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

Project Number DE-FE0009299

Steven Bryant

The University of Texas at Austin

U.S. Department of Energy

National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and
Infrastructure for CCS

August 20-22, 2013

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)

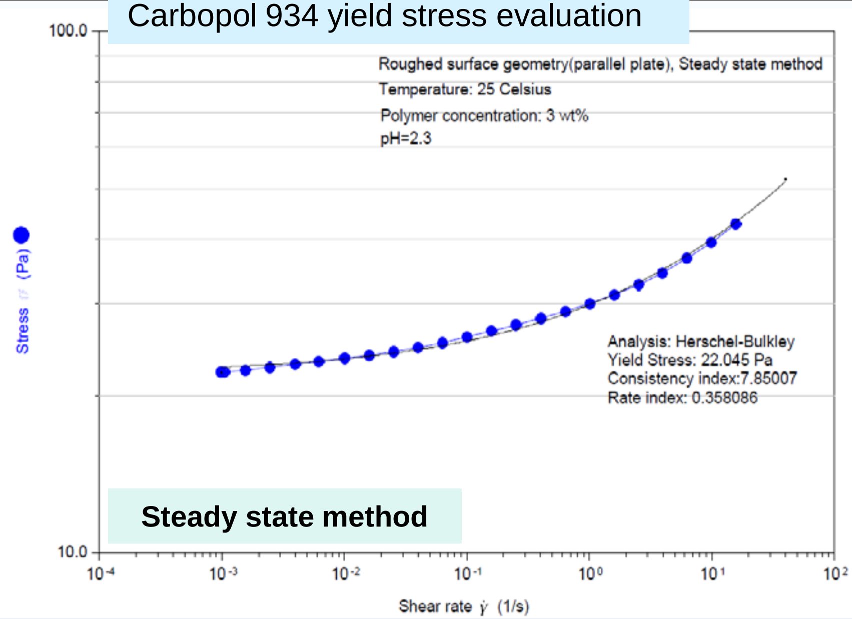
- Overall objective: determine performance of pH-triggered polymer gelant as sealant for leakage paths along a wellbore
- Success criteria
  - Capability of pH-triggered gels to stop brine leaks at constant pressure gradient
  - Validated model of acid-consuming reactions and their rates
  - Validated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

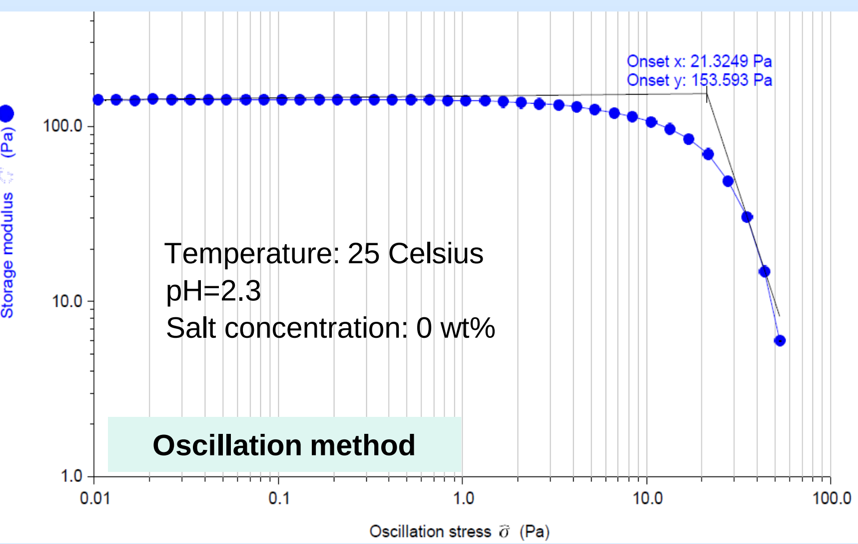
Technical Status

- Gelant and gel rheology measurement and modeling (Mohammad Shafiei)
- Gelant placement in cement fracture experiments (James Patterson)
- Gelant placement reactive transport modeling (Jostine Ho)

