Development of Nanoparticle-Stabilized Foams to Improve Performance of Water-less Hydraulic Fracturing

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Presentation Outline

• Benefit to the Program
• Project Overview
  – Goals and Objectives
  – Background and Motivation
  – Success Metric
• Technical Status
  – 3 Key Findings Elaborated
  – Work in Progress
• Accomplishments to Date
• Summary
Benefit to the Program

• **Goal:** Reducing water usage in hydraulic fracturing without reducing stimulation performance

• **Benefits statement:** The research project is developing high gas fraction (>0.9, “*ultra dry*”) CO$_2$-in-water and N$_2$-in-water foams suitable for hydraulic fracturing. Such foams could drastically reduce water use per fracture.
Project Goal: Establish Novel Frac Fluid Technology to Reduce Water Consumption

Project Objective: Develop nanoparticle-stabilized CO$_2$-in-water (C/W) and N$_2$-in-water (N/W) foams suitable for hydraulic fracturing treatment.

Foam quality = $V_{\text{gas}}/V_{\text{total}}$

Ultra Dry Foams to Reduce Water Consumption

Water usage in hydraulic fracturing could be reduced by over 90% by using ultra-dry foams. The foams are stabilized using nanoparticles, surfactants and polymers.
Background and Motivation

• Three drivers
  – Hydraulic fracturing essential technology for current, future hydrocarbon production
  – Unconventional oil and gas reservoir development requires
    • Dense well spacing
    • Many frac stages per well

• Standard base fluid for hydraulic fracturing is fresh water
  – Competition for water in arid regions
  – Water use, disposal in wet regions
  – Water additives that reduce leak-off form gel on fracture face (impede production)
Success Metric

• **Baseline: fracturing fluids**
  • Currently at use 20-30% of water or more
  • Should be *viscous enough* to carry sand, but also allow *easy clean up* before production

• **Proposed technology response:** use *substantially* less water per frac by using ultra dry foams
Key finding 1: ultra dry foams with nanoparticles (NPs), surfactant and polymer

- Very low water (“ultra dry”) supercritical CO$_2$-in-water foams:
  - 90% - 98% CO$_2$ by volume
  - with high viscosity on the order of 100 cP and
  - long lifetime of hours
- Stabilized with mixtures of:
  - silica nanoparticles
  - lauramidopropyl betaine (LAPB) surfactant and
  - partially hydrolyzed polyacrylamide (HPAM) polymer
- Foams at typical conditions of hydraulic fracturing of 2 % KCl brine and 50 °C could potentially reduce water consumption for fracturing by orders of magnitude.
Key finding 1: Ultra Dry Foams with NPs, Surfactant and Polymer

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Foam Generation and Viscosity Measurements

Hagen–Poiseuille equation

\[ \mu_{app,capillary} = \frac{\pi \cdot \Delta P \cdot R^4}{8 \cdot q \cdot L} \]
Apparent Viscosity of C/W Foams in 2 % KCl brine at shear rates of 200 s\(^{-1}\), 3000 psi and 50 °C.
95% v/v C/W foams stabilized with mixtures of 0.88% HPAM, 0.08% LAPB, with and without 1% silica NP.

NPs increase the apparent viscosity and stability of foam. NPs:

- Decrease bubble size by factor of 2
- Increase foam stability against Ostwald Ripening
- Irreversibly adsorb to C/W interface, creating an elastic interface
High Pressure Foam Suspends Sand

- 90% quality, 2000 psi
- Presence of the proppant grains does not affect the foam stability
- The dry foam has enough strength and stability to carry the proppant in potential fracturing applications

Key finding 1: Mechanisms

• High continuous phase and surface viscosities produced as a result of opposite charge between surfactant and polymer

• CO₂/brine IFT reduced from 20 mN/m to 5 mN/m at 50 °C, 3000 psia

• Low lamellae drainage rates and low coalescence

• Small bubble size leads to high viscosity of 150-270 cP at 0.90-0.98 quality, at 200 s⁻¹

• NPs increase the apparent viscosity and stability of foam
Key finding 2: Ultra Dry Foams with Viscoelastic Aqueous Phases

- Stabilized with **viscoelastic aqueous phase**
  - high viscosity (100 cP at 100 s\(^{-1}\)),
  - high quality (> 0.9) C/W foams
  - with **long lifetime** (>3 hrs)

- Fine bubbles (20 µm) were stabilized at high quality up to 0.98

- **Significance:** Simplified, ultra dry foams formed with sodium lauryl ethoxylated sulfate (SLES) surfactant **without** polymer **could potentially be enough** to carry out fracturing.

