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

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U.S. Department of Energy

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Carbon Storage R&D Project Review Meeting
Transforming Technology through Integration and Collaboration

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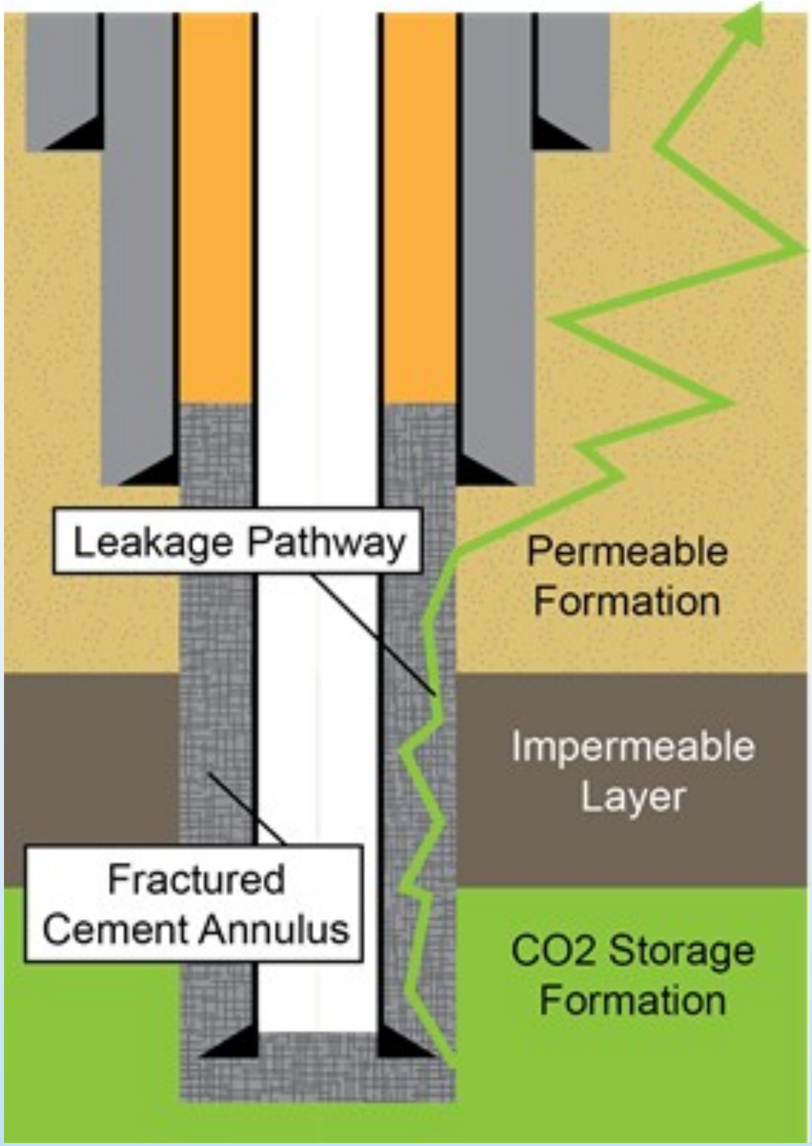
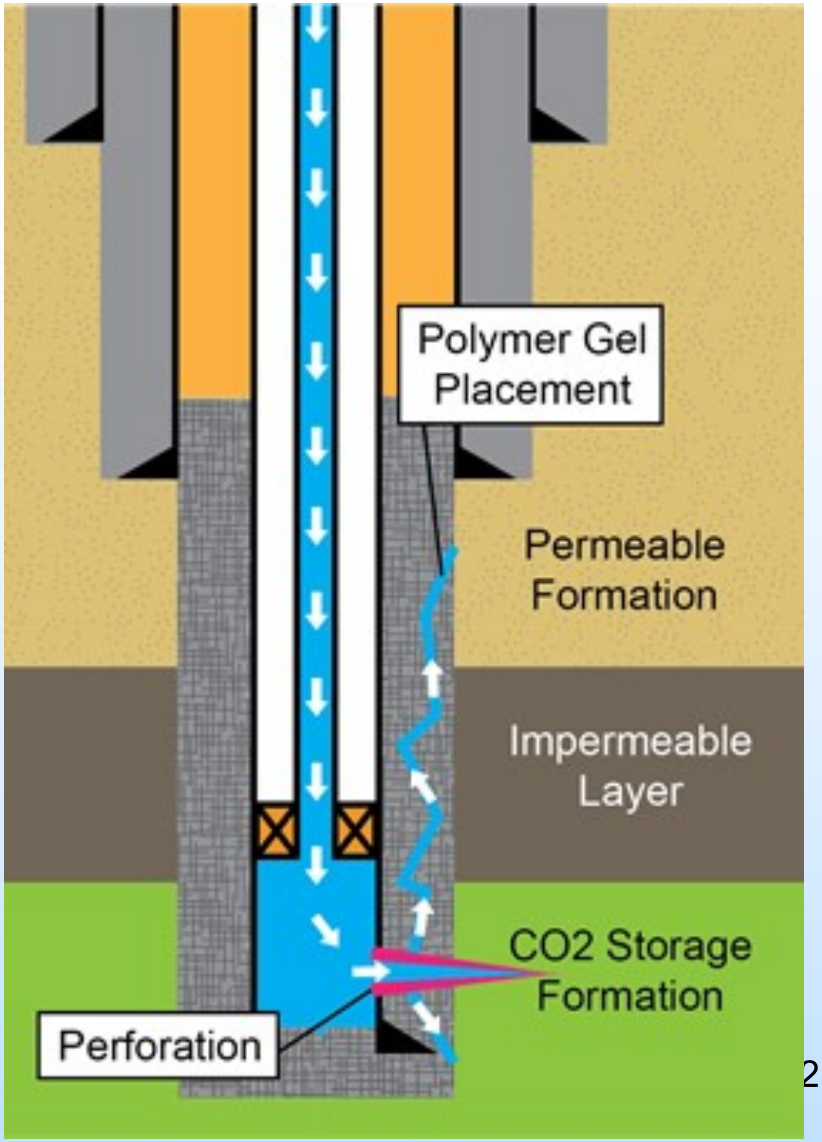
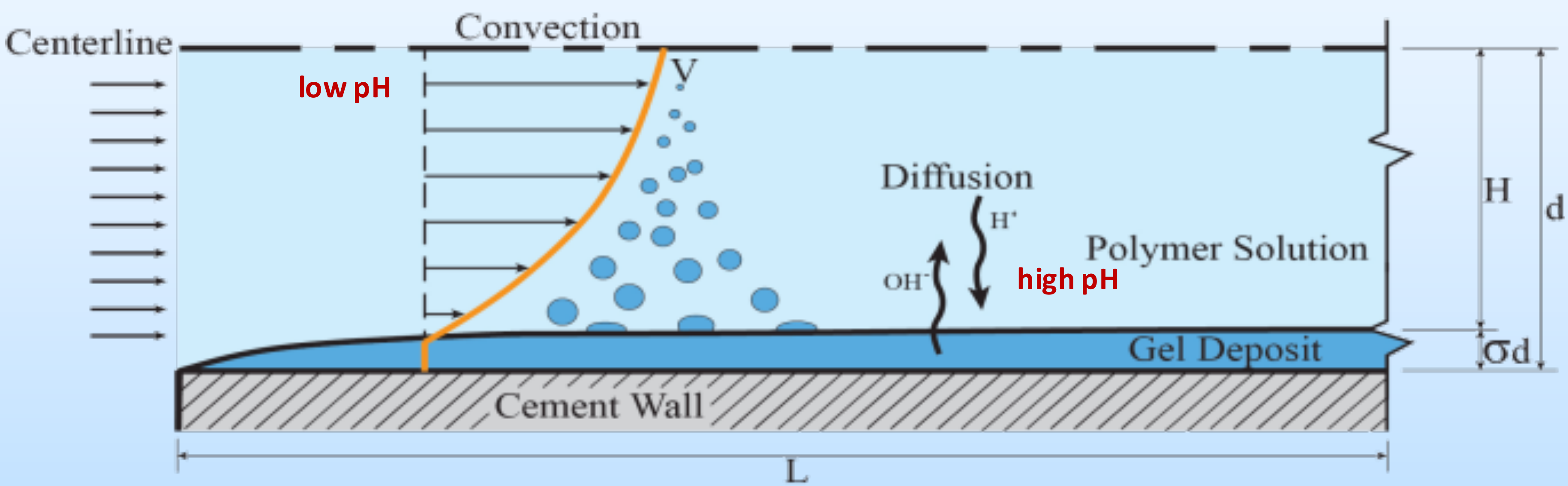
Overview


Leakage Pathway
Permeable Formation
Impermeable Layer
Fractured Cement Annulus
CO2 Storage Formation


Polymer Gel Placement
Permeable Formation
Impermeable Layer
CO2 Storage Formation
Perforation

Mechanism for pH Triggered Polymer Gel

- 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, allows rapid propagation of the low-viscosity solid microgel
- Subsequent shut-in allows formation of gel with high yield-stress throughout the fracture, blocking any leakage flow



Benefit to the Program

Program goals: 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. We test a novel pH-triggered polymer gelant which improves existing technologies:

(i) placement of the gelant is straightforward, even into narrow gaps which allow leakage but will not admit a cement slurry,

(ii) gelant is converted to gel only after contacting the cement and that contains leakage path. Benefit to storage community would be new technology that would work best where current technology has greatest difficulty.

