Development and Evaluation of Re-crosslink Preformed Particle Gel System for Low-to-Medium Temperature Reservoirs

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Outline

• Development of RPPG
• Evaluation of New Batch Commercial Product
• Development of New Products
• Summary
• Acknowledgements
Development of RPPG

<table>
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<tr>
<th>Products</th>
<th>CRPPG &amp; Microsphere</th>
<th>L-RPPG</th>
<th>mRPPG, Alg-IPNG, and etc.</th>
</tr>
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<tr>
<td>CRPPG</td>
<td>2013.10</td>
<td>2015.4</td>
<td>2017.4</td>
</tr>
<tr>
<td>L-RPPG, mRPPG, and (H)RPPG</td>
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</table>

**Tasks**

- **80°C (CRPPG)**
  - 1.5 to 15 d
- **Room temperature 23°C (L-RPPG for ConocoPhillips)**
  - More difficult
  - 1yr lab +1yr pilot production
- **Micro-RPPG & Nano-RPPG**
- **Mid-temperature (>65°C) Reservoir**
  - (M)RPPG
  - L-RPPG pilot production evaluation
- **L-RPPG, mRPPG, and (H)RPPG Thermo-stability test**
- **RPPG Improvement (nano-composite, fiber, resorcinol, and etc.)**
  - (H)RPPG
Q & A of Last JIP Meeting

Q 1: Summary slide comparing RPPG-1, L-RPPG, (M)RPPG, & (H)RPPG would be helpful
A 1: The RPPGs are compared in the next page.

Q 2: (H)RPPG was introduced only at the end of presentation, no mention of it in timeline on slide 4. Why was it not included in test results on slides 11 to 14?
A 2: A more comprehensive study has been given to (H)RPPG (renamed as Alg-IPNG in this study).

Q 3: Does Missouri S&T intend to experiment with added fibers to increase the ultimate strength of the L-RPPG?
A 3: Some preliminary results will be provided in the study.

Q 4: We would be interested in exploring a particle that would be suitable for a steam flood (~450 °F)
A 3: Thermo-stability evaluation for another product has been done at 150 °C / 302 °F by my colleague.
## Summary of RPPGs

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Specifications</th>
<th>Applicable focus</th>
<th>Swelling ratio</th>
<th>Re-crosslink Temperature (°C)</th>
<th>Starting re-crosslinking time (h)</th>
<th>Thermo-stability: Started to degrade or deform</th>
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<tbody>
<tr>
<td>L-RPPG</td>
<td>Copolymer</td>
<td>Low temperature (23°C)</td>
<td>23 to 30</td>
<td>23 to 80</td>
<td>3 to 15</td>
<td>350 days @ 40°C; 350 days @ 65°C; 200 days @ 80°C; 3 days @ 100°C</td>
</tr>
<tr>
<td>(M)RPPG</td>
<td>Copolymer</td>
<td>Mid temperature (65-80°C)</td>
<td>25 to 30</td>
<td>65 to 80</td>
<td>4 to 16</td>
<td>350 days @ 40°C; 350 dayse @ 65°C; 300 days @ 80°C; 10 days @ 100°C</td>
</tr>
<tr>
<td>Alg-IPNG (H)RPPG</td>
<td>Interpenetrating structure</td>
<td>High temperature (100°C)</td>
<td>10 to 20</td>
<td>65 to 100</td>
<td>40 to 55</td>
<td>150 days @ 100°C</td>
</tr>
</tbody>
</table>

- **Additional request:**
  Help COP evaluate the newest batch products of Daqing Company
Research Topics

• **Topic I:** New Batch RPPG Evaluation  
  (Motivation: Newest Batch shows abnormal stickiness)

• **Topic II:** Fiber-introduced RPPG (F-RPPG)  
  (Motivation: Enhance re-crosslinked gel strength)

• **Topic III:** Inter-penetrating network RPPG (Alg-IPNG)  
  (Motivation: Medium-temperature product development)

• **Topic IV:** Enhanced Alg-based Gel (R-RPPG)  
  (Motivation: Medium-temperature product development)
Topic I: New Batch RPPG (COP-1) Evaluation

- Received sample list:
  - RPPG(1E-105) x2 (#1 and #2)
  - Arctic Diesel x1
  - 2% KCl brine x2
Tasks & Parameters

- **Tasks:**
  - a. Compare swelling of COP-1 with Batch 5
  - b. Conduct experiment in stationary mode or a shaker
  - c. Horizontal + shake
  - d. Vertical + shake

(Prepare samples with concentration of 0.5, 0.75 and 1.0 lb/gal)

- **Swelled Ratio Control:**
  - Initial gel/brine ratio calculation:
    - 0.5 lb/gal = 2.1 g/35 mL
    - 0.75 lb/gal = 3.15 g/35 mL
    - 1.0 lb/gal = 4.2 g/35 mL
a. Comparison of COP-1 and Batch 5