- SLES allows for more control over triggering destabilization of foams upon depressurization.
Entanglement of Wormlike Micelles Imparts Viscoelasticity

https://www1.ethz.ch/ilw/vt/research/projects/viviane

Surfactant packing parameter

\[ p = \frac{v}{a_0 l_c} \]

\( v \): volume of surfactant tail
\( l_c \): length of surfactant tail
\( a_0 \): area of surfactant head group

Lower crossing frequency means higher entanglements.

Maxwell Model
Linear Viscoelasticity

\[ G'(\omega) = \frac{\omega^2 \tau^2_R}{1 + \omega^2 \tau^2_R} G_0 \]
\[ G''(\omega) = \frac{\omega \tau_R}{1 + \omega^2 \tau^2_R} G_0 \]
Wormlike Micelles Provide Higher Disjoining Pressure and Slower Drainage

- Drainage driven by pressure difference:
  \[
  V = -\frac{d h_f}{d t} = \frac{h_f^2}{3 \mu_e R_f^2} \Delta P_{film}
  \]

  \[
  \Delta P_{film} = 2(P_c - \Pi_d)
  \]

  \(\Pi_d\) (disjoining pressure) = van der Waals, electrostatic repulsion and repulsive steric or hydration.

- \(P_c\) increases as \(CO_2\) volume fraction (\(\phi\)) increases
  \[
  P_c \approx \frac{\gamma}{R_v \sqrt{1-\phi}}
  \]

- Wormlike micelles provides higher disjoining pressure: bulkier (more steric repulsion)

- High aqueous phase viscosity lowers drainage: maintain thicker lamellae.

Ivanov and Kralchevsky, 1997
Langevin, 2000
Foam Viscosity

at room temperature, 3000 psia and 200 s⁻¹

(a)

Foam Viscosity (cP)

Internal Phase Volume Fraction
Foam Texture

- SLES + CDMA 2% KCl
- SLES 2% KCl
- SLES DIW

\( \phi = 0.80 \)
\( \phi = 0.95 \)
\( \phi = 0.98 \)
Key Findings 2: Mechanisms

- Increased continuous phase and surface viscosity by wormlike micelles and polyelectrolytes
  - The wormlike micelles were formed by raising the packing parameter of SLES with salt and protonated C\textsubscript{10}DMA, as shown by cryo-TEM, and large values of the zero-shear viscosity and the dynamic storage and loss moduli.

- Lower lamella drainage rate by immobile interface and high continuous phase viscosity

- Reduced coalescence and Ostwald ripening possibly due to thick film and elastic interface

- Improved foam stability by dense packing surfactant or nanoparticle (at interface) or polyelectrolyte

Key finding 3: Numerical Assessment of Reservoir Behavior

- Larger foam viscosity generated wider fractures with smaller fracture half-length: less leak-off
- Fracture cleanup simulations show that fracturing fluid cleanup for foam based fracturing fluids could take the order of 10 days
  - Compare viscous fracpad which could take up to 1000 days
- Finite difference model combines:
  - Gas and water flow in matrix and fracture
  - Mechanistic accounting of foam generation and coalescence (population balance, Kam & Rossen)
  - Simplistic fracture geometry (KGD model)

Fracture Geometry (width and half-length)

Water

Viscous frac pad

CO₂
Larger Foam Viscosity Generated Wider Fractures with Smaller Fracture Half-length
Fracture Geometry is Tunable Based on Viscosity

Foam 70% Low Vis.

Foam 90% Low Vis.

Foam 95% Low Vis.
### Fracture Cleanup / Water Saturation

<table>
<thead>
<tr>
<th>Water</th>
<th>1 day</th>
<th>2 days</th>
<th>7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vis Fracpad</td>
<td>Foam 70%</td>
<td>Foam 70%</td>
<td>Foam 70%</td>
</tr>
<tr>
<td>Low Vis.</td>
<td>High Vis.</td>
<td>Low Vis.</td>
<td>High Vis.</td>
</tr>
<tr>
<td>Foam 90%</td>
<td>Foam 90%</td>
<td>Foam 90%</td>
<td>Foam 90%</td>
</tr>
<tr>
<td>High Vis.</td>
<td>Low Vis.</td>
<td>High Vis.</td>
<td>Low Vis.</td>
</tr>
</tbody>
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Work in Progress

• Results replicated with $N_2$ foams
  – Foam quality, stability and texture very similar
  – **Hypothesis to be tested:** depressurization triggers foam destabilization due to compressibility

