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

Project Number DE-FE0013723

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Carbon Storage and Oil and Natural Gas Technologies Review Meeting
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Presentation Outline

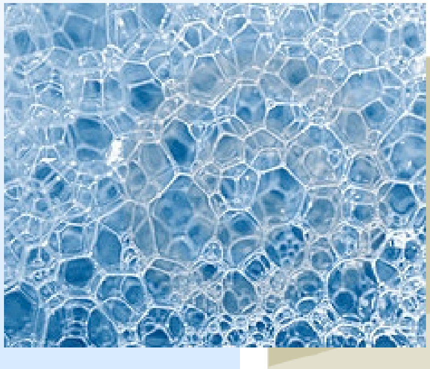
- Benefit to the Program
- Project Overview
  - Goals and Objectives
  - Background and Motivation
  - Success Metric
- Technical Status
  - 3 Key Findings Elaborated
  - Work in Progress
- Accomplishments to Date
- Summary

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.

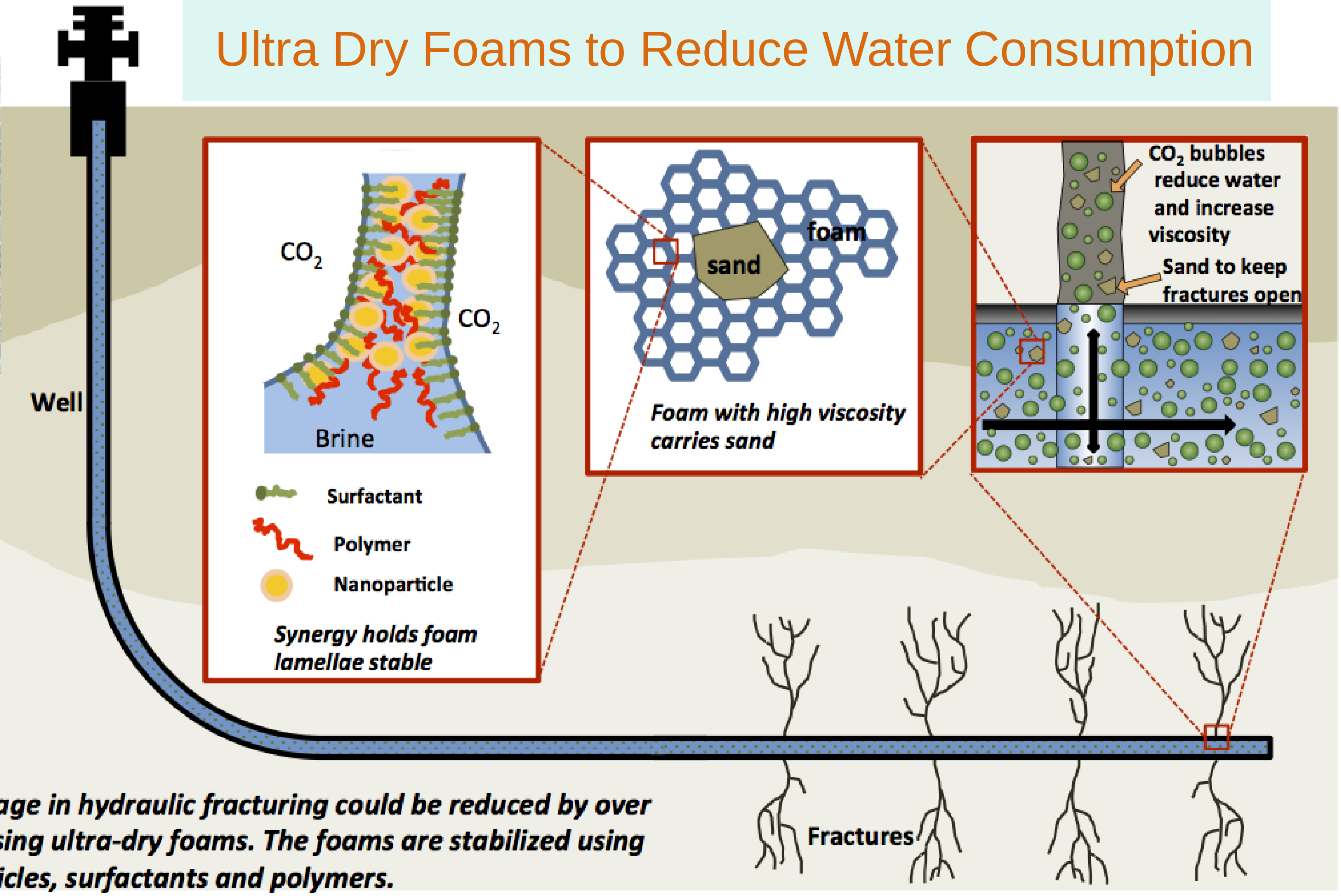
Project Goal: Establish Novel Frac Fluid Technology to Reduce Water Consumption

