Novel Materials for Robust Repair of Leaky Wellbores in CO$_2$ Storage Formations

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Overview
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

<table>
<thead>
<tr>
<th>Project Goals</th>
<th>Success Criteria</th>
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<tbody>
<tr>
<td>1. Determine optimal gelant composition/rheology</td>
<td>1. Validated model of gel rheology including at elevated temperature</td>
</tr>
<tr>
<td>2. Test capability of optimal formulation in fractured cement cores to withstand pressure gradient applied with acidic brine and CO₂</td>
<td>2. Capability of pH-triggered gels to stop brine leaks at constant pressure gradient</td>
</tr>
<tr>
<td>3. Develop reactive transport models</td>
<td>3. Validated model of acid-consuming reactions and their rates</td>
</tr>
<tr>
<td>4. Develop plan for deploying material in field</td>
<td>4. Tested plan in bench-scale field</td>
</tr>
</tbody>
</table>
1. Gelant Rheology

\[ \sigma = \sigma_y + K \gamma^{n} \]

- **Newtonian Model**
- **Power Law Model**
- **Bingham Plastic Model**
- **Herschel-Bulkley Model**
1. Rheology of gelant/gel (Carbopol 934)

\[ \sigma = \sigma_y + K \gamma^n \]
1. Yield stress function of pH and concentration
1. Rheology of gelant/gel (Carbopol 934)

\[ \sigma = \sigma_y + K \gamma^l \]
\[ \sigma_y, K, n = f(c_p, pH, salinity) \]
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/CO₂ imposed pressure gradient
2. Holdback Pressure Gradient

- Q = 0.25 mL/min
- Max holdback Pressure
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$_5$P$_3$O$_{10}$ Pre-treatment

<table>
<thead>
<tr>
<th>Core Type</th>
<th>Experiment</th>
<th>Aperture (mm)</th>
<th>Pre-treatment Time</th>
<th>Polymer Shut-in time</th>
<th>Max Pressure holdback Gradient (psi/ft)</th>
<th>Holdback Fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement-cement</td>
<td>6CF-36</td>
<td>0.436</td>
<td>24 hours</td>
<td>2 weeks</td>
<td>32.3</td>
<td>pH4 brine</td>
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<tr>
<td>Cement-cement</td>
<td>6CF-39</td>
<td>0.463</td>
<td>10 minutes</td>
<td>2 weeks</td>
<td>104.1</td>
<td>pH4 brine</td>
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<tr>
<td>Cement-plastic</td>
<td>6FP-34</td>
<td>0.313</td>
<td>24 hours</td>
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<td>Cement-plastic</td>
<td>10FP-35</td>
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<td>Cement-plastic</td>
<td>10FP-37</td>
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<td>12 hours</td>
<td>1 week</td>
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<td>Cement-plastic</td>
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<td>10FP-L2*</td>
<td>0.525</td>
<td>10 minutes</td>
<td>1 hour</td>
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<td>Cement-plastic</td>
<td>10FP-M2*</td>
<td>0.530</td>
<td>10 minutes</td>
<td>1 hour</td>
<td>15</td>
<td>DI water</td>
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<td>Fractured Cement in</td>
<td>6CH-39</td>
<td>0.423</td>
<td>10 minutes</td>
<td>24 hours</td>
<td>&gt; 60</td>
<td>CO$_2$</td>
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<td>Hassler Coreholder</td>
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Average holdback ~ 60 psi/ft
2. Gel strength function of gel shut-in times (Na$_5$P$_3$O$_{10}$ Pre-treatment)

Residual Na$_5$P$_3$O$_{10}$ 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

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

- \( C \): dimensionless proton concentration
- \( C_0 \): initial polymer proton concentration, \( C_0 = 1 \)
- \( C_w \): cement wall proton concentration, \( C_w << 1 \)
- \( D \): diffusivity of \( H^+ \) in water

Gel layer thickness

- Particle diffusion deposition rate:
  \[ j_{\text{dep}} = D_{\text{gel}} \frac{(C_p - C_{\text{gel}})}{H} \]
- Shear Removal ablation rate:
  \[ j_{\text{abl}} = A \tau_w \]

\( j_{\text{dep}} \gg j_{\text{abl}} \) for gel growth

Deposit thickness:

\[ \sigma_d = f(j_{\text{dep}}, j_{\text{abl}}, t) \]

\( C = C_0 \) at entrance

\( C = C_w \) at cement surface

\( C = C_c \) at gel layer surface
3. Simulation model and results

**Rheology**

\[
\tau_y (Pa) = -3.83c_p (pH - 2)^2 + 43.93c_p (pH - 2)
\]

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

\[n : 0.37\]
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
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
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 Ca²⁺ 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

<table>
<thead>
<tr>
<th>Phase</th>
<th>Task</th>
<th>Milestone</th>
<th>YEAR 1</th>
<th>YEAR 2</th>
<th>YEAR 3</th>
<th>Interdependencies</th>
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### Interdependencies
- **Project management across all tasks**
- **Develop protocol for testing capability of gel to stop leaks**
- **Use protocol from Task 2.1 to test gels for range of conditions relevant to geologic storage**
- **Develop reactive transport model that accounts for effluent pH measurements in Tasks 2.2 and 2.3**
- **Apply model from Task 3.1 to validate reaction rate constants against data from Tasks 2.2 and 2.3**
- **Develop model gelant rheology and gel yield stress**
- **Apply model from Task 4.1 to measurements from Tasks 2.2 and 2.3**
- **Develop model that integrates components from Tasks 3 and 4 and data from Task 2**
- **Apply model from Task 5.1**
- **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