• Results replicated at 90°C

• Environmentally responsible surfactants
Foam Morphology of 1% Surfactant in Different Salt Conc. at 90°C and 3000 psi

<table>
<thead>
<tr>
<th></th>
<th>70Q</th>
<th>95Q</th>
<th>98Q</th>
</tr>
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<tbody>
<tr>
<td>DI</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
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<tr>
<td>2%KCl</td>
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<td>API</td>
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</tbody>
</table>

- Increasing salt concentration increases the aqueous phase viscosity, which in turn helps decreasing the initial bubble sizes especially at very high qualities.
- Smaller bubble sizes give rise to higher foam viscosity.
Aqueous Phase Rheology with 1% w/v Single Surfactant that Makes Wormlike Micelles

Aqueous rheology at 25°C and ambient pressure

Complex rheology at 25°C and ambient pressure

- Aq. phase viscosity at 25°C and ambient pressure incr. with salt conc.: more entangled wormlike micelles
- The crossing of the lose and storage modulus indicates the entanglement of the wormlike structure: more entangled wormlike micelles cross at lower ang. frequency.
Foam Generated with 1% w/v Single Surfactant that makes Wormlike Micelles at a Shear Rate of 200/s

Foam vs. salt at 90°C and 3000psi

- Aq. phase viscosity increases raises C/W foam viscosity as expected theoretically
- Stable foams maintained up to 90°C even with very high foam quality:
  - reduced lamellae drainage from wormlike micelles
  - thicker lamellae resist Ostwald ripening and coalescence
Accomplishments to Date

- Successful creation and characterization of viscous, ultra dry CO$_2$ and N$_2$-in-water foams:
  - Stable at high temperature and pressure
  - Can carry proppant
  - Could significantly reduce water use
  - Environmentally friendly surfactants possible
Synergy Opportunities

– Need to test fracturing behavior in the lab and field (Sharma, Tokunaga, Winterfield)

– Reservoir / geomechanics simulators currently cannot model ultra dry foam (Wheeler, Nakagawa, Sharma)
Summary

– Key Findings
– Lessons Learned
– Work in Progress
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• Model combines:
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  – Fracture geometry generated using existing software
  – Mechanistic accounting of foam generation and coalescence (population balance)

Lessons Learned: Technology basis for stabilizing and viscosifying foams

Most advanced ultra dry CO₂-in-water foams are stabilized with a viscoelastic aqueous phase

- Key finding 2: viscoelastic anionic wormlike micelles
- Key finding 1a: mixtures of anionic NPs and cationic surfactant
- Key finding 1b: mixtures of anionic NPs, anionic polyelectrolyte and low conc. cationic surfactant
Lessons Learned: Technology basis for stabilizing and viscosifying foams

Compare to ultra dry CO$_2$-in-water foams are stabilized with NPs, surfactant and polymer

- Key finding 2: viscoelastic anionic wormlike micelles
- Key finding 1a: mixtures of anionic NPs and cationic surfactant
- Key finding 1b: mixtures of anionic NPs, anionic polyelectrolyte and low conc. cationic surfactant
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- Results replicated at 90°C
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- Environmentally responsible surfactants
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Appendix

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

- Maša Prodanović¹ (PI)
- Keith Johnston² (co-PI)
- Chun Huh¹ (co-PI)
- PhD Students: Shehab Alzobaidi², Chang Da²
- Graduated students: Zheng Xue², Andrew J. Worthen²
- Postdoctoral researcher: Ali Qajar¹

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²Chemical Engineering, UT Austin
Project Schedule

• **Year 1 (Start 10/2013)**
  - Task 1 – Project Management, Planning, and Reporting
  - Task 2 – Development of high viscosity C/W foams
  - Task 3 – Development of materials/techniques for N/LHC foams

• **Year 2**
  - Task 4 – Development of C/W foams with tunable stability
    - Overall, above and beyond successful; two technologies, nanoparticles not always necessary
  - Task 5 – Development of high viscosity N/LHC foams with particles
    - (abandoned – safety concerns, See Continuation Proposal, July 2015 for details)

• **Year 3 (End 10/2016)**
  - (Revised) Task 6 – Further characterization of ultra dry C/W foams
  - Task 7 – Development of N/W foams with nanoparticles–viscoelastic surfactants

✓ Overall tasks on schedule, however no-cost extension requested:
  ✓ Students graduated at the end of BP2, new PhD student trained and now productive
Bibliography

Peer reviewed:


Conference paper: