, before the Ca-polymer formation

– Lessons Learned
  - Visual flow cell experiments show that dynamics of competing formation of swollen gel layer and Ca-polymer layer controls the gelant transport in the fracture
  - To properly model the long-distance transport of gelant, not only the diffusion of OH^{-} and Ca^{++} and subsequent formation of swollen gel and ca-polymer, but also their areal distribution should be accounted for

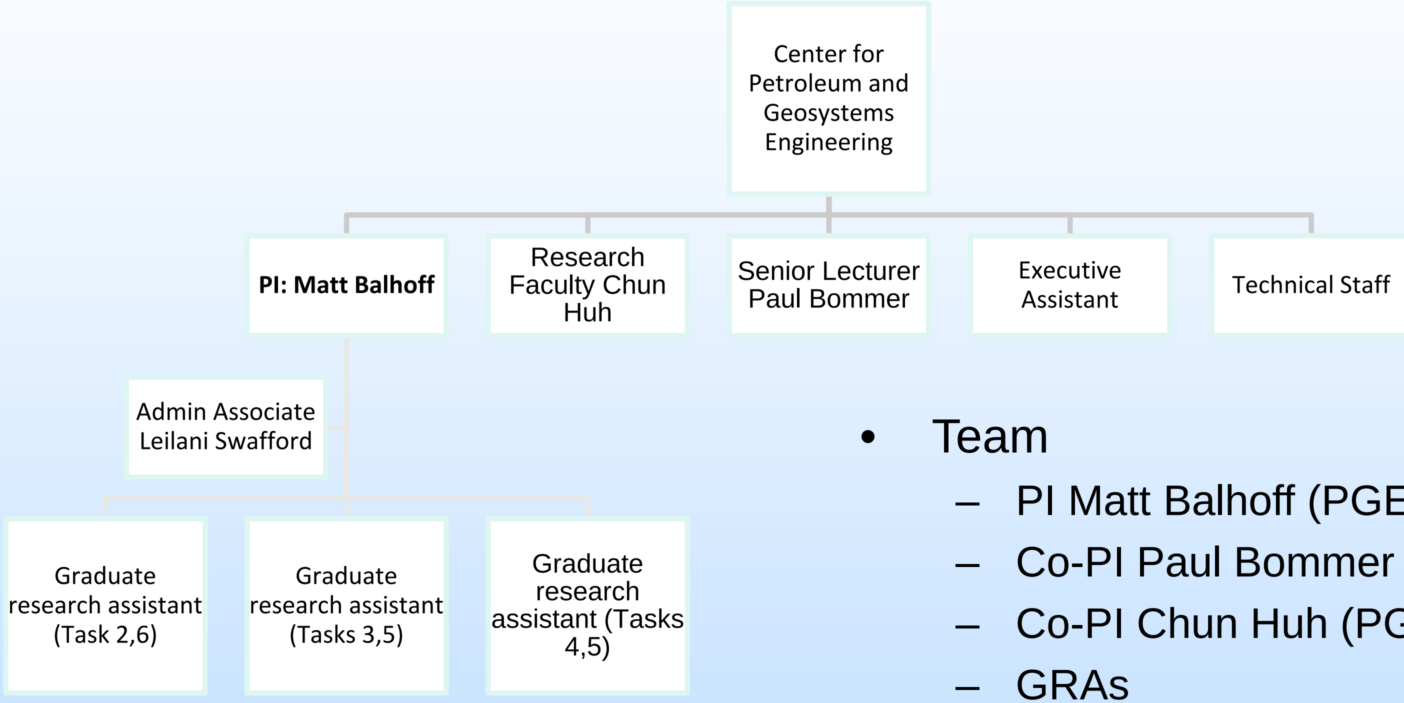
Summary

– Future Plans
  - Gelant transport experiments
    – Develop protocol to optimize the gelant concentration and injection rate; and the chelating agent pre-flush concentration and bank size, for (i) successful transport of gelant to the entire length of fracture; and (ii) the resultant gel's flow blockage ability
    – Test the gel's flow blockage integrity when the fracture boundary is subjected to supercritical CO_2
  - Gelant reactive transport modeling
    – Extend the current 2-D model to account for Ca-polymer formation
    – Extend to 3-D to describe development of the areal distribution of swollen gel layer and Ca-polymer layer
  - Gelant/gel rheology
    – Parameterize Herschel-Bulkley constants in terms of polymer concentration, pH, salinity, Ca^{++}, and temperature for modeling

Appendix

– These slides will not be discussed during the presentation, but are mandatory

Organization Chart



- Team
  - PI Matt Balhoff (PGE)
  - Co-PI Paul Bommer (PGE)
  - Co-PI Chun Huh (PGE)
  - GRAs
    - James Patterson (PGE: MS ‘14)
    - Jostine Ho (PGE)
    - Mohammad Shafiei (ChE)
    - Balhoff’s modeling team (PGE)
  - Collaborator Roger Bonnecaze (ChE)

- Organization
  - Center for Petroleum and Geosystems Engineering
  - Cockrell School of Engineering
  - The University of Texas at Austin

Gantt Chart

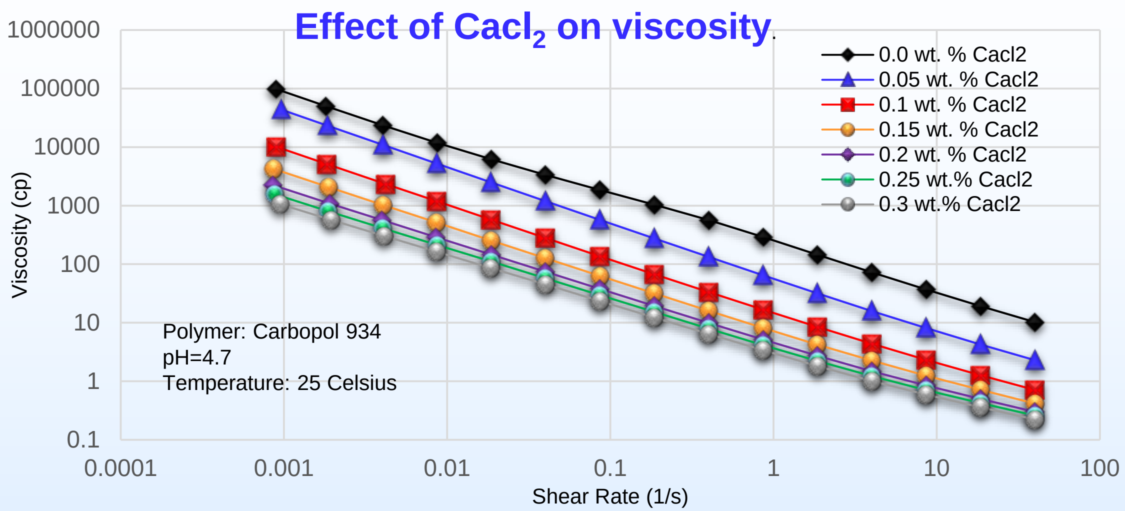
AUG 2014

Phase	Task	Mile-stone	YEAR 1				YEAR 2				YEAR 3				Interdependencies
			1	2	3	4	1	2	3	4	1	2	3	4	
1	1														Project management across all tasks
	2.1	1.A		X											Develop protocol for testing capability of gel to stop leaks
	2.2	1.B					X								Use protocol from Task 2.1 to test gels for range of conditions relevant to geologic storage
	2.3														
	3.1														Develop reactive transport model that accounts for effluent pH measurements in Tasks 2.2 and 2.3
	3.2	1.C						X							Apply model from Task 3.1 to validate reaction rate constants against data from Tasks 2.2 and 2.3
	4.1														Develop model gelant rheology and gel yield stress
	4.2	1.D								X					Apply model from Task 4.1 to measurements from Tasks 2.2 and 2.3
2	5.1	2.A										X			Develop model that integrates components from Tasks 3 and 4 and data from Task 2
	5.2														Apply model from Task 5.1
	6	2.B										X			Use optimal gelant formulations found in Task 2 to test resistance to CO2

Bibliography

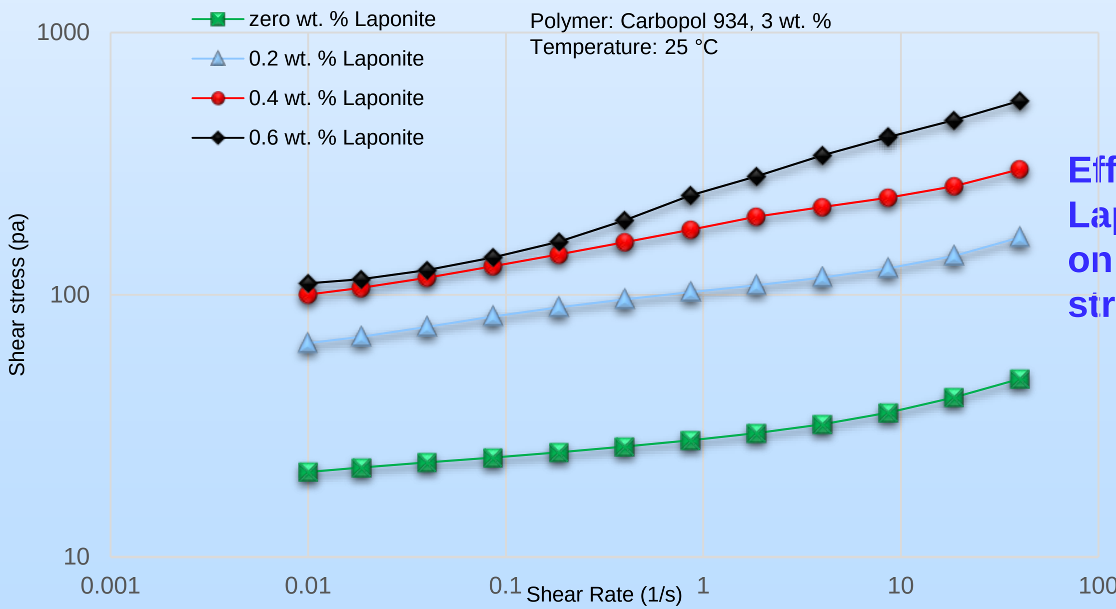
- A paper based on MS Thesis by James Patterson (2014), “Viscosification and solid deposition during reactive transport in a fracture” is ready for submission
- A paper on development of rheological correlations for pH-triggered polymer is in preparation

Use of Nano-clay to Enhance Gel's Yield Stress

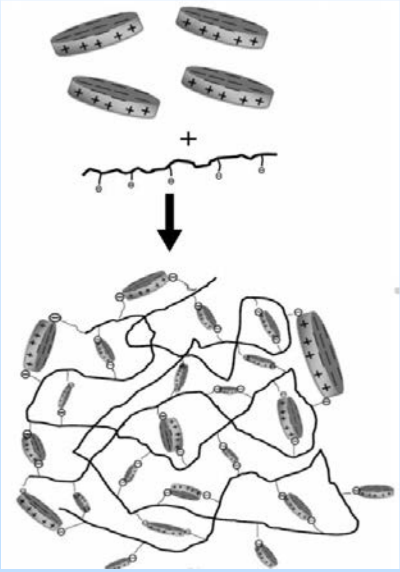


Association of Ca^{++} ion with COO^{-} anion of polymer causes contraction of polymer network.

Addition of a small amount of nanao-clay found to help maintain gel's yield stress at conditions gel de-swelling would occur otherwise.



Effect of Laponite on shear stress.



Interaction between Laponite and polymer
(P. Tongwa and et al., *J. appl. Poly. Sci.*, **128**, 787-794 (2013)).

Effect of NaCl Concentration on Gelant/Gel Viscosity