Project Overview: determine performance of pH-triggered polymer gelant as sealant

Project Goals

1. Determine optimal gelant composition/rheology

2. Test capability of optimal formulation in fractured cement cores to withstand pressure gradient applied with acidic brine and CO_2

3. Develop reactive transport models

4. Develop plan for deploying material in field

Success Criteria

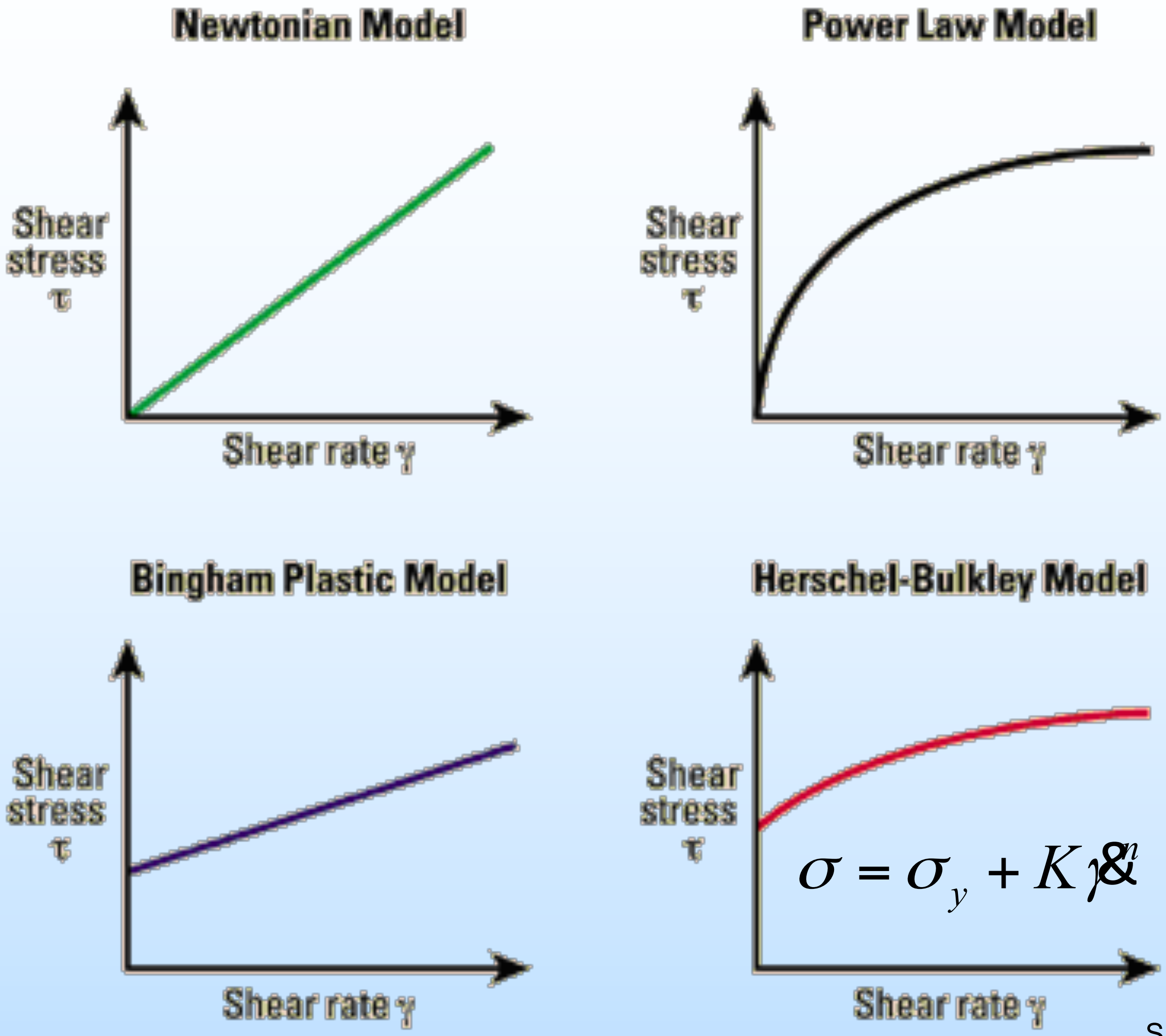
1. Validated model of gel rheology including at elevated temperature

2. Capability of pH-triggered gels to stop brine leaks at constant pressure gradient

3. Validated model of acid-consuming reactions and their rates

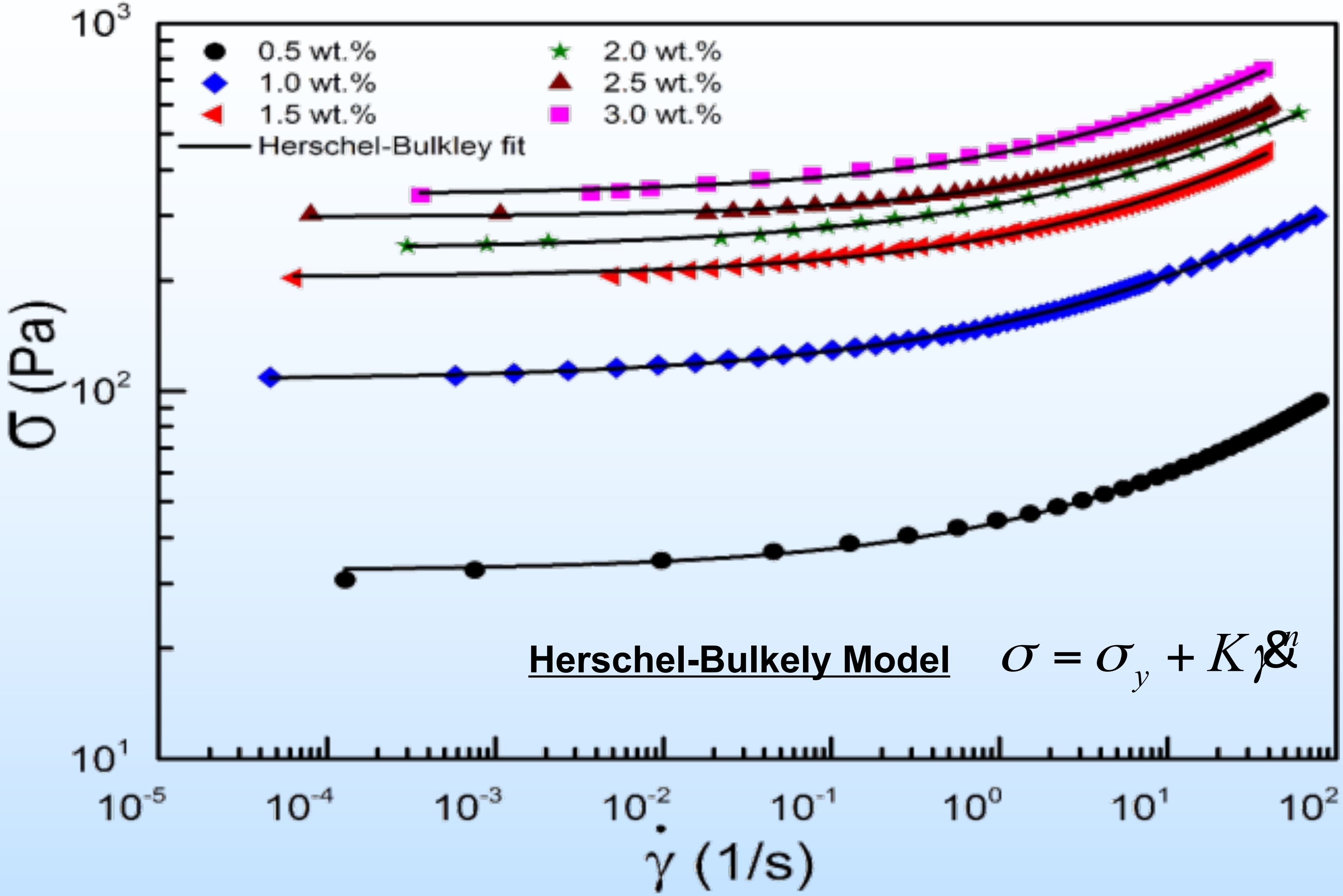
4. Tested plan in bench-scale field

1. Gelant Rheology

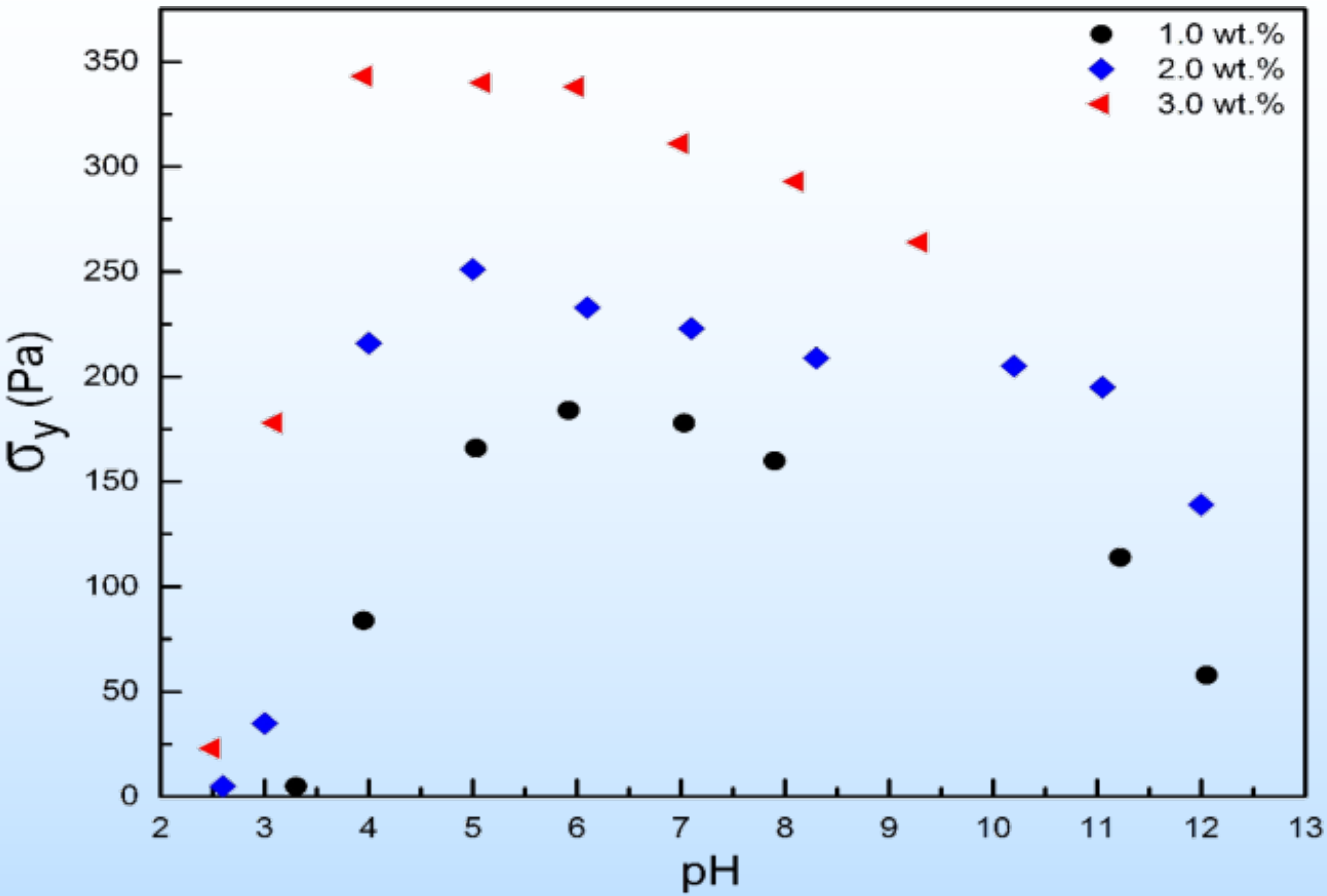


SLB oilfield dictionary

1. Rheology of gelant/gel (Carbopol 934)



1. Yield stress function of pH and concentration



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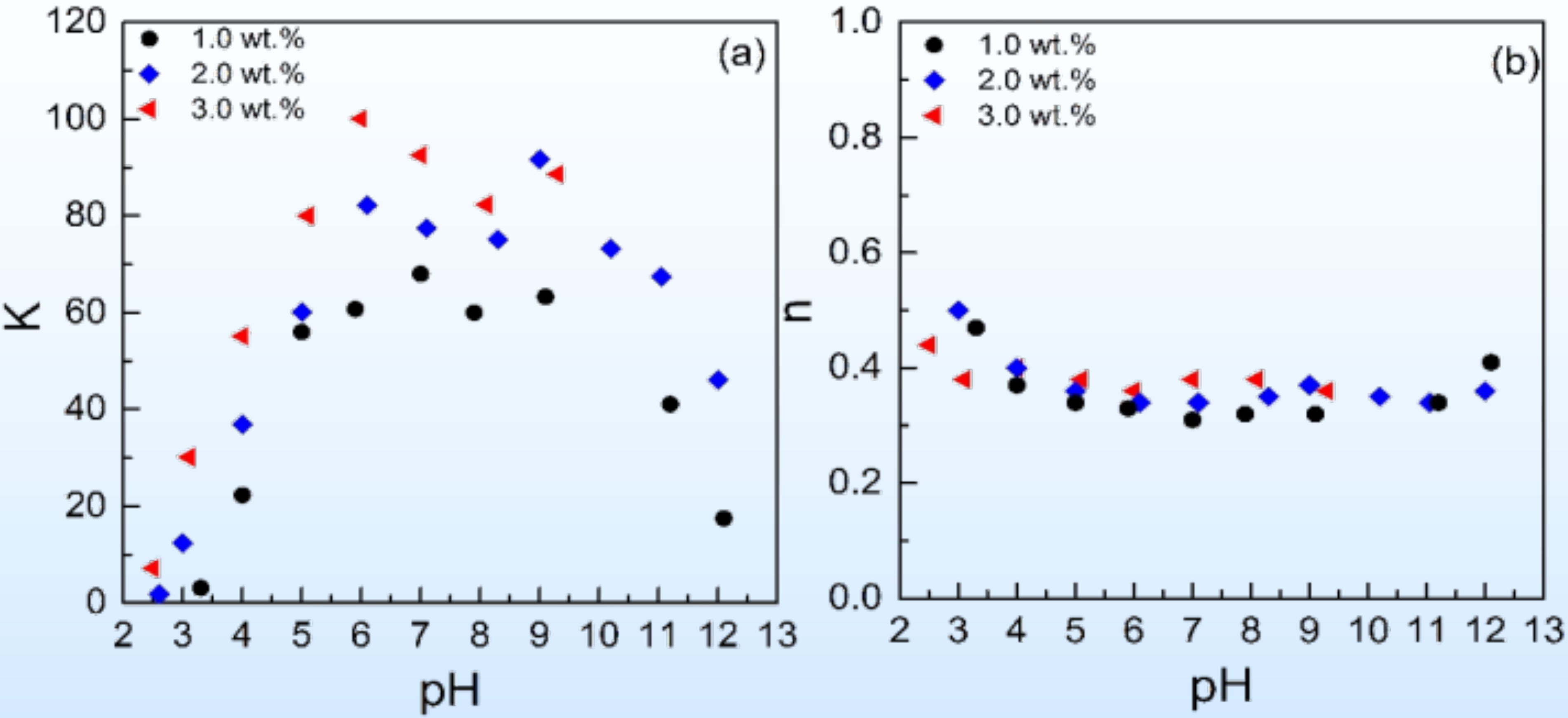
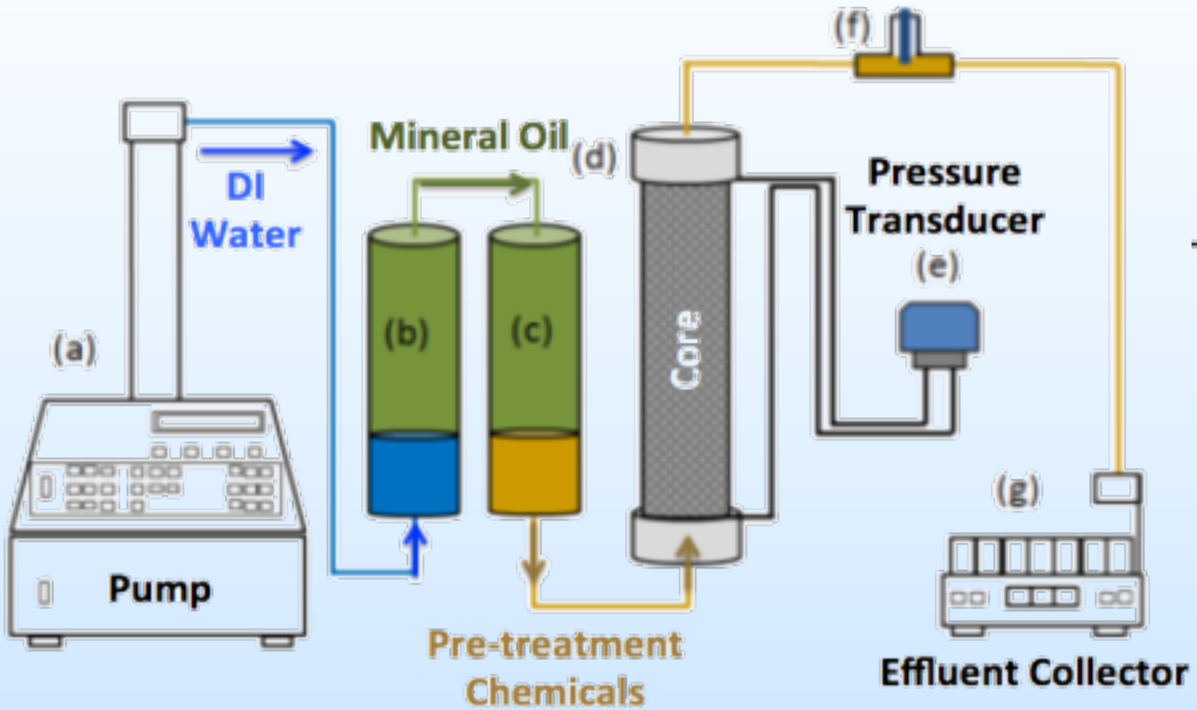


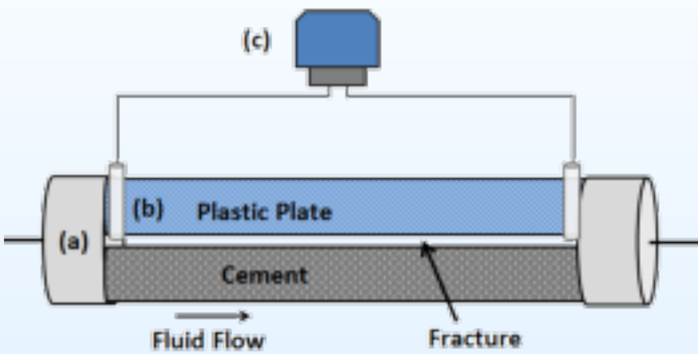
$$\sigma = \sigma_y + K\dot{\gamma}^n \qquad \sigma_y, K, n = f\left(c_p, pH, salinity\right)$$

2. Injecting pH Triggered Polymer Gelant through Fractured Cement

Key performance measures:

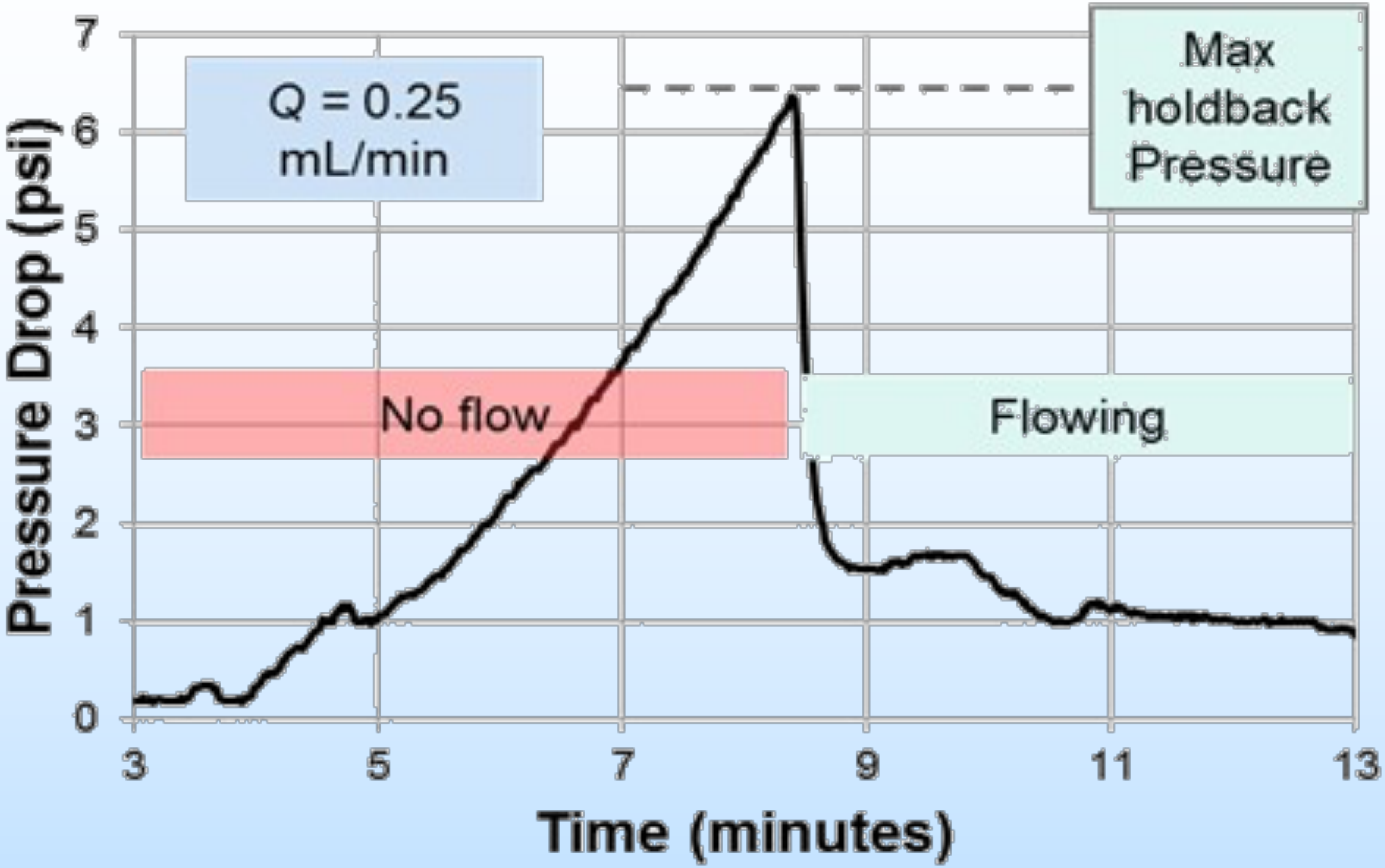
- Placing low viscosity reactive polymer into the entire length of narrow leakage paths, so that flow blocking gel is formed after shut in
- Ability of gelled polymer to withstand brine/ CO_2 imposed pressure gradient





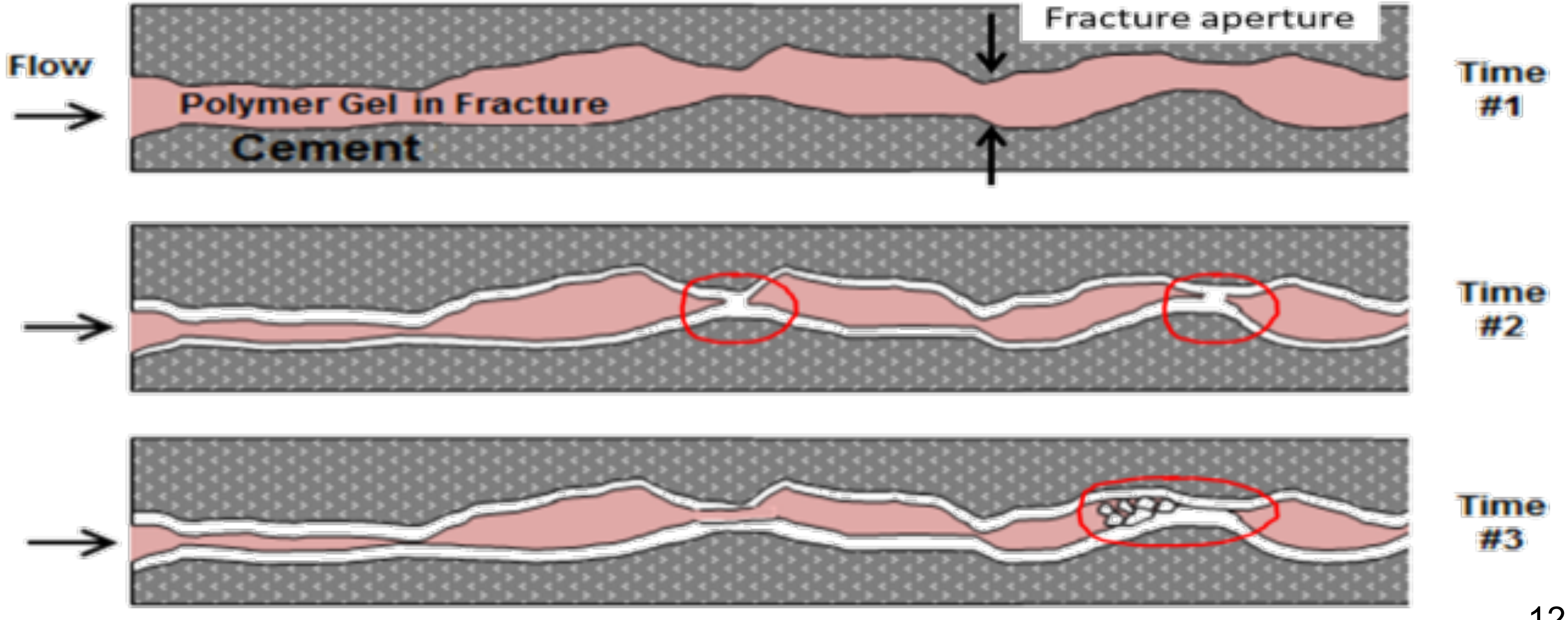
Brazilian Test

2. Holdback Pressure Gradient



2. Formation of white syneresis detrimental

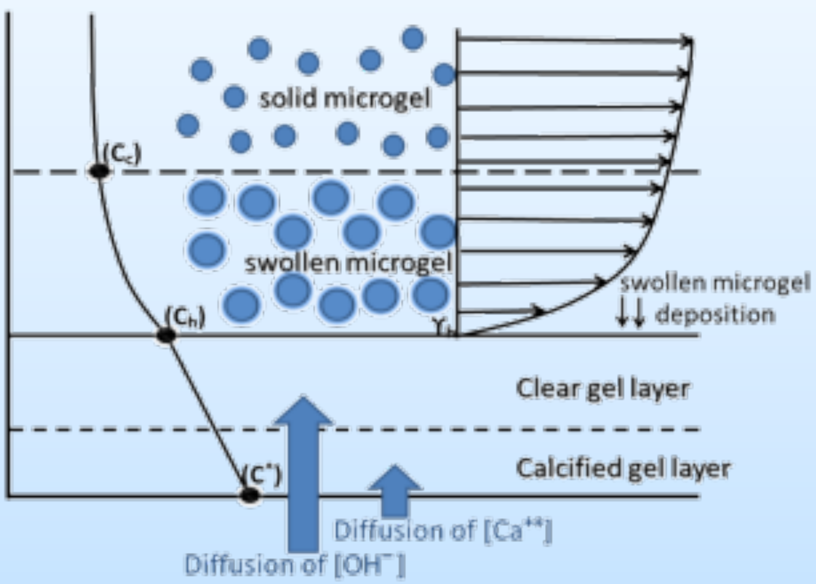
In addition to OH^-, Ca^{++} ion also diffuses out from cement, which causes the contraction of swollen gel network. Water expelled from the contracted gel sometimes forms water channel

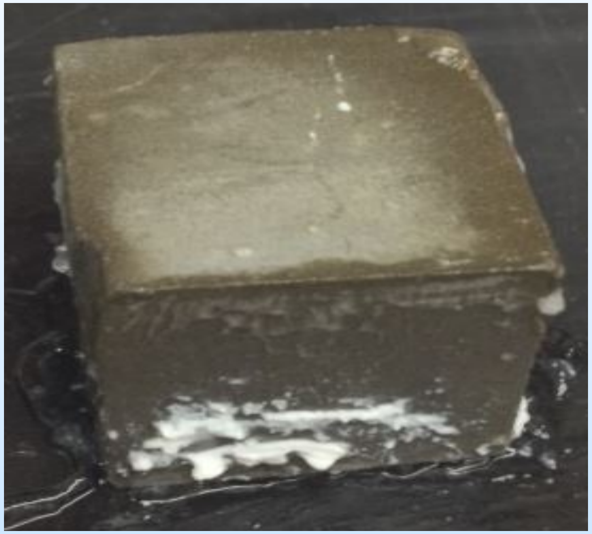


2. Modified process to remedy complication

- Fracture is pre-flushed with a small bank of chelating agent, such as HCl, EDTA or Na triphosphate, 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