- **Results:**
  - The swelling kinetic curve is almost the same at vertical-tube situation. However, equilibrium swollen ratio of Batch 5 reaches 39 which is higher than COP-1 (31).
  - After immersed in 2%KCl brine, the COP-1 become more **sticky** than Batch 5.
b. COP-1 Conduct experiment in both shaking and stationary mode

First 100-min

Particle size: 2-4 mm
0.5 lb/gal
23.9 °C /75°F
2% KCl

1. Start to re-crosslink
2. “Slow-down” swelling
b. Conduct experiment in both shaking and stationary mode (cont.)

• Results:

1. Shaking prolongs the starting re-crosslinking time (compared two samples); The starting re-crosslinking time is around 1 h

2. A “slow-down” swelling is observed after the swelling ratio reached 15

3. “Fully swollen time” for horizontal+shake sample is 300 min while for horizontal-only sample is around 400 min
c. Place samples in horizontal + Shake

First 100-min
Particle size: 2-4 mm
23.9 °C / 75°F
2% KCl
c. Place samples in horizontal + Shake (cont.)

• Results:

1. “Fully swollen time” measurement:
   - 0.5 lb/gal : 300 min
   - 0.75 lb/gal : 150 min
   - 1.0 lb/gal : 50 min

2. No unabsorbed/free brine is observed at the top of the gels.
d. Place samples in vertical + Shake

First 100-min
Particle size: 2-4 mm
23.9°C/75°F
2% KCl

500 min
75°F
d. Place samples in vertical + Shake (cont.)

• Results:

1. “Fully swollen time” measurement:
   - 0.5 lb/gal : 400 min
   - 0.75 lb/gal : 300 min
   - 1.0 lb/gal : 100 min

2. Unabsorbed/free brine is observed at the top of the gels.

3. In this condition, the gels are unevenly swelled since re-crosslinking happened. The tube diameter may also affect the swelling result.
Sectional Summary

• The result shows that COP-1 and Batch 5 products perform similar swelling kinetics in 2% KCl solution. However, the equilibrium swollen ratio of COP-1 reaches 31, which is lower than Batch 5 (39);

• COP-1 is more sticky than the Batch 5 products.

• Compared with stationary condition, the COP-1 swell with shaking performs higher fully swollen ratio and shorter fully swollen time; For the sample at stationary condition, unabsorbed/free water is observed in the tubes after the swelling stopped.

• COP-1 in horizontal-placed tubes demonstrate more complete swelling process than the samples in the vertical-placed tubes resulting in higher equilibrium swelling ratios.
**Topic II: Re-crosslink RPPG (F-RPPG)**

**Preparation of F-RPPG**

- **One-pot free-radical polymerization**
  - Monomer(s)
  - Crosslinker(s)
  - Initiator(s)
  - Fiber
  - 40°C water bath
  - Semi-product (bulky gel)
  - Dry, grind & screen
  - F-RPPG

- **F-RPPG Applicable Focus**
  - Improve strength of L-RPPG
  - Solve the placement problem caused by gravity (Ze Wang’s presentation)

**Schematic of F-RPPG synthesis**

*Super-Sweep Fine® Fiber* (FORTA: [www.super-sweep.com](http://www.super-sweep.com))

*Re-crosslinked gel (0.03% Fiber)*
Effect of Fiber Concentration

Swelling Kinetic and Equilibrium

Effect of Fiber Concentration

- **Results:**
  - 0 to 0.06% → swelling rate ↓
  - 0.06 to 0.12% → swelling rate ↑

G' and G” measurement

- **Results:**
  - 0 to 0.03% → G’ ↑
  - 0.03 to 0.12% → G’ ↓

(Fibers reduce the polymer contact area of the F-RPPG)
• **Results:**
  
  - No blasting (pumping) recorded
  - Slight effect on swelling
Sectional Summary

- Adding Fiber can adjust the swelling kinetics and strength of the re-crosslinked gel.

- F-RPPGs with fiber concentration 0.03 and 0.06% perform highest G’.

- Initiator concentration can influence the G’ of the re-crosslinked gels.
Introduction of Alg-IPNG

How to synthesize Alg-IPNG particles?

- One-pot free-radical polymerization (solution polymerization).
- Procedures:
  (a) Preparation of a solution containing monomer(s), crosslinker(s), and Alginate;
  (b) Deoxygenation
  (c) Adding initiator(s)
  (d) Aging in a 50°C oven
  (e) Post-treatment (dry, grind, and screen)

Alg-IPNG Applicable Focus:
- 80 to 100 °C
- Reinforced-strength (delayed)
Inter-penetration & Ca-Alg Crosslinks

- **Inter-penetrating structure (IPN) advantages:**
  - High strength
  - Stable swelling
  - Multiple stimuli-response

- **Ca-Alginate crosslink**
  - Configuration
    - (G rich & M rich)

**Poly(acrylamide-co-vinyl acetate)**

**G monosaccharides**
\(\alpha\)-L-gulopyranuronate

**M monosaccharides**
\(\beta\)-D-mannopyranuronate

- **Ca-Alg crosslink**

- **Immersion in CaCl\(_2\) brine**

**Inter-penetration & Ca-Alg Crosslinks**
Results:

- Brine salinity effect
- Brine type effect (disproportionately)
Re-crosslinking Measurement

- Re-crosslinking Results:
  - Re-crosslinking started in 60 h
  - Temperature ↑ → starting time ↓
  - Temperature ↑ → Interval time ↓
    (20:1 to 40:1)
  - Swelled ratio ↑ → Interval time ↑
  - High G’

Alg-IPNG particles
(Particle size: 2-4 mm)

Alg-IPNG solution

Re-crosslinked gel

Immersed in 1% NaCl brine

100 °C, 12 h

Lyophilization

SEM picture

1 μm

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Thermo-stability Characterization

- Results:
  - Extra-swelling of Alg-IPNG (40:1 sample at 100 °C)
  - Only Alg-IPNG (Swelled ratio = 20:1) remains stable (100%) after 150-d aging
  - Alg-IPNG shows better thermo-stability than RPPG at 100 °C
  - Decomposition/Degradation starts from the gel/air surface
Thermo-stability Characterization (cont.)

L-RPPG
40:1
3 d → 80 d → 150 d

L-RPPG
20:1
3 d → 80 d → 150 d

Alg-IPNG
40:1
3 d → 80 d → 150 d

Alg-IPNG
20:1
3 d → 80 d → 150 d

Na⁺
polymer
Sectional Summary

• IPN structure has been introduced to Alg-IPNGs which help to improve the strength (G’) by absorbing Ca\(^{2+}\) and forming Ca-Alg crosslinks.

• Ca-Alg crosslinks can influence both the swelling behavior and the strength (G’) of the Alg-IPNGs.

• Alg-IPNGs can re-crosslink to form a bulky gel.

• Compared with previous products (L-RPPG, F-RPPG, and etc.), Alg-IPNG performs a better thermo-stability at high temperature.
Topic IV: Enhanced Alg-based Gel (R-RPPG)

- R-RPPG Applicable Focus:
  - Stable swelling behavior
  - High-T (>100°C)

- R-RPPG particles:
  - Green & dark
  - Resorcinol-embedded

Inter-penetrating structure
Resorcinol
Copolymers
R-RPPG particles

Semi-product (Resorcinol)
Solidification

5-day aging
100 °C/212°F
Swelling Kinetic and Equilibrium

Particle size: 2-4 mm
23.9°C/75°F
1% NaCl

Swelling ratio $V_t/V_0$

Time (h)

Results

- Not sensitive to brine type and concentration (except for 5% NaCl)

G’ & G” measurement

Solution type

DIW 1% NaCl 5% NaCl 5% CaCl2

Results

- Soft
- Not sensitive to brine type and concentration
Re-crosslinking Measurement

- **R-RPPG re-crosslinking**
  - **Results**:
    - Delayed re-crosslinking
    - Temperature $\uparrow \rightarrow$ starting time $\downarrow$
    - Temperature $\uparrow \rightarrow$ Interval time $\downarrow$
    - Swelled ratio $\uparrow \rightarrow$ Starting time $\uparrow$
    - Low $G'$ (compare with Alg-IPNG)
Thermo-stability Characterization

- Results:
  - Started to re-crosslink in day one
  - R-RPPG showed a delayed swelling
  - Gas created in the re-crosslinked gel (sample 20:1)
  - No decomposition/degradation so far

Sectional Summary

- R-RPPG performs more stable swelling behavior in various brines than Alg-IPNG.

- R-RPPGs have lower G’ before or after re-crosslinking than Alg-IPNG. However, the G’ of the re-crosslinked gel increased as the increase of the temperature.

- R-RPPG shows a delayed swelling at 100°C.
Summary

• New batch product (COP-1) shows a more sticky property than the previous products.

• Adding Fiber into the L-RPPG to form F-RPPG which can improve the strength and swelling kinetics of the gel.

• Alg-IPNGs can absorb Ca$^{2+}$ and form Ca-Alg crosslinks. The re-crosslinked gel maintains good thermo-stability.

• R-RPPG can has higher $G'$ when put in the higher temperature environment.

• Both F-RPPG and Alg-IPNG demonstrate stable swelling kinetics which is independent to brine type and concentration.
Acknowledgement

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Thank you / Questions