pH-triggered gelant is Herschel-Bulkley fluid for wide range of conditions

Carbopol 934 yield stress evaluation





capability of stopping leak

ease of placement

$$\tau = \tau_y + K\dot{\gamma}^n$$

τ_y:yield stress

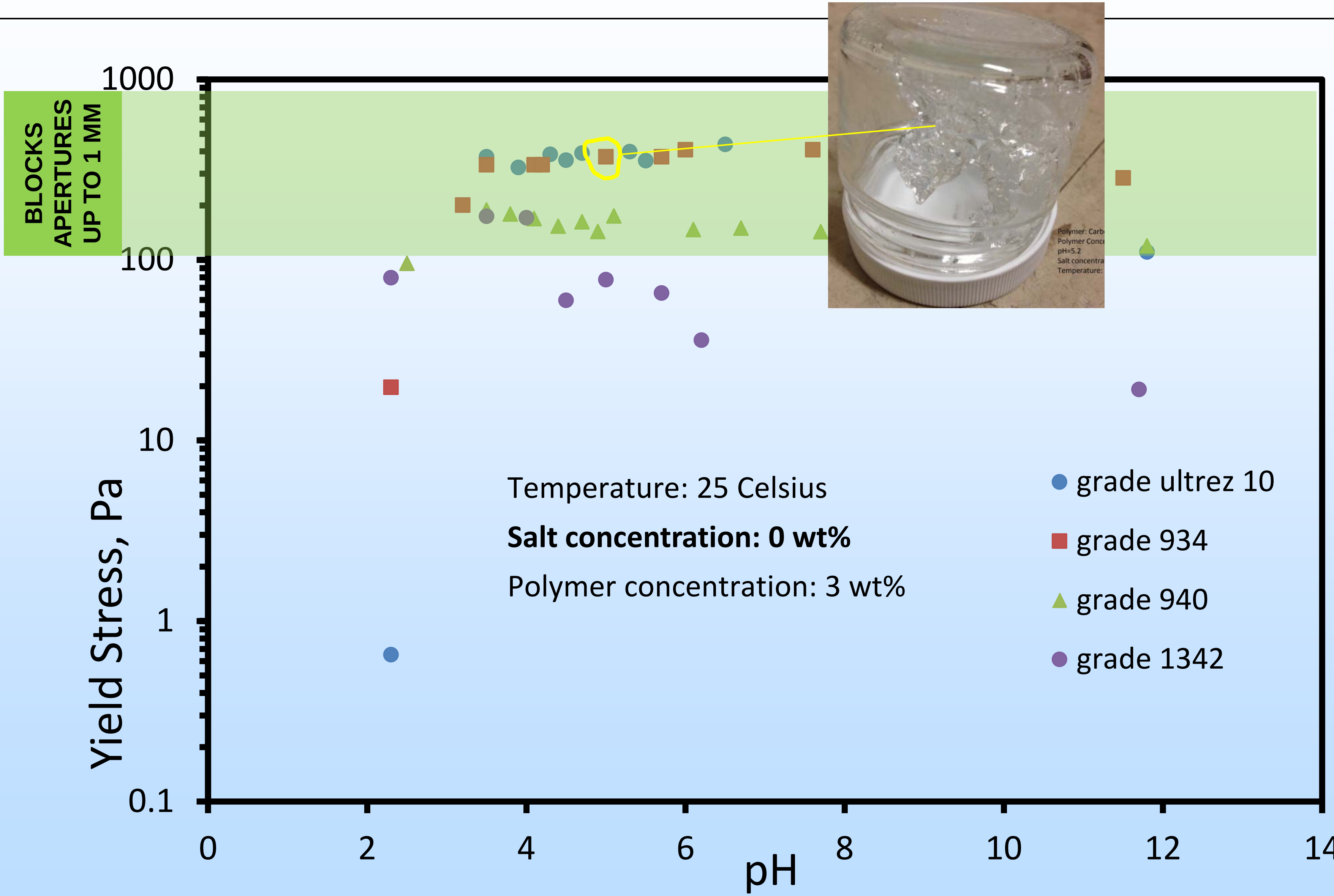
K: consistency index

n: fluid behavior index

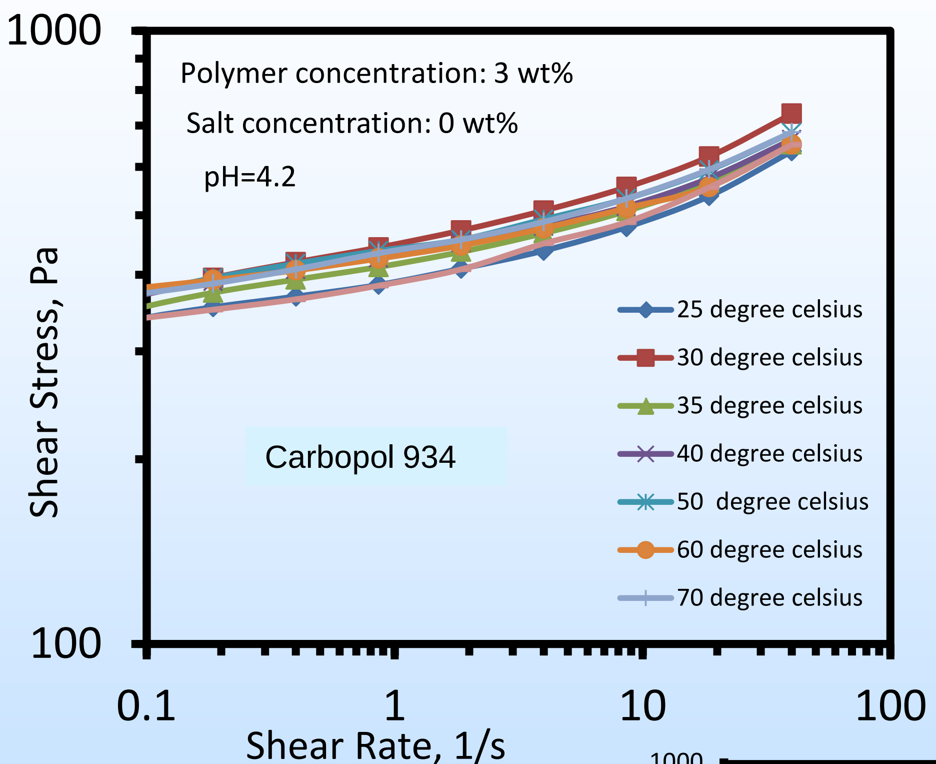
AR G2 Rheometer

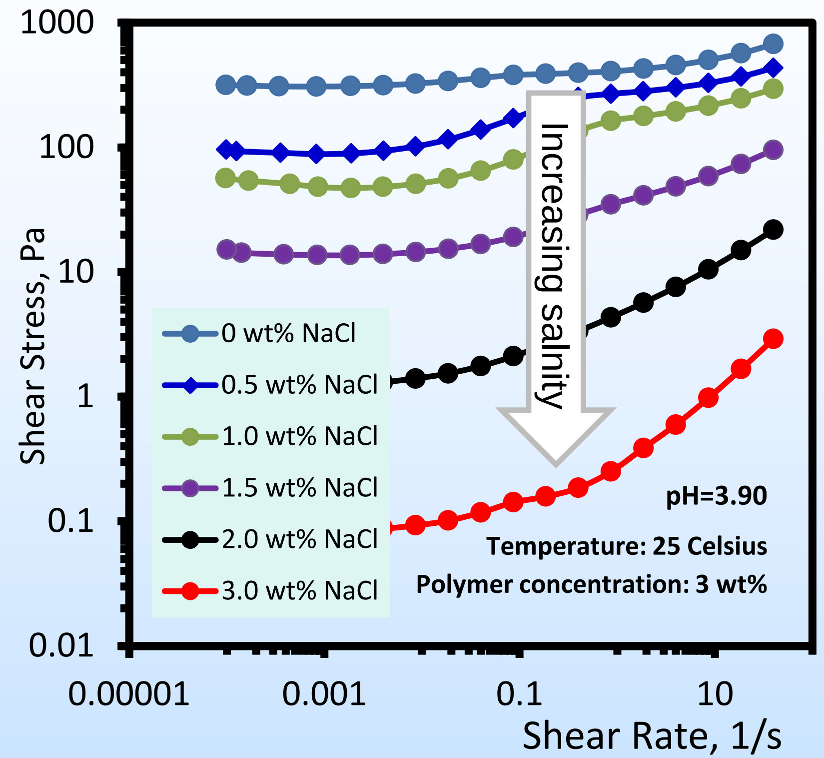
- Measurements from 25 C to 70 C
- Rough surface needed for reliable yield stress measurement
- Methods give same yield stress values for our gelants for wide range of conditions

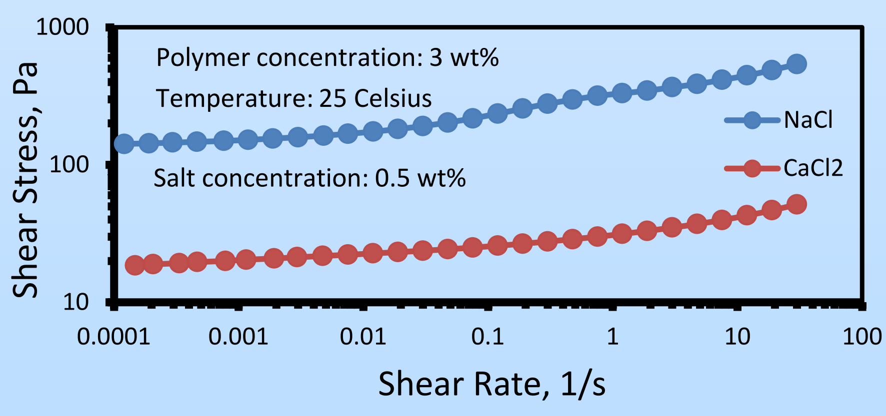
Gelant rheology shows useful yield stress values at pH expected in situ



Gelant rheology weak function of *T*, strong function of salinity and divalent cation

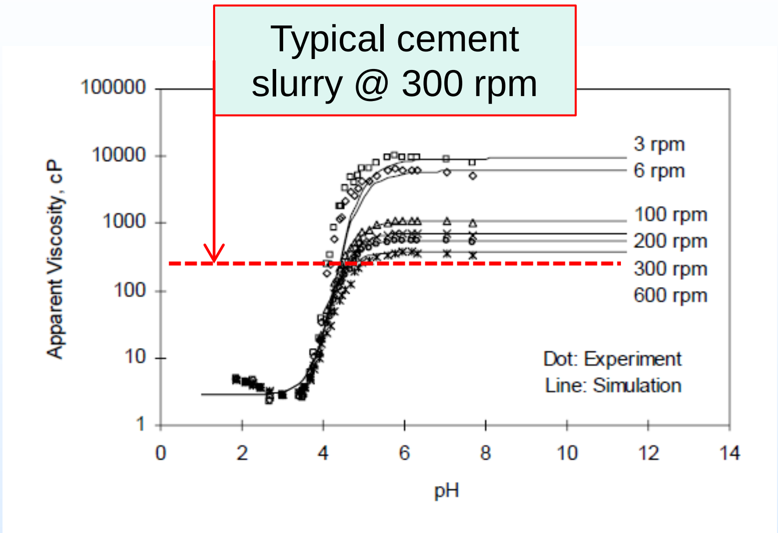


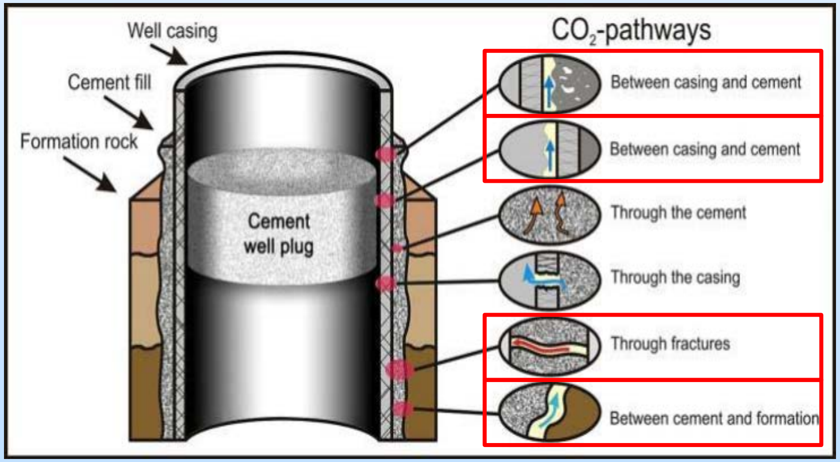




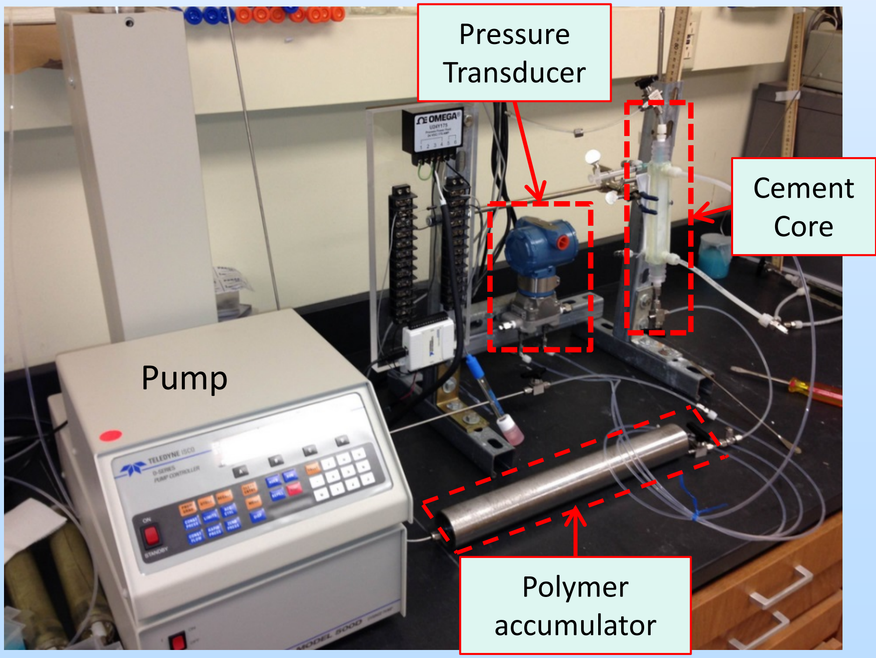
Injecting pH Triggered Polymer Gelant through Fractured Cement

- **Project goal**: feasibility of placing low viscosity reactive polymer into narrow leakage paths which will block flow after shut in
- **Key performance measure**: ability of gelled polymer to withstand brine/ CO_2 imposed pressure gradient



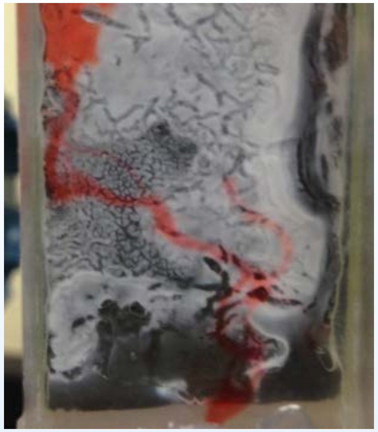


after Nordbotten and Celia, Geological Storage of CO2, 2012

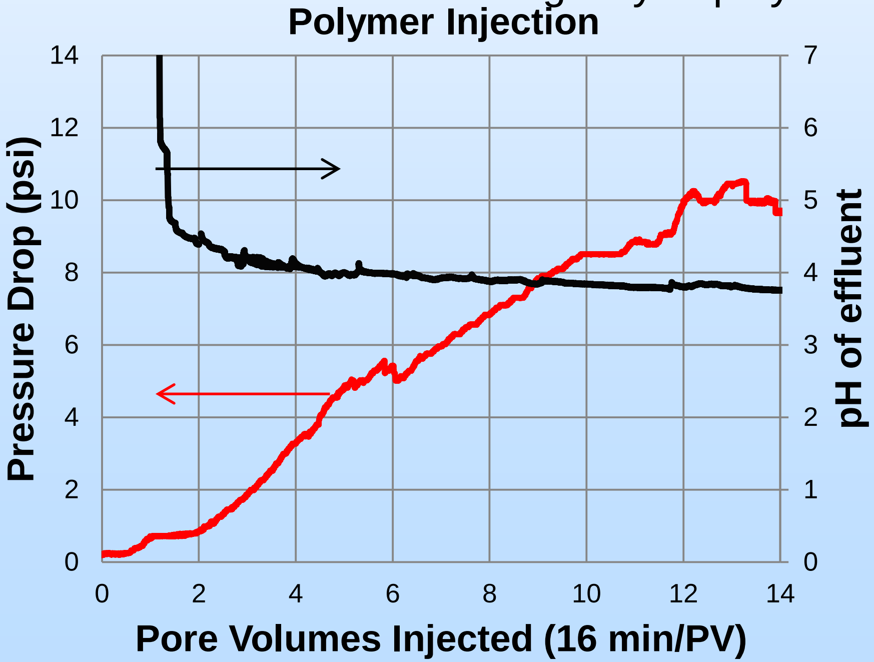


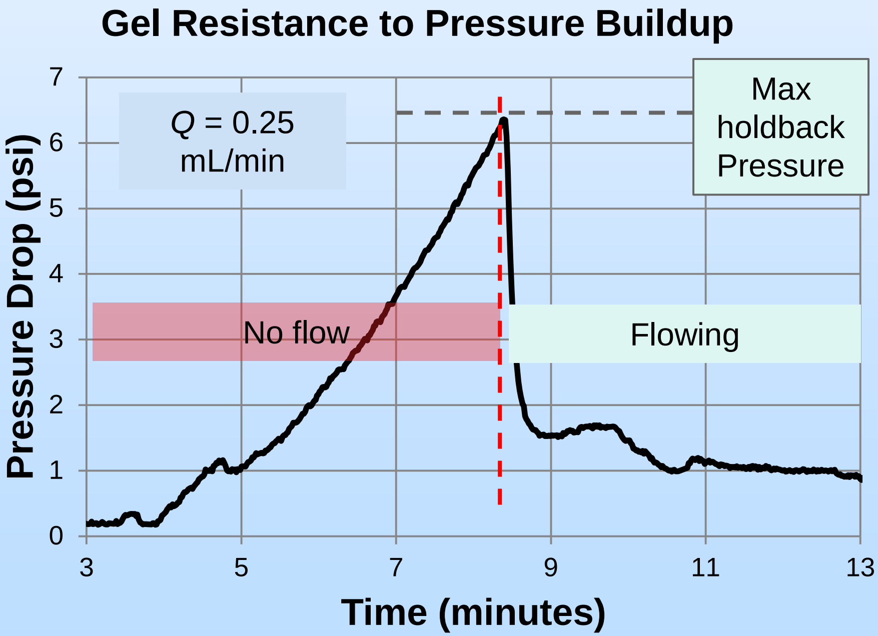
Investigation Methods and Data Gathered

- Poly(acrylic acid) polymer injected into epoxied fractured 6” cement cores; pressure drop and effluent pH are measured; cores are visually inspected
- 4 days of shut in, then
  - Inject brine to determine maximum gel holdback pressure gradient
  - Or apply constant pressure to determine longevity of polymer seal



Brine (red) channeling through gelled polymer





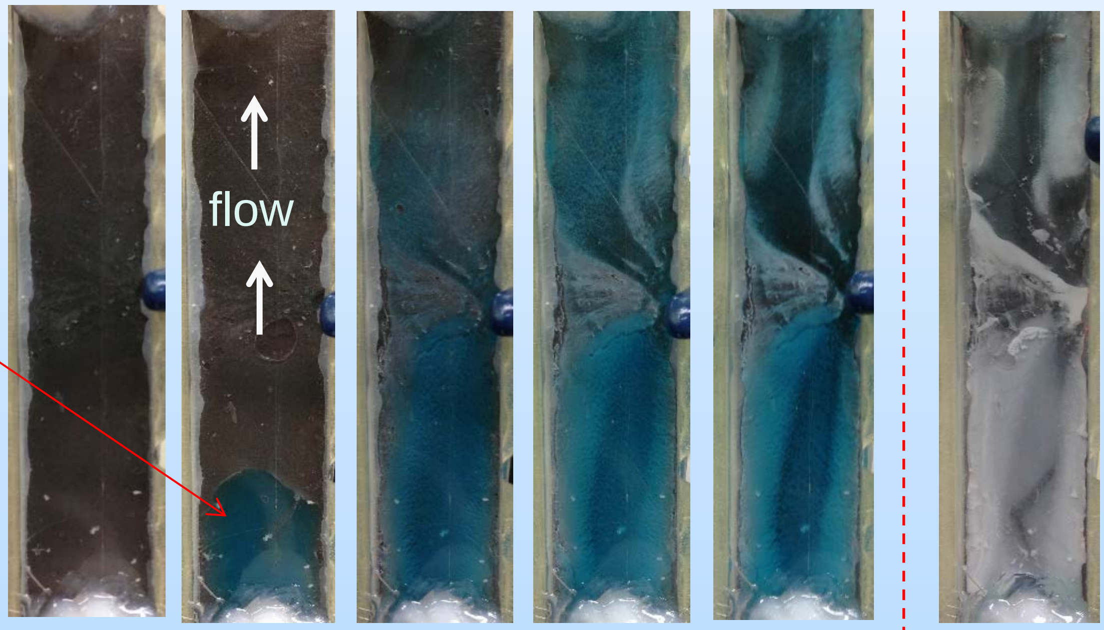
Gelant placement experiments indicate useful properties

- When it works, it works well:
  - Polymer reacts to deposit sponge-like solid on cement face, blocking flow
  - Polymer gel can hold back **up to 18 psi/ft pressure gradient**; can hold back a **6 psi/ft gradient for up to 6 weeks** (so far)
  - When maximum gradient exceeded, **effective permeability ~1000** times smaller than original
- Occasional failure to prevent brine flow; cause under investigation

Progression of polymer (dyed blue) gellation in cement fracture

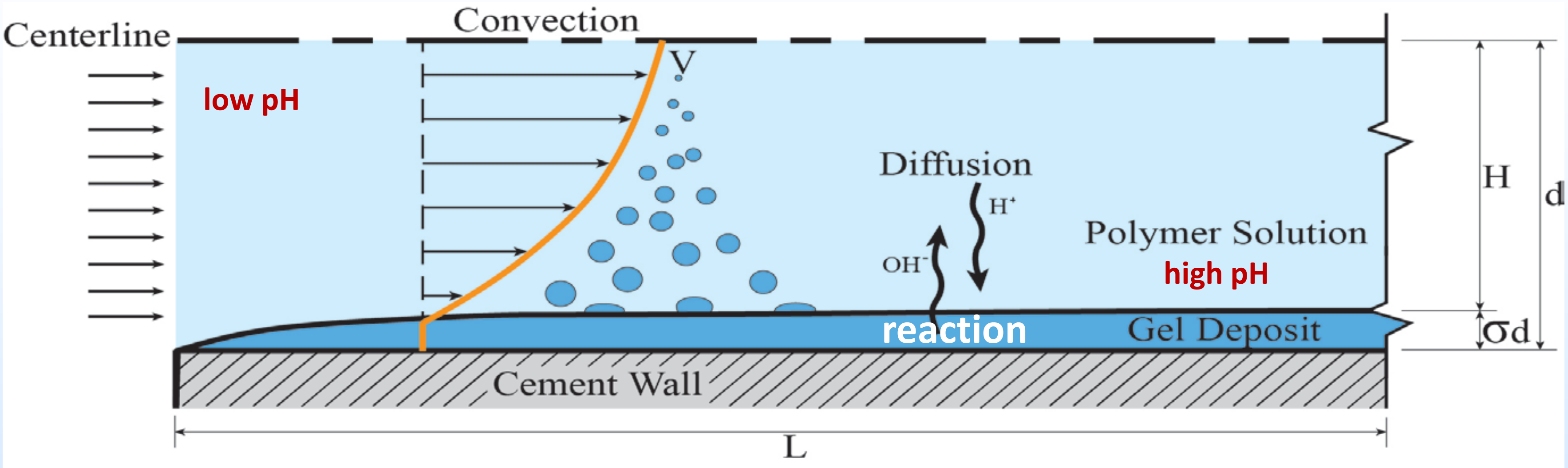
Polymer (dyed blue): 3 wt% Carbopol 934; 0.0 % NaCl

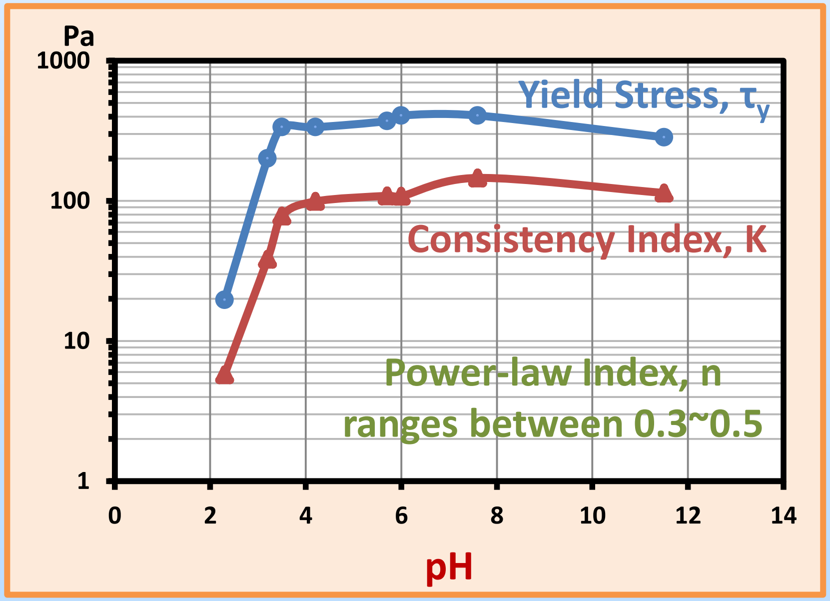
Flow rate: 0.07 mL/min (~1 cm/min)
Temperature: 22º C

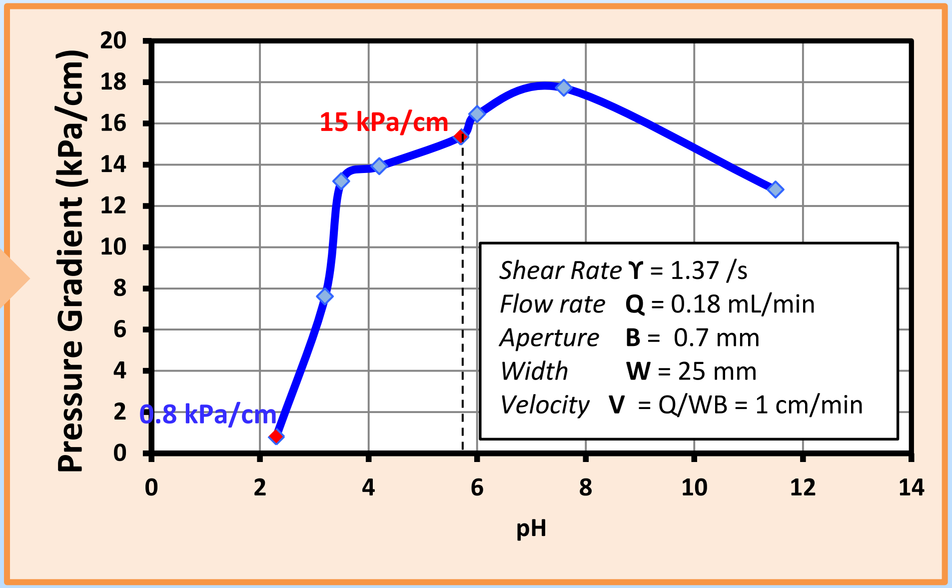


t = 0 min 0 PV | t = 5 min .3 PV | t = 29 min 1.8 PV | t = 50 min 3.2 PV | t = 98 min 6.2 PV | Shut in 48 hours

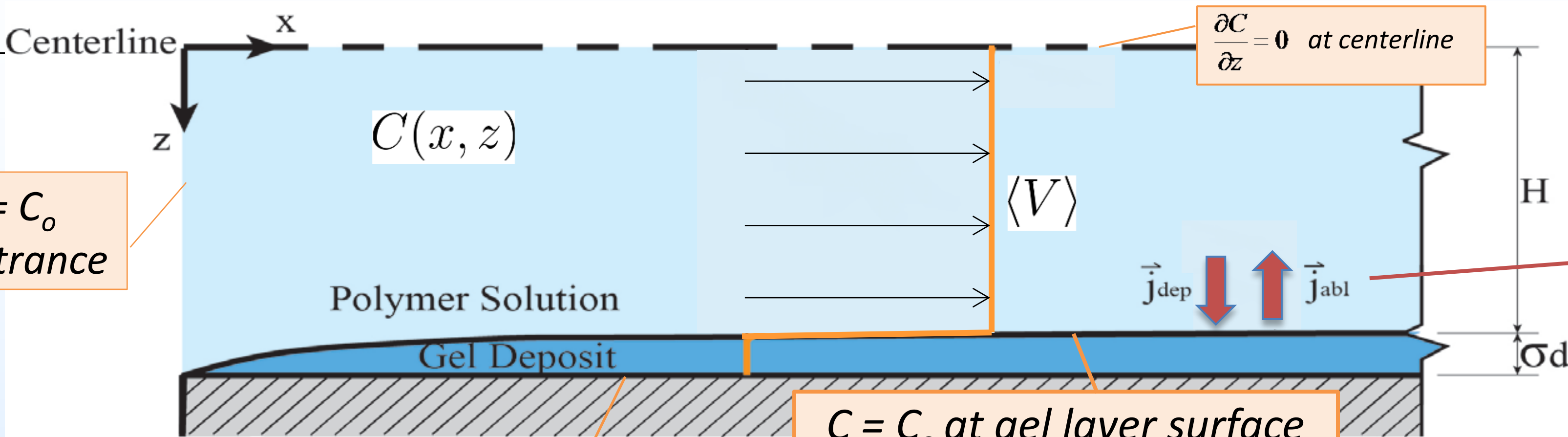
Model couples reactive transport and rheology







Model in fast-reaction plug-flow limit



$\frac{\partial C}{\partial z} = 0$ *at centerline*

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

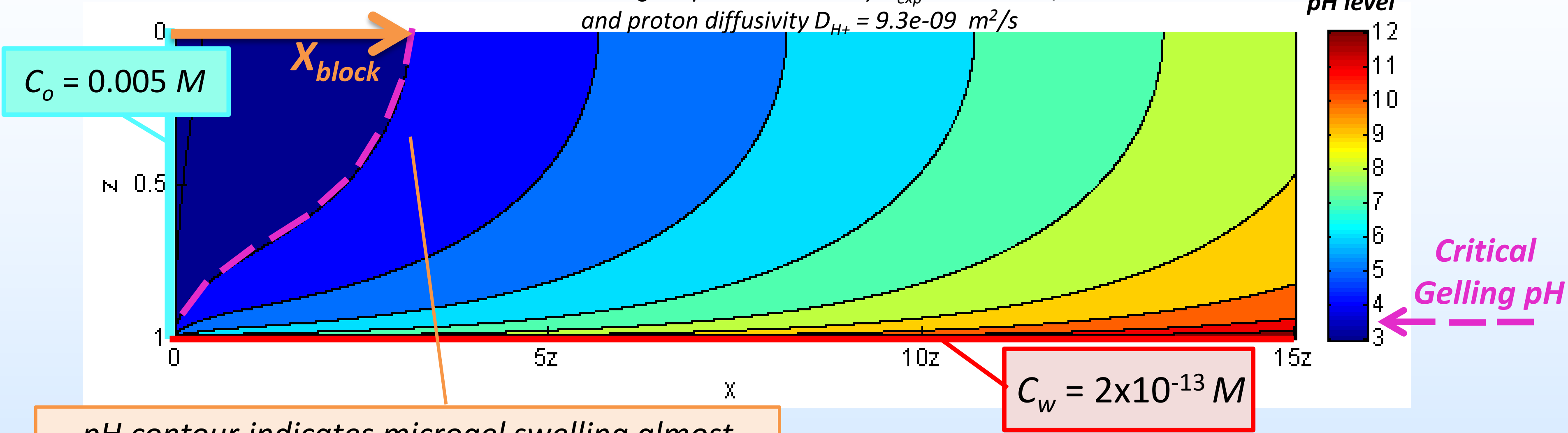
Deposit thickness:

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

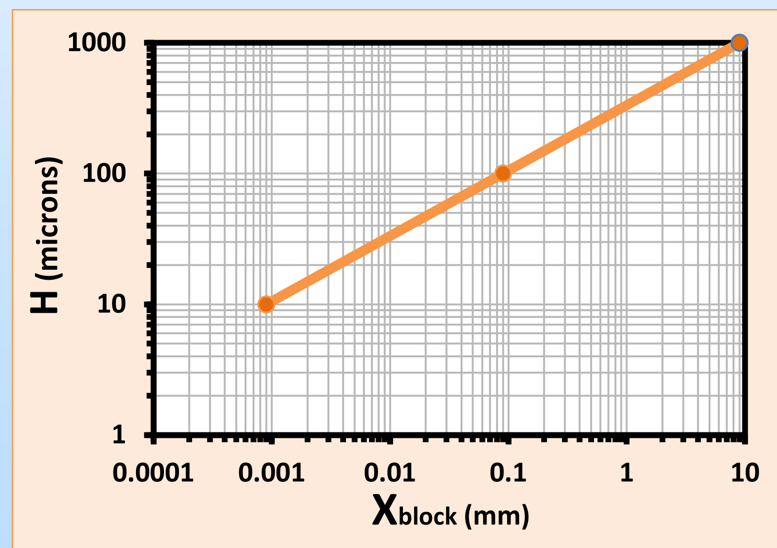
C_p: microgel concentration in polymer solution, C_{gel}: swollen gel concentration, D_{gel}: swollen gel diffusivity, A: ablation rate constant, τ_w: wall shear stress at z = H

Expect gelant→gel in short distance in fast-reaction plug-flow limit

with average experiment velocity V_{exp} = 1.6e-04 m/s
and proton diffusivity D_{H+} = 9.3e-09 m²/s



pH contour indicates microgel swelling almost immediately at the fracture entrance (gelling distance << fracture aperture)



However, experimental data shows that polymer could travel a longer distance before complete gel-up of the fracture channel. This imply that future modification of the model needs to account for the following key phenomena to better predict gelling behavior:

- *neutralization reaction rate at polymer solution and swollen gel contact*
- *diffusivity of the calcified gel layer between cement surface and swollen gel deposition*

Accomplishments

- Developed apparatus and protocol for gelant placement in model fractures in cement
- Developed apparatus for visual inspection of gelant placement process, gel transition and breakdown pathway
- Developed conceptual and mathematical model for gelant placement
- Developed protocol for evaluating key rheological characteristics of pH-triggered gelants
- Evaluated rheology for family of gelants for wide range of conditions

Summary

- Key Findings
  - Carbopol family of pH-triggered polymer gelants has rheology useful for stopping leaks along wellbore/rock interface
  - Gelant placement experiments in cement show rapid neutralization of acidic injected polymer solution
  - Reactive transport model indicates rate of reaction at cement wall likely to dominate placement process
- Lessons Learned
  - Visual flow cell experiments show geometric configuration of gelant placement, gel transition more complicated than we thought
  - Yield stress rapidly declines as brine salinity, hardness increase
  - Gel completely fails to block flow in some experiments

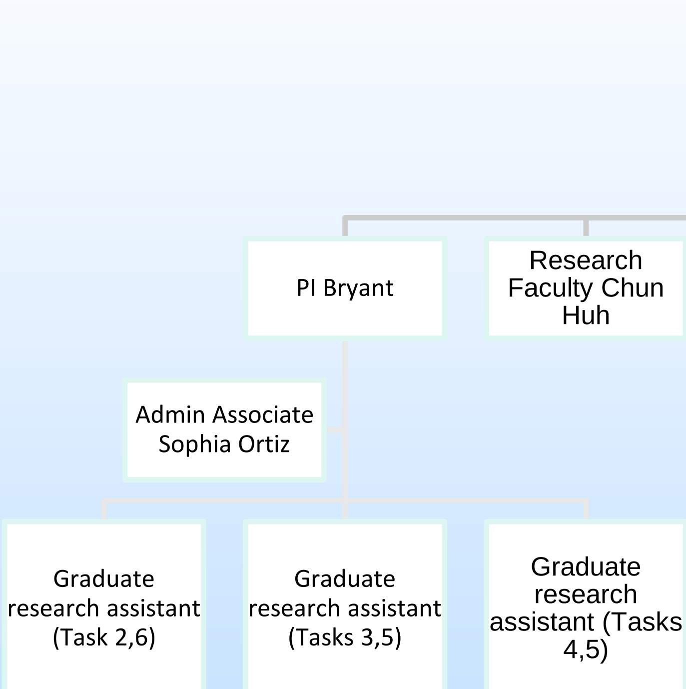
Summary

- Future Plans
  - Gelant transport experiments
    - Placement at elevated temperature (kinetics of neutralization)
    - Find cause of failure to resist flow
  - Gelant reactive transport modeling
    - Extend to surface reaction
    - Include coupling to rheology
  - Gelant/gel rheology
    - Characterize as function of polymer concentration
    - Parameterize Herschel-Bulkley constants in terms of composition
    - Verify that rheometer-derived Herschel-Bulkley constants predict pressure/flow rate relationships in flow experiments

Appendix

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

Organization Chart



- Team
  - PI Steven Bryant (PGE)
  - Co-PI Paul Bommer (PGE)
  - Co-PI Chun Huh (PGE)
  - GRAs
    - James Patterson (PGE)
    - Jostine Ho (PGE)
    - Mohammad Shafiei (ChE)
  - Collaborator Roger Bonnecaze (ChE)

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

Gantt Chart

AUG 2013

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

No publications as of 16 Aug 2013

(None anticipated at this time because project started 1 Oct 2012)