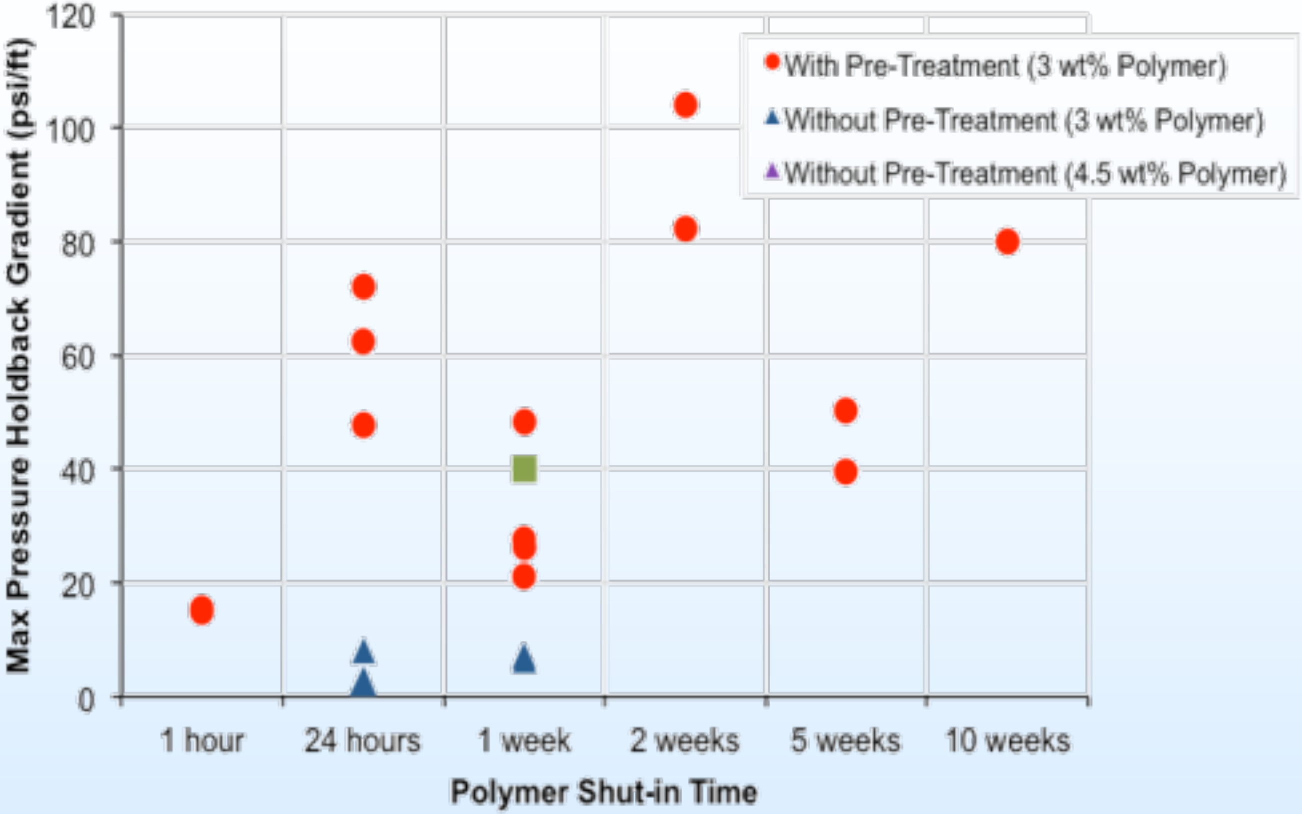
24 hour pre-soak

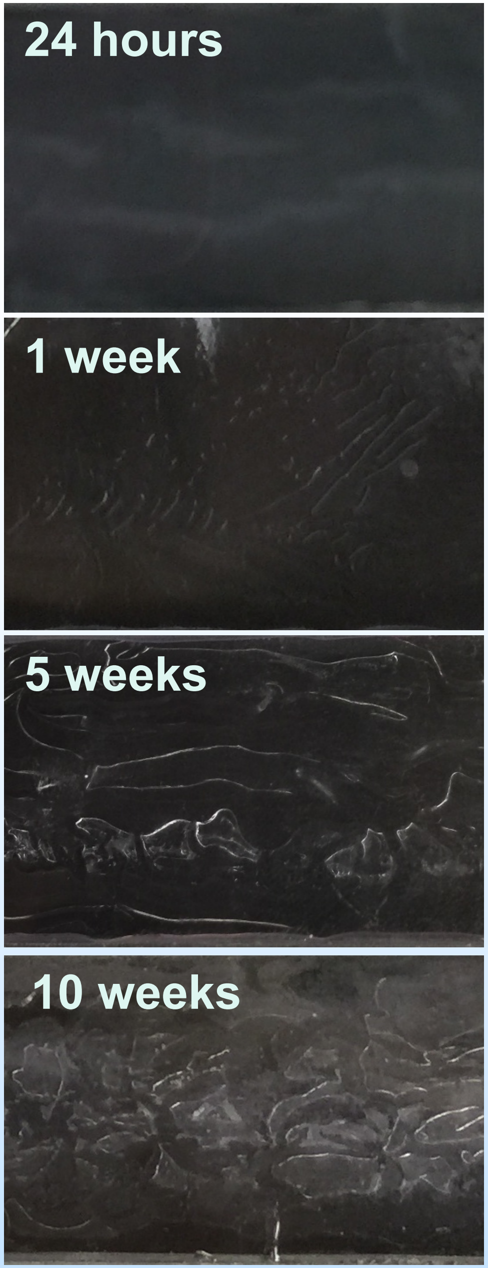
2. Coreflood Experiments with $Na_5P_3O_{10}$ Pre-treatment

Core Type	Experiment	Aperture (mm)	Pre-treatment Time	Polymer Shut-in time	Max Pressure holdback Gradient (psi/ft)	Holdback Fluid
Cement-cement	6CF-36	0.436	24 hours	2 weeks	82.3	pH4 brine
	6CF-39	0.463	10 minutes	2 weeks	104.1	pH4 brine
Cement-plastic	6FP-34	0.313	24 hours	24 hours	72	DI water
				10 weeks	80	DI water
	10FP-35	0.218	--	1 week	21	DI water
	10FP-36	0.255	24 hours	24 hours	47.6	DI water
	10FP-37	0.209	12 hours	1 week	27.6	DI water
	10FP-38	0.228	6 hours	24 hours	62.4	DI water
				5 weeks	39.6	DI water
	10FP-38P	0.277	6 hours	5 weeks	50.4	DI water
	10FP-39V	0.274	10 minutes	1 week	26.3	DI water
	10FP-S1	0.547	10 minutes	1 week	48.4	pH4 brine
	10FP-L2*	0.525	10 minutes	1 hour	15.4	pH4 brine
	10FP-M2*	0.530	10 minutes	1 hour	15	DI water
Fractured Cement in Hassler Coreholder	6CH-39	0.423	10 minutes	24 hours	> 60	CO_2

Average holdback ~ 60 psi/ft

2. Gel strength function of gel shut-in times ($Na_5P_3O_{10}$ Pre-treatment)

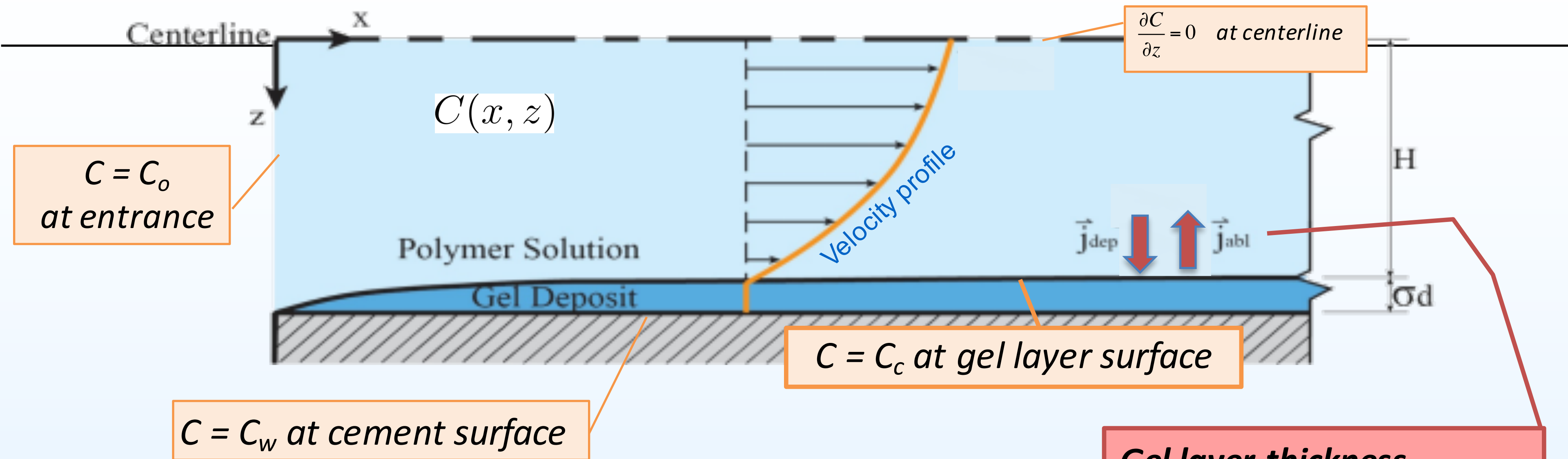




Residual $Na_5P_3O_{10}$ slowly reacts with polymer gel forming bubbles

- Initially lowers yield stress, but maintains desirable gel strength
- As air/gas in bubbles gradually dries up gel inside the fracture, yield stress gradually increases.

3. 2-D gelant transport modeling in model fracture



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:*

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

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

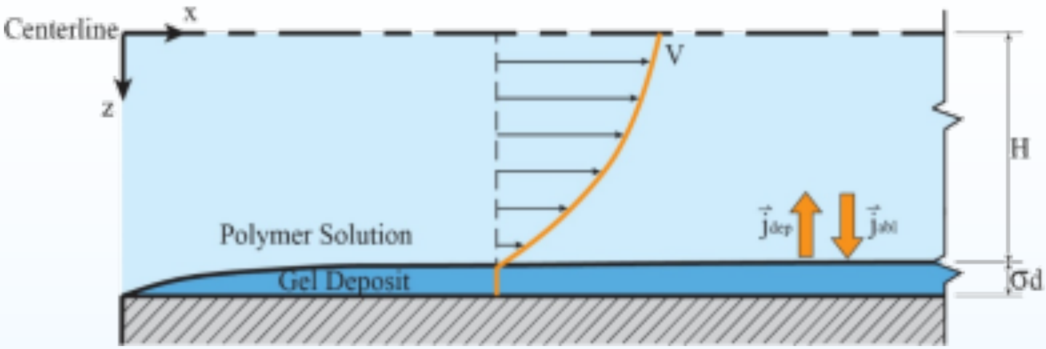
j_{dep} >> j_{abl} for gel growth

Deposit thickness:

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

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

3. Simulation model and results



Rheology

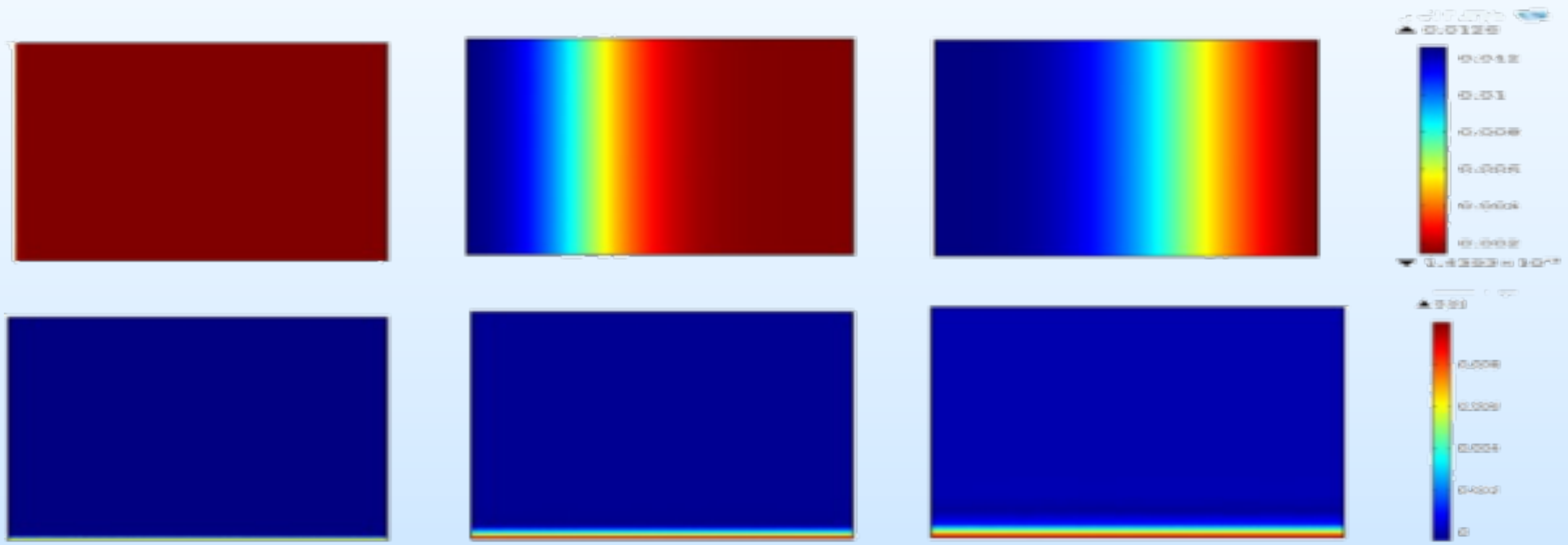
$$\tau_y\,(Pa) = -3.83c_p(pH-2)^2 + 43.93c_p(pH-2)$$

$$K\,(Pa.s^n) = -0.954c_p(pH-2)^2 + 11.84c_p(pH-2) + 0.001$$

$$n:\ 0.37$$

Polymer concentration

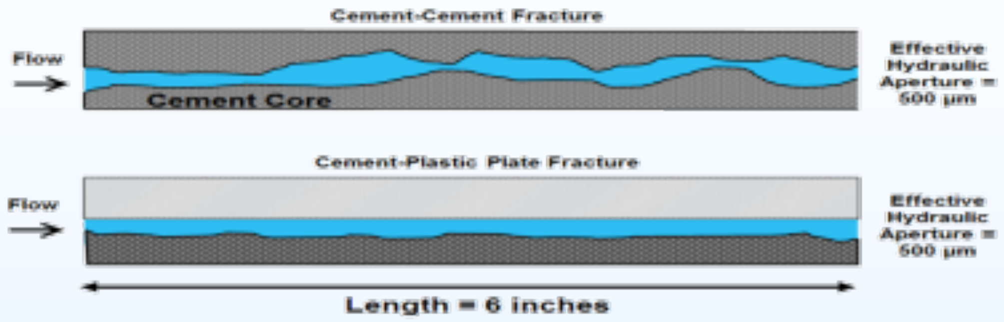
Hydroxide concentration

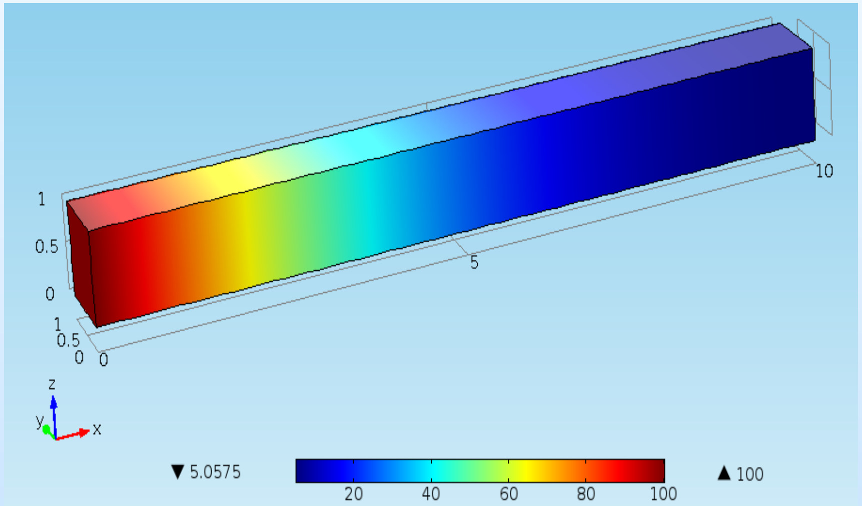


$t_D=0$ $t_D=0.5$ $t_D=1$

3-D gelant transport modeling in “real” fracture

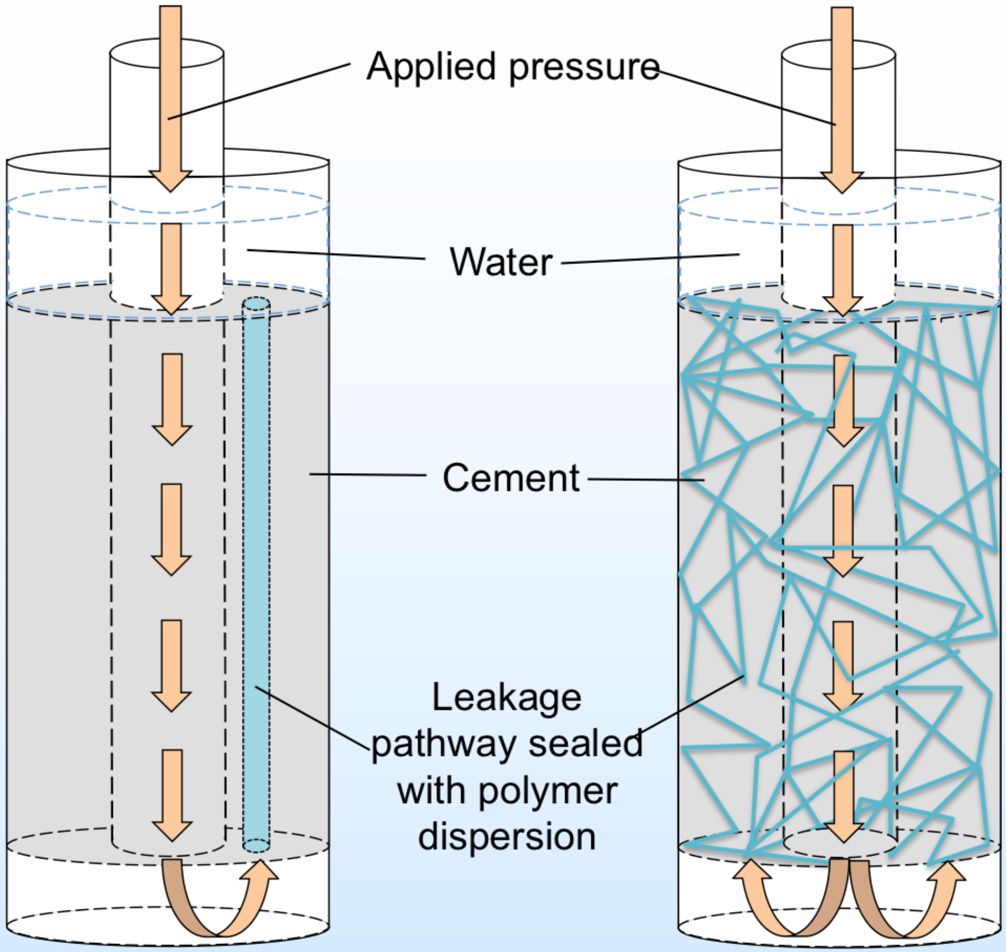
- Due to areal variation of fracture gap width, formation of gel layer and Ca-polymer layer is not uniform
- Formation of Ca-polymer layer from contraction of swollen gel generates low-viscosity water channel





3D simulation of polymer concentration

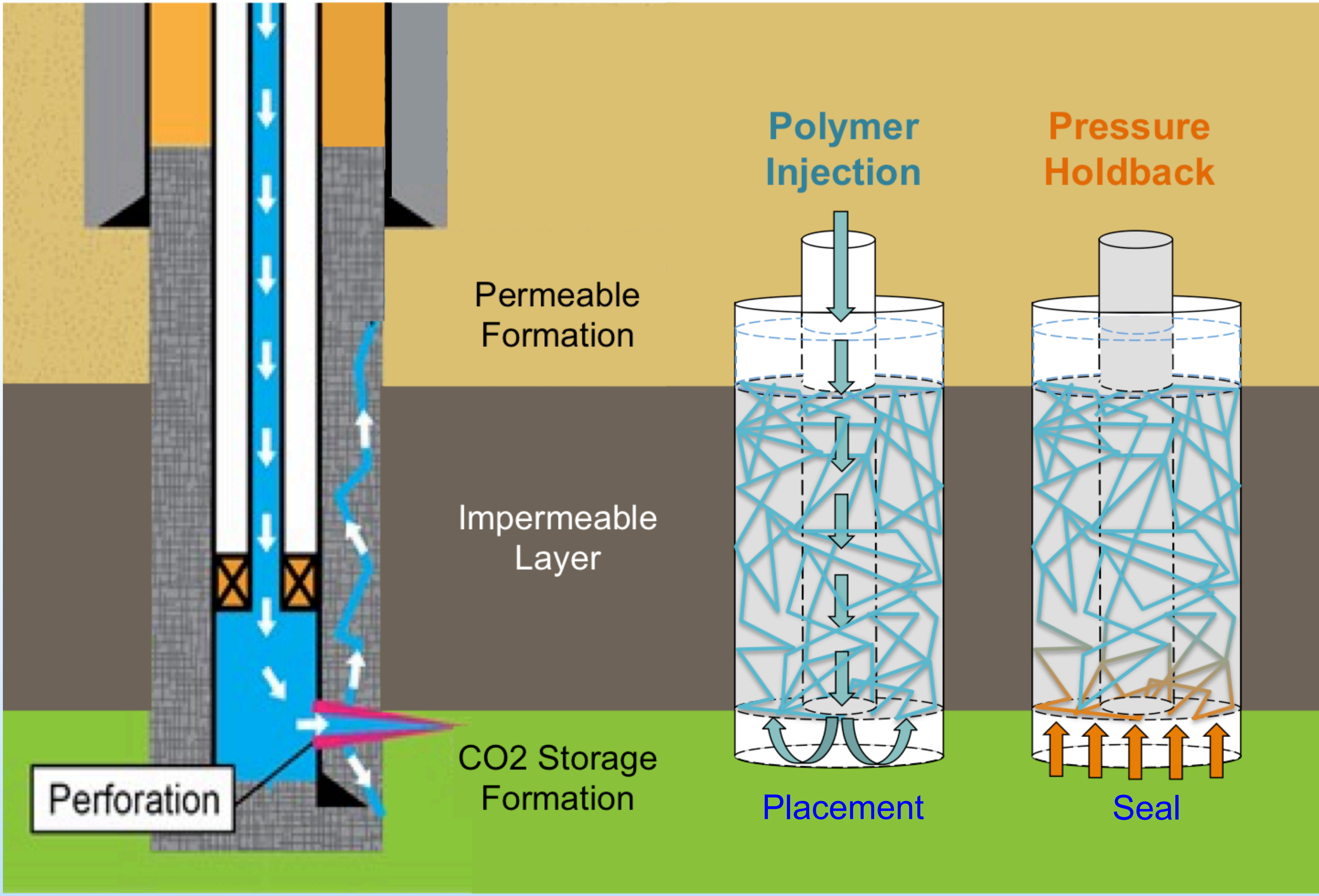
4. Bench Test for Field Preparation



Channel pathway:
- ✓ Held constant 15 psi/ft for one week
- ✓ Maximum breakthrough at 72 psi/ft

Fractured pathway:
- ✓ Held constant 15 psi/ft for one day
- ✓ Still holding pressure

4. Field Application Analogy

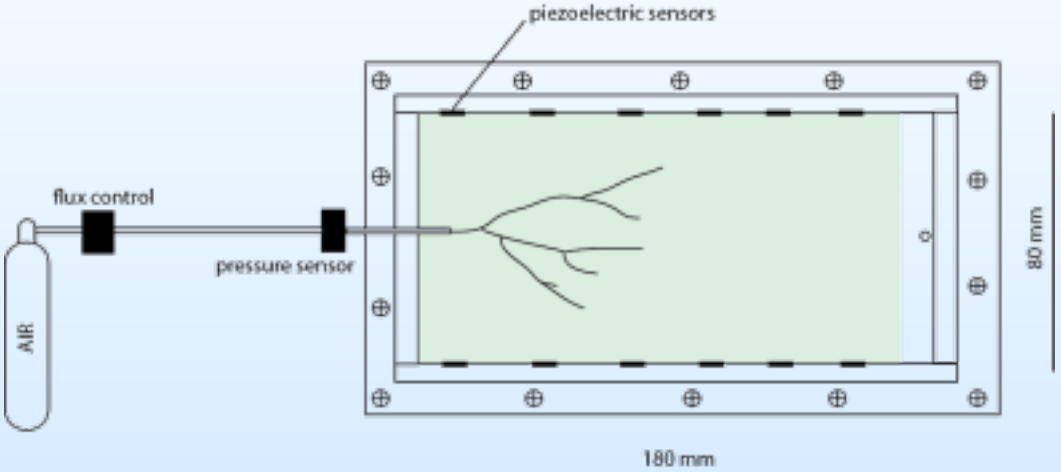


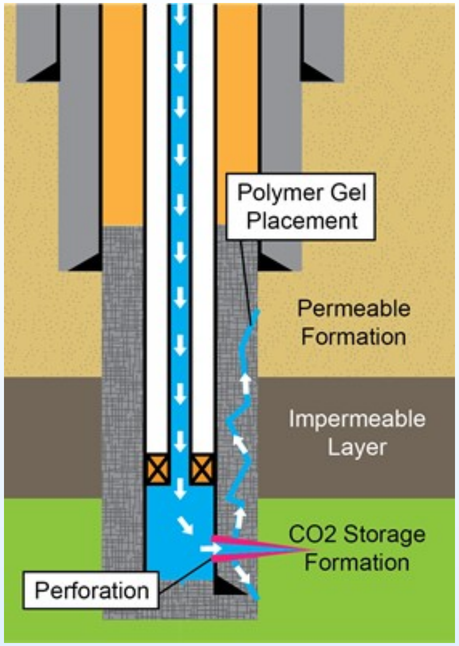
Accomplishments to Date

- Evaluated rheology (non-Newtonian viscosity of gelant & yield stress of gel) for family of gelants for wide range of conditions
- 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
- Successfully bench-tested a simple field plan

Synergy Opportunities

1. Use of Carbopol gel in fracture propagation experiments in DOE EFRC (CFSES)





2. Field Trials

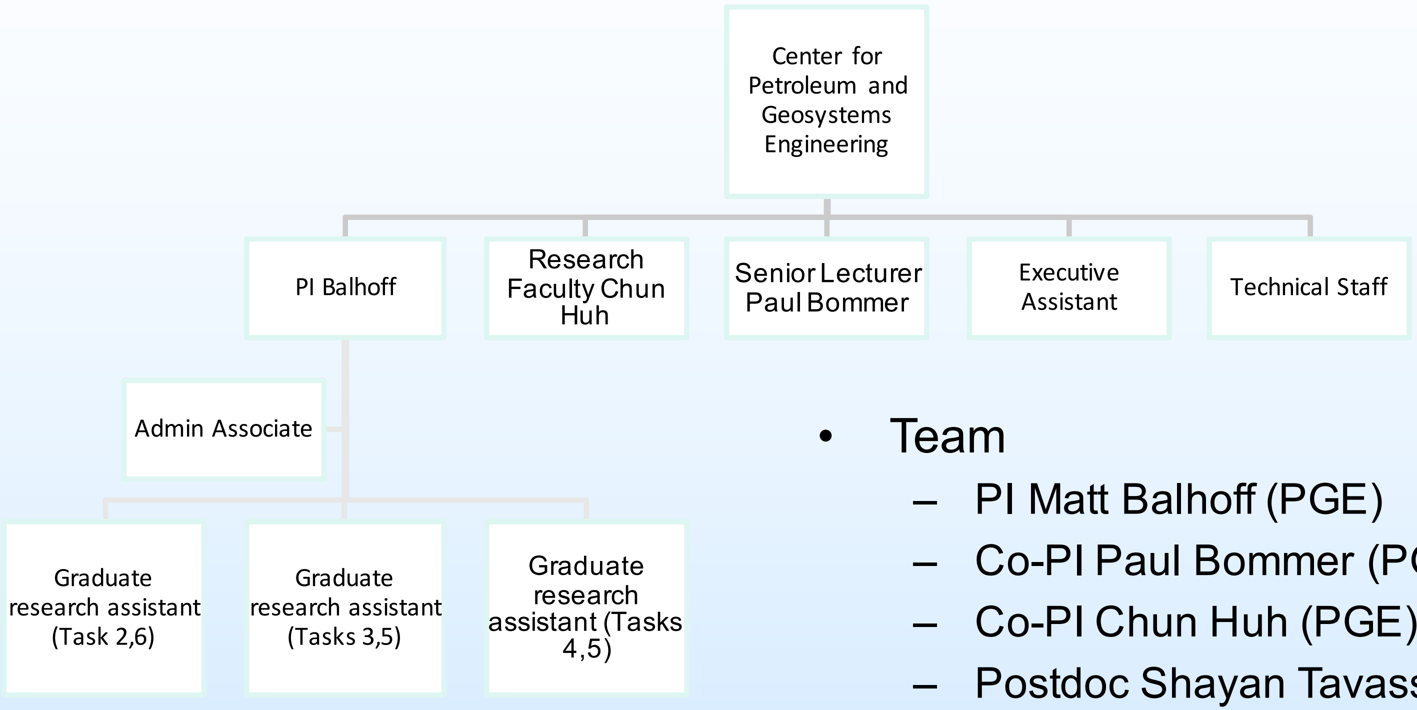
Summary

– Key Findings
  - pH-triggered polymer gelants (Carbopol) useful for stopping leaks along wellbore/rock interface
  - Chelating agent pre-flush allows the gelant propagation through fracture, before the Ca-polymer formation. Sodium Triphosphate > EDTA

– Lessons Learned
  - Flow cell experiments show that hold back pressure is dependent on use of chelating agent and time
  - Transport modeling should include pH and concentration dependent rheology, viscosity-dependent diffusion, and 3D; diffusion of OH^- and Ca^{++} and subsequent formation of swollen gel and ca-polymer

– Future Work
  - Quantitative 3D modeling to predict long-term hold back
  - Development of a field plan in both shallow and deep wells

Organization Chart



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

- Team
  - PI Matt Balhoff (PGE)
  - Co-PI Paul Bommer (PGE)
  - Co-PI Chun Huh (PGE)
  - Postdoc Shayan Tavassoli
  - GRAs
    - Jostine Ho (PGE)
    - Mohammad Shafiei (ChE)
  - Collaborator Roger Bonnecaze (ChE)

Gantt Chart

AUG 2015

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

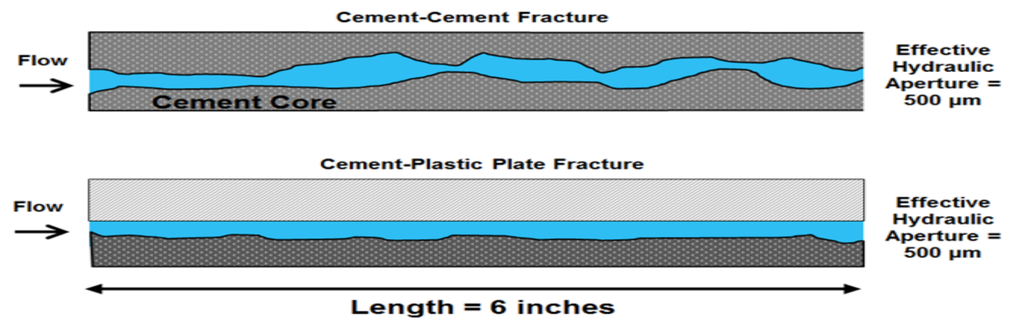
Bibliography

Ho, J.F., Patterson, J.W, Tavassoli, S. Shafei, M., Balhoff, M.T., Huh, C. Bommer, P.M., Bryant, S.L., "The Use of a pH-Triggered Polymer Gelant to Seal Cement Fractures in Wells", *SPE Drilling and Completions*, in review

3-D gelant transport modeling in “real” fracture

- Due to areal variation of fracture gap width, formation of gel layer and Ca-polymer layer is not uniform
- Formation of Ca-polymer layer from contraction

  of swollen gel generates 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

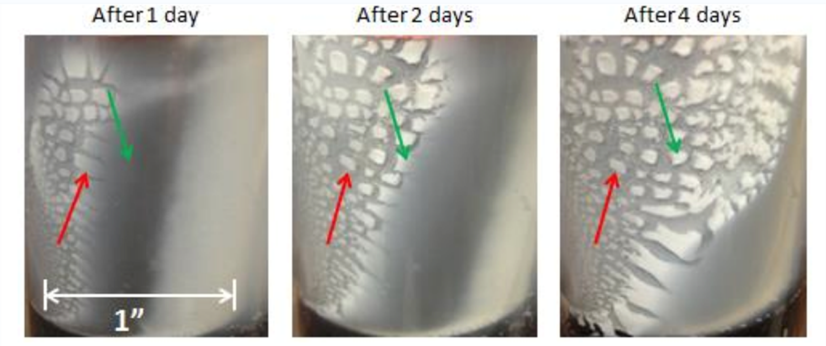
(2) Ca^{++} and chelating agent

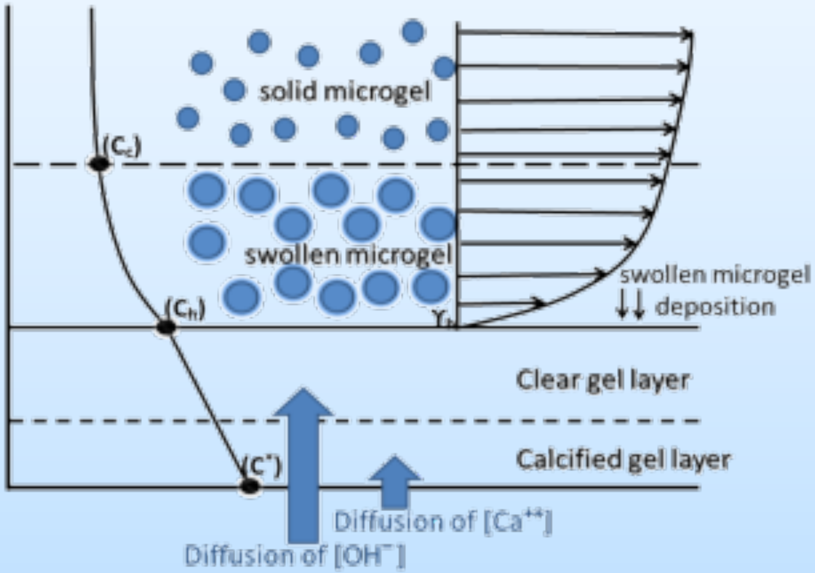
Technical Status

- 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/Shayan Tavassoli)
  - *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*

2. Formation of White Syneresis Detrimental

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





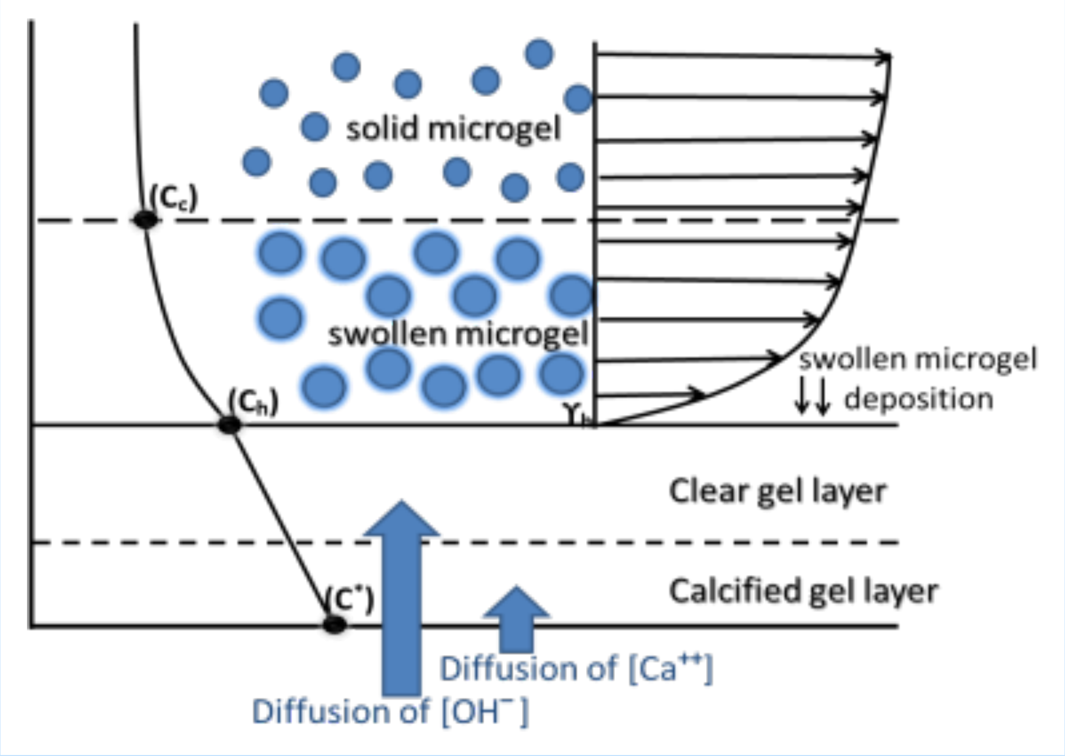
2-D modeling of competing formation of gel layer and Ca-polymer layer

- After swollen gel layer formation (due to OH^- diffusion), slow diffusion of Ca^{++} causes contraction of gel network with expulsion of water/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

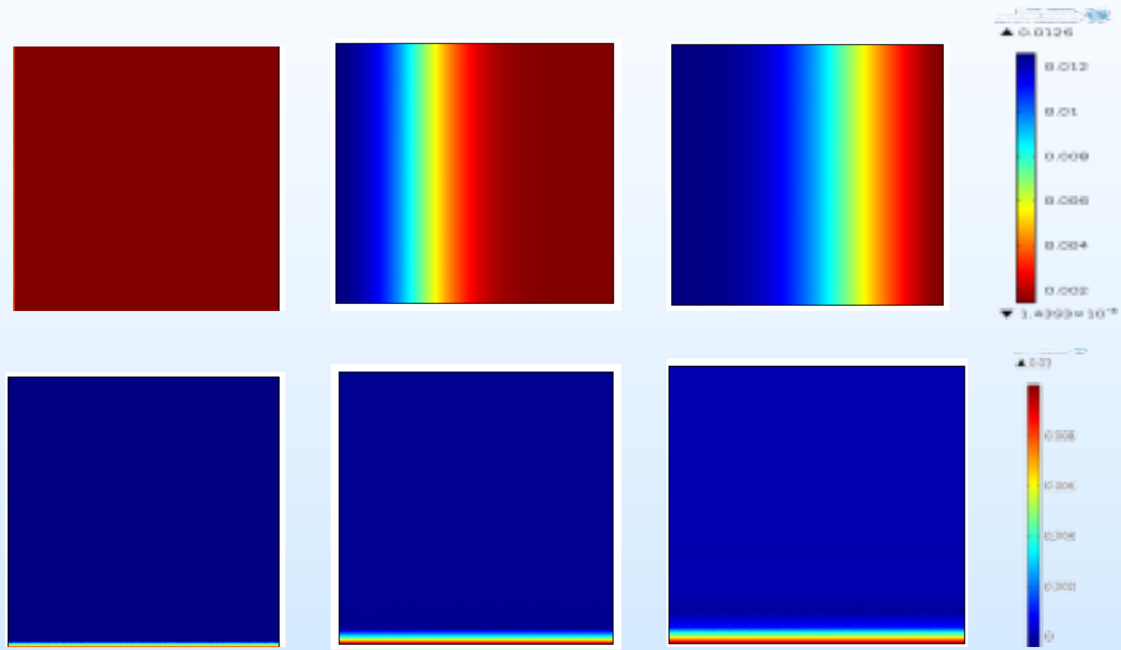
Model Formulation

- 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

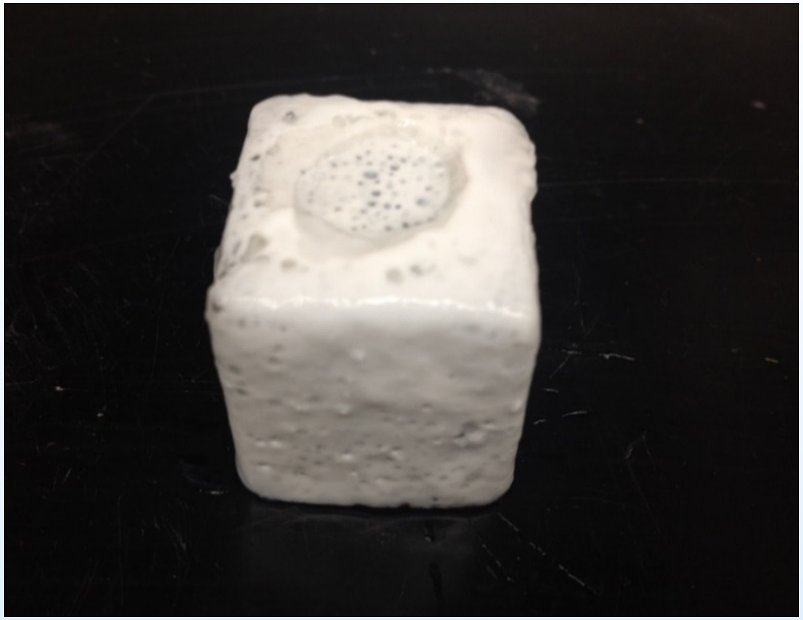


Simulation Model – Polymer Concentration

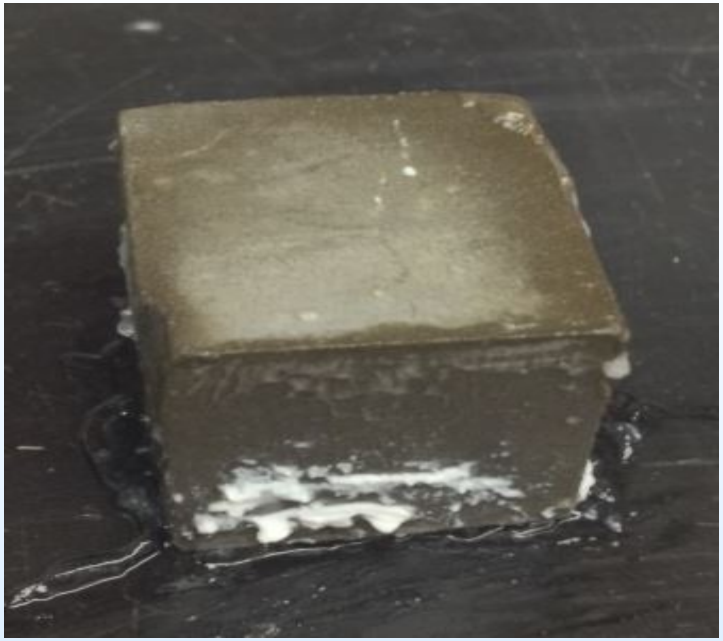


t_D=0 t_D=0.5 t_D=1

2. Modified process to remedy complication



2 hour pre-soak



24 hour pre-soak