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 $=V_{gas}/V_{total}$

Ultra Dry Foams to Reduce Water Consumption



Synergy holds foam lamellae stable

Foam with high viscosity carries sand

CO_2 bubbles reduce water and increase viscosity

Sand to keep fractures open

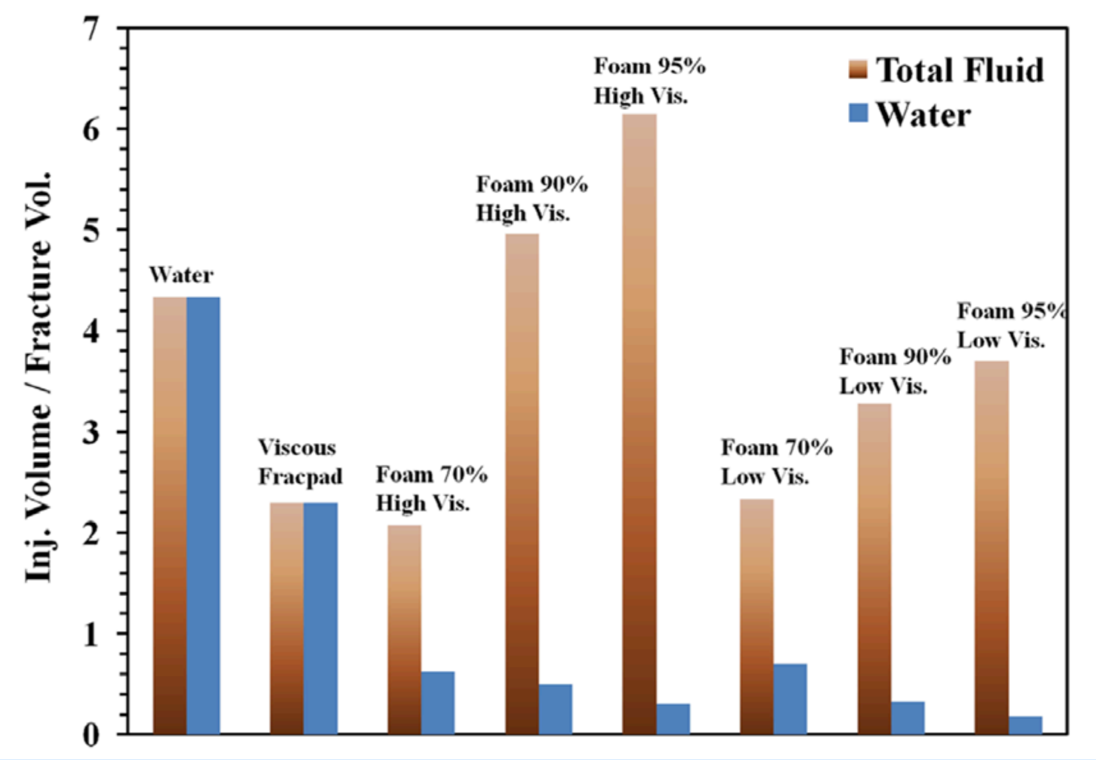
Water usage in hydraulic fracturing could be reduced by over 90% by using ultra-dry foams. The foams are stabilized using nanoparticles, surfactants and polymers.

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 ^oC could potentially reduce water consumption for fracturing by orders of magnitude.

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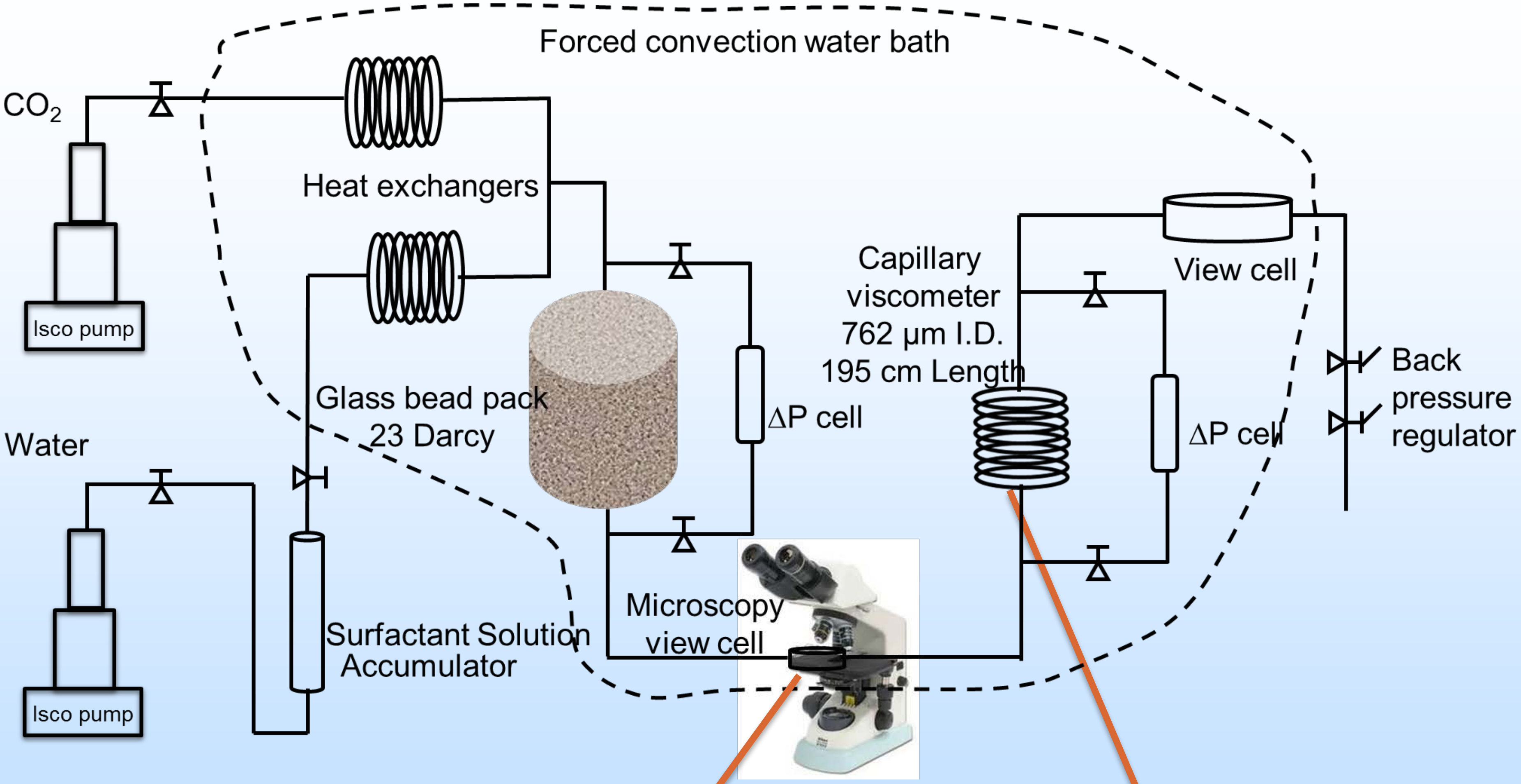
"Viscosity and stability of ultra-high internal phase CO2-in-water foams stabilized with surfactants and nanoparticles with or without polyelectrolytes", Z. Xue, A. Worthen, A. Qajar, I. Robert, S. L Bryant, C. Huh, M. Prodanović, K. P. Johnston, Journal of Colloid and Interface Science 461 (2016) 383-395

Foam Generation and Viscosity Measurements



Forced convection water bath

CO_2

Isco pump

Heat exchangers

Water

Isco pump

Glass bead pack
23 Darcy

ΔP cell

Surfactant Solution
Accumulator

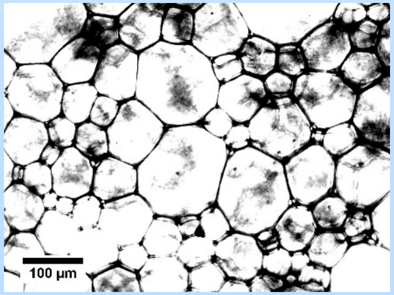
Microscopy
view cell

Capillary
viscometer
762 μm I.D.
195 cm Length

View cell

ΔP cell

Back
pressure
regulator

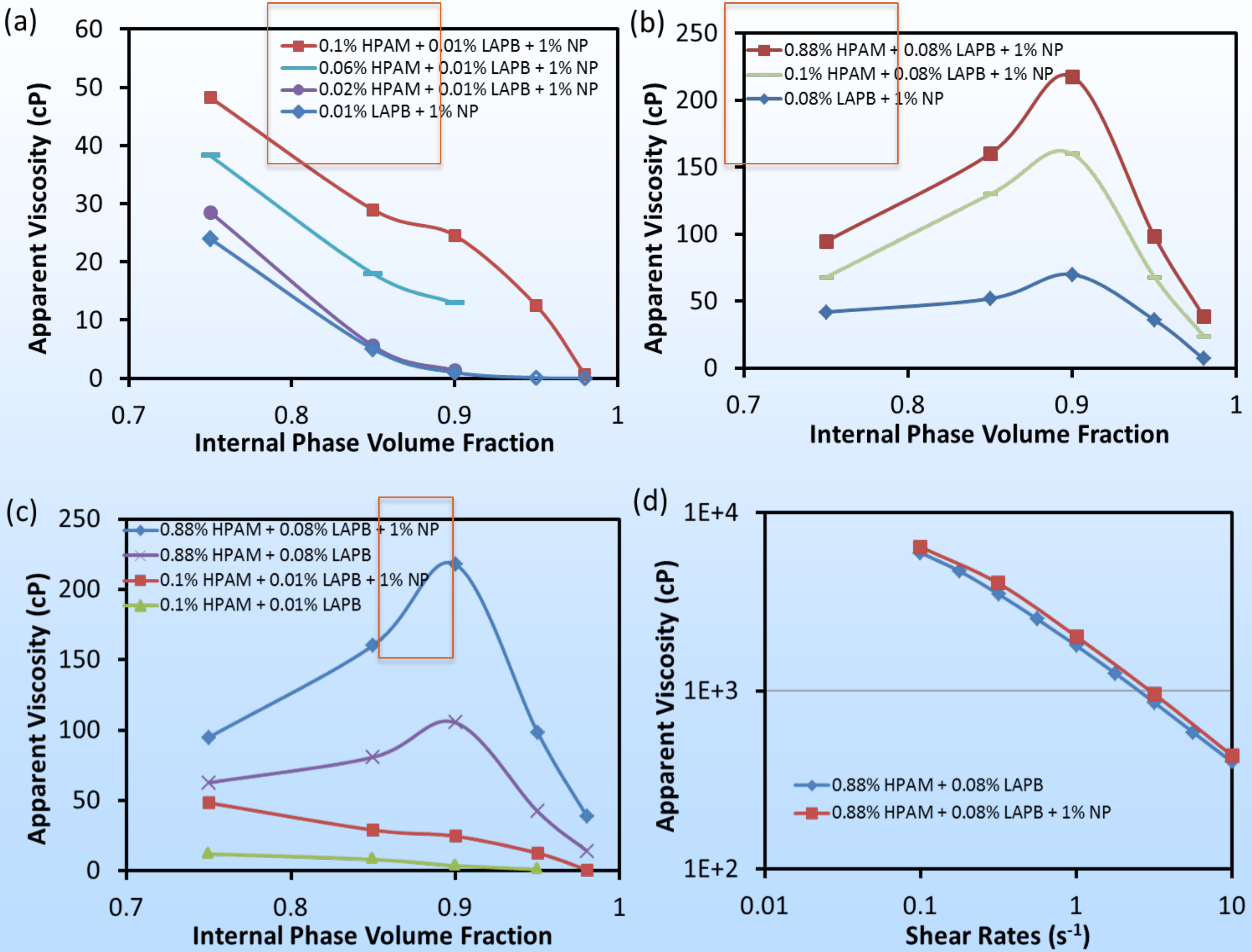


Hagen–Poiseuille equation

$$\mu_{app,capillary} = \frac{\pi \cdot \Delta P \cdot R^4}{8 \cdot q \cdot L}$$

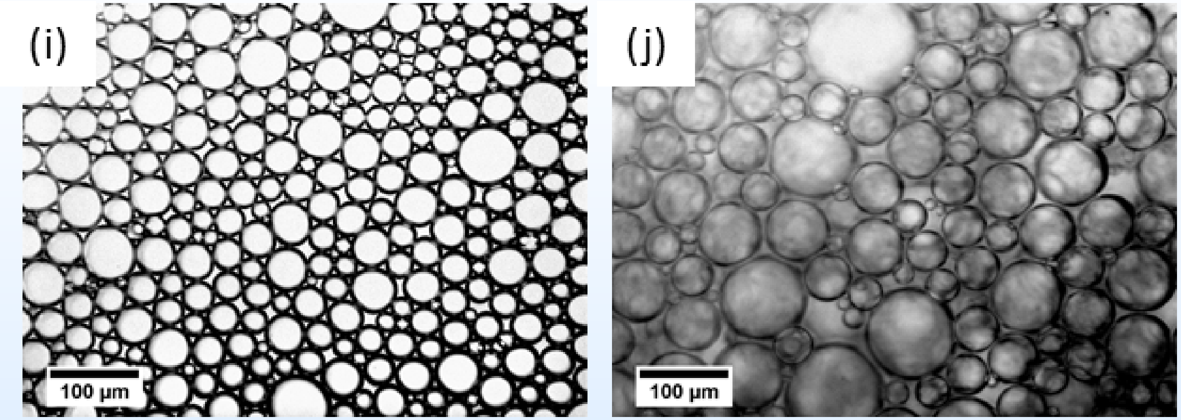
Apparent Viscosity of C/W Foams in 2 % KCl brine

at shear rates of 200 s^{-1}, 3000 psi and 50 ^{o}C.



Example Micrographs of C/W Foams

3000 psia, 2% KCl brine and room temperature.



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

Right after foam generated

One day later

- 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

C. Da, Z. Xue, A. J. Worthen, A. Qajar, C. Huh, M. Prodanovic, and K. P. Johnston, "Viscosity and Stability of Dry CO2 Foams for Improved Oil Recovery," in SPE Improved Oil Recovery Conference Proceedings, Tulsa, OK, 2016, p. Paper number 179690.

Key finding 1: Mechanisms

- High continuous phase and surface viscosities produced as a result of opposite charge between surfactant and polymer
- CO_2/brine IFT reduced from 20 mN/m to 5 mN/m at 50 ^oC, 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

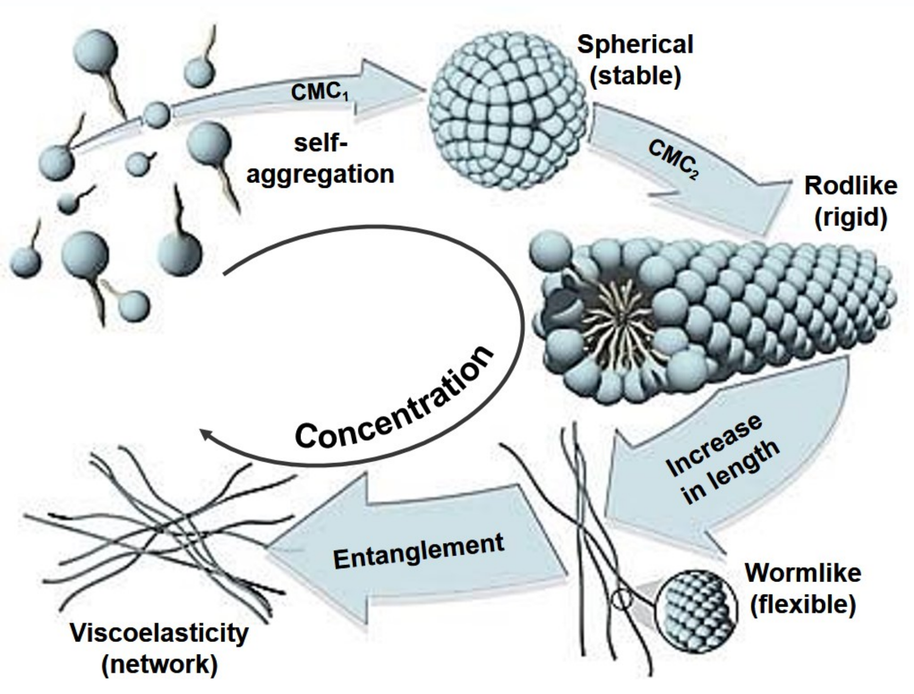
- Stabilized with **viscoelastic aqueous phase**
  - **high viscosity (100 cP at 100 s^{-1}),**
  - **high quality (> 0.9)** C/W foams
  - with **long lifetime (>3 hrs)**

- 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

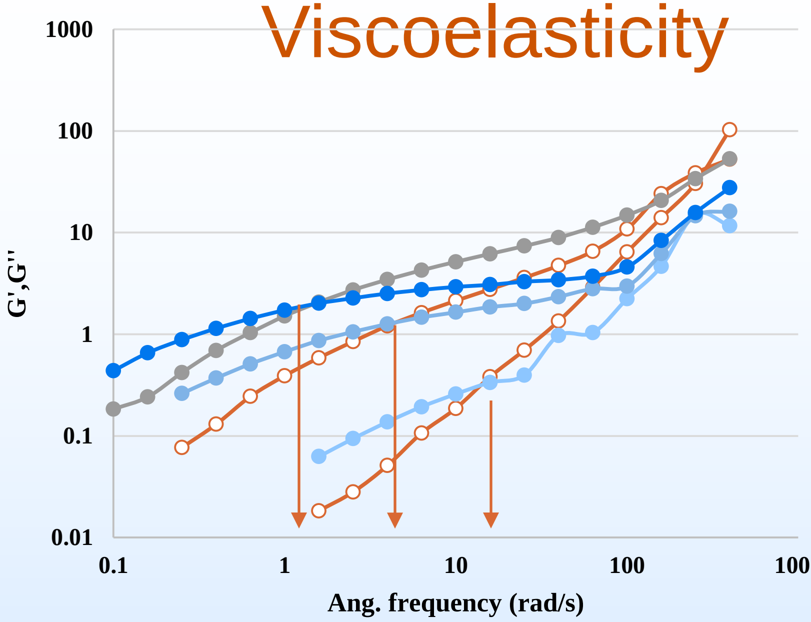


https://www1.ethz.ch/ilw/vt/research/projects/viviane/

surfactant packing parameter

$$p = v/a_0 l_c$$

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



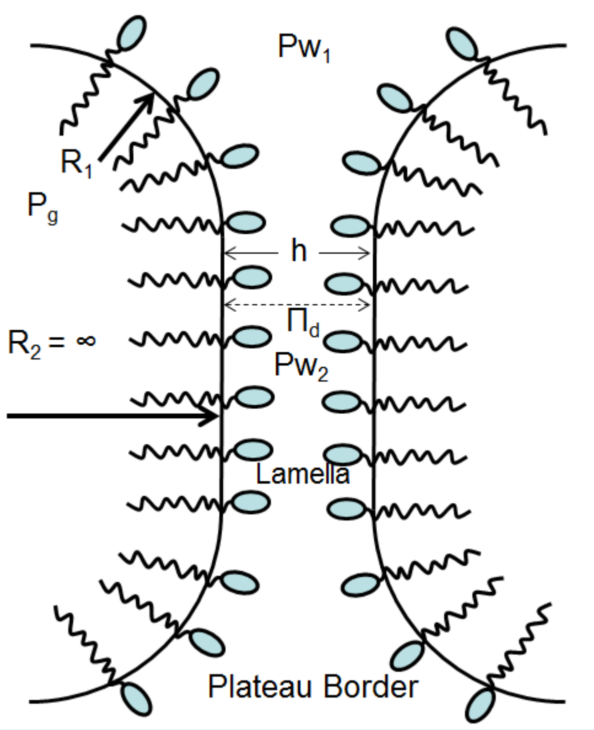
Lower crossing frequency means higher entanglements.

Maxwell Model
Linear Viscoelasticity

$$G'(\omega) = \frac{\omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2} G_0$$

$$G''(\omega) = \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2} G_0$$

Wormlike Micelles Provide Higher Disjoining Pressure and Slower Drainage



- Drainage driven by pressure difference:

$$V = -\frac{dh_f}{dt} = \frac{h_f^2}{3\mu_e R_f^2}\Delta P_{film}$$

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

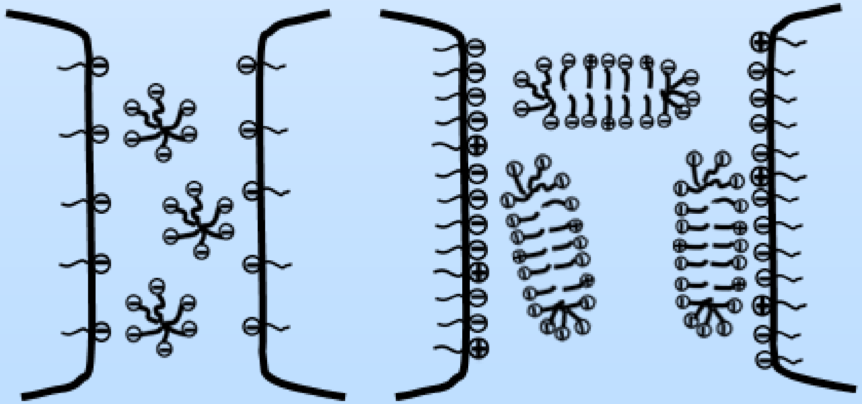
Πd (disjoining pressure) = van der Waals, electrostatic repulsion and repulsive steric or hydration.

P_c increases as CO_2 volume fraction (ϕ) 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.

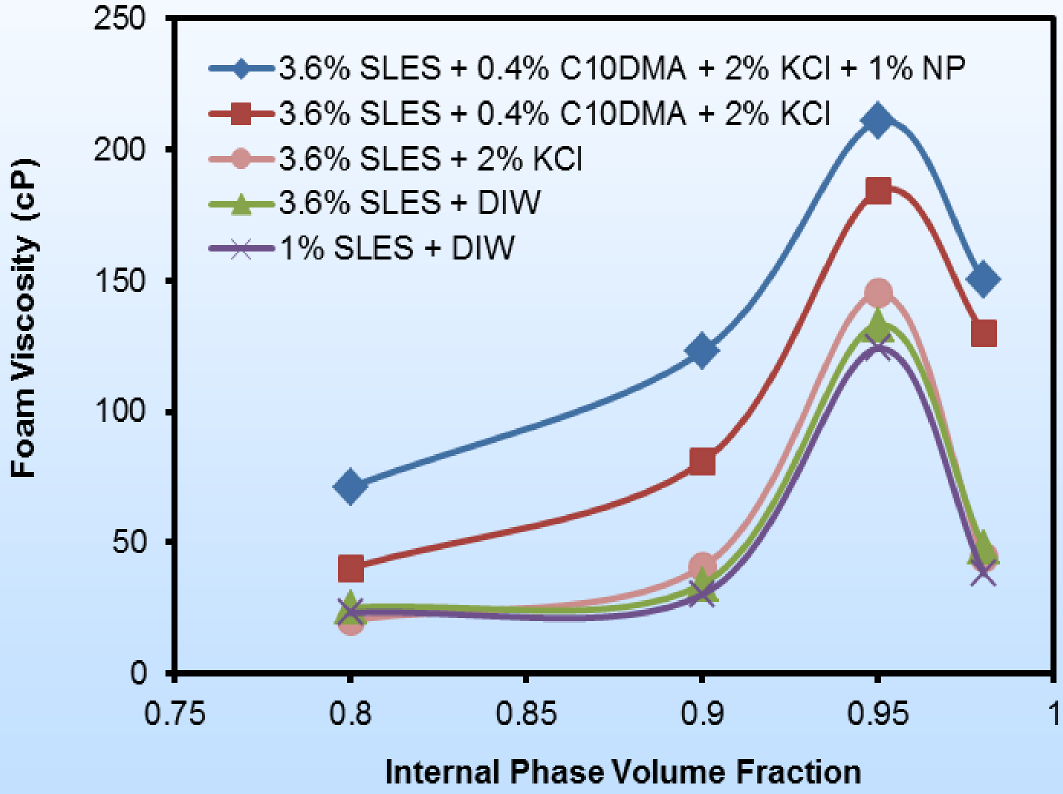


Ivanov and Kralchevsky, 1997
Langevin, 2000

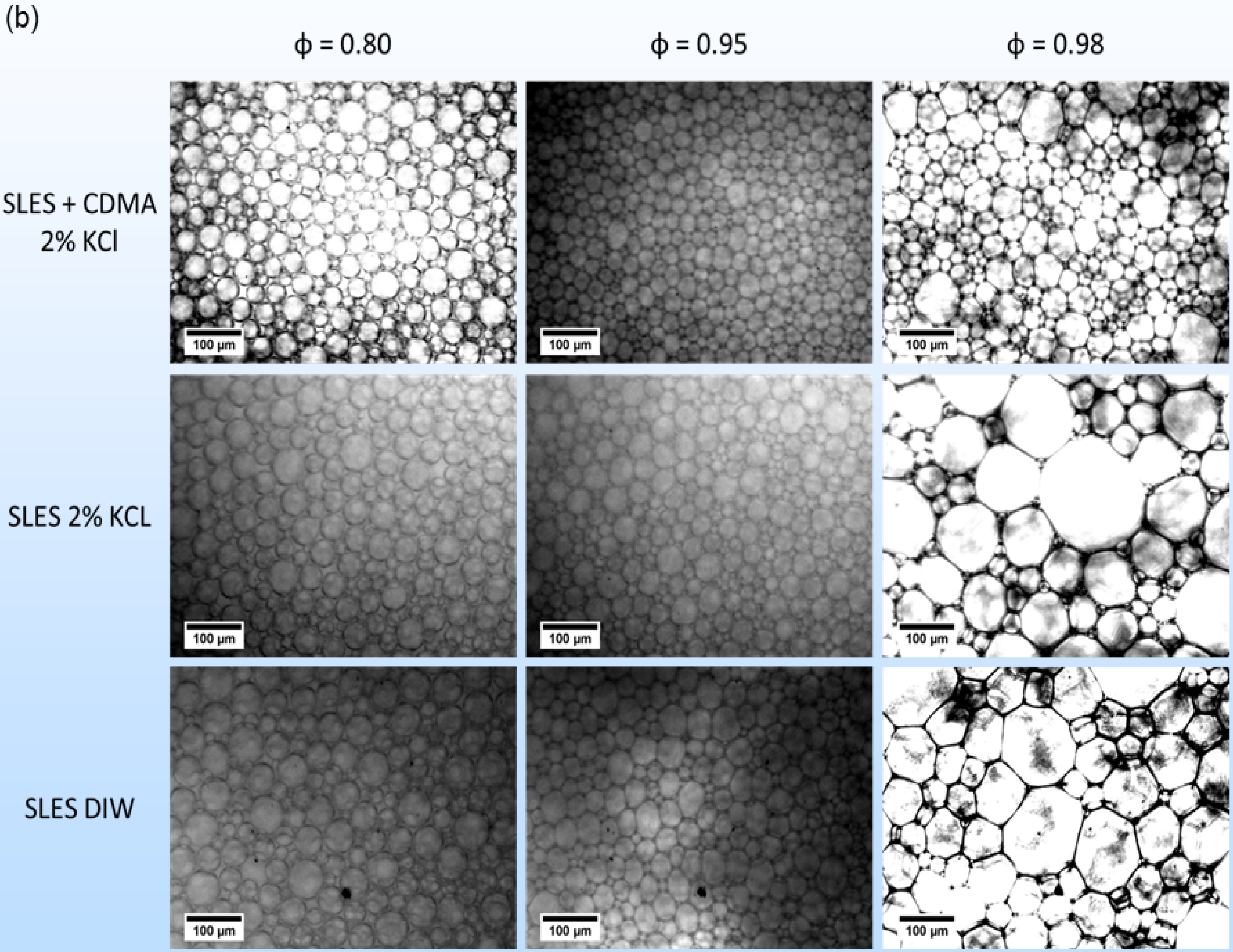
Foam Viscosity

at room temperature, 3000 psia and 200 s^{-1}

(a)



Foam Texture



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_{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

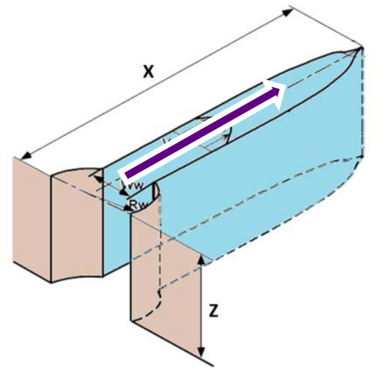
"Ultra dry carbon dioxide-in-water foams with viscoelastic aqueous phases", Z. Xue, A. J. Worthen, A. Qajar, I. Robert, C. Huh, M. Prodanović, K. P. Johnston, Langmuir, 2016, 32, 28-37

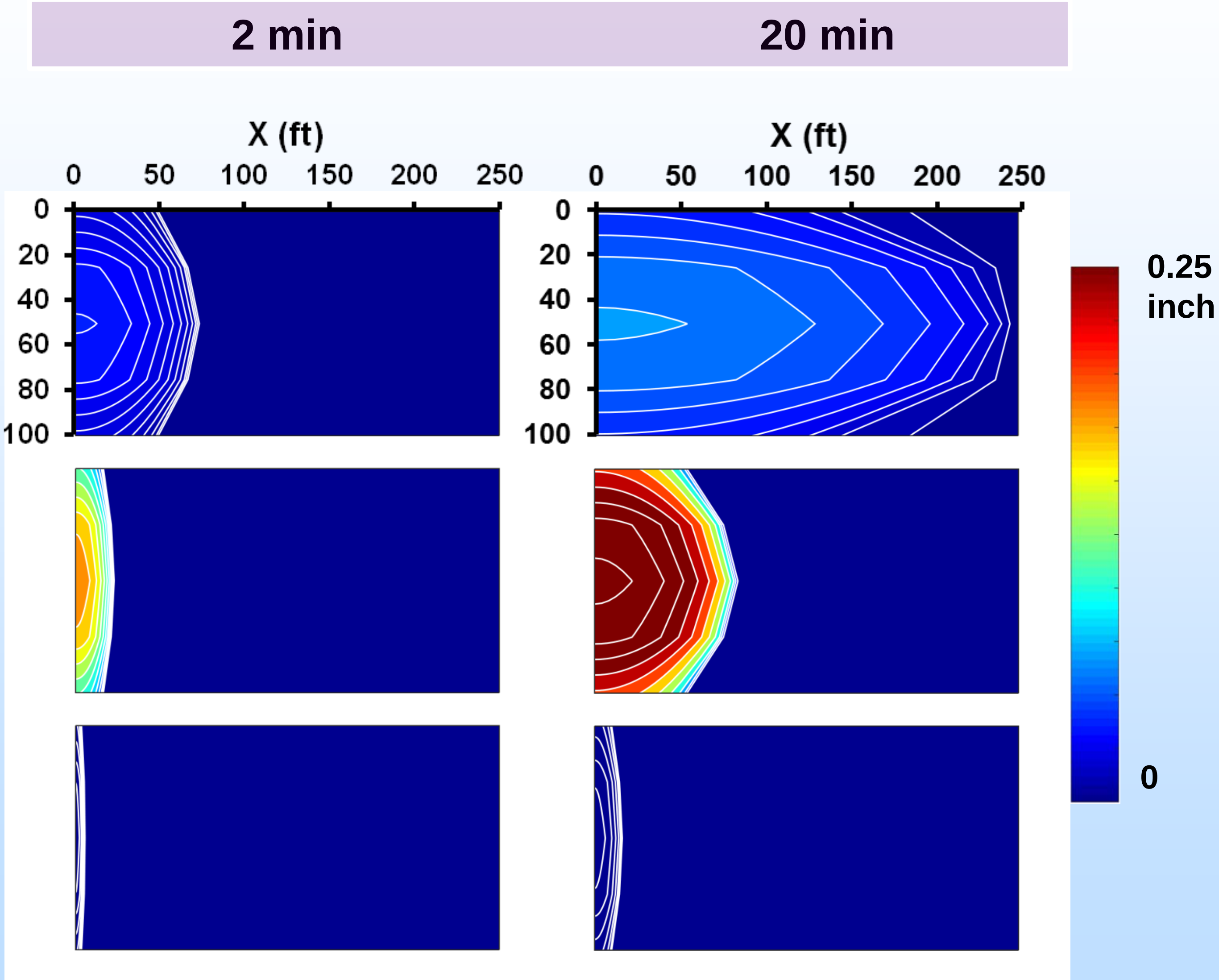
Key finding 3: Numerical Assessment of Reservoir Behavior

- 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)

“Modeling fracture propagation and cleanup for dry nanoparticle-stabilized-foam fracturing”, Ali Qajar, Zheng Xue, Andrew J Worthen, Keith P Johnston, Chun Huh, Steven L Bryant, Maša Prodanović, submitted to Journal of Petroleum Science and Engineering 146 (2016) 210-221

Fracture Geometry (width and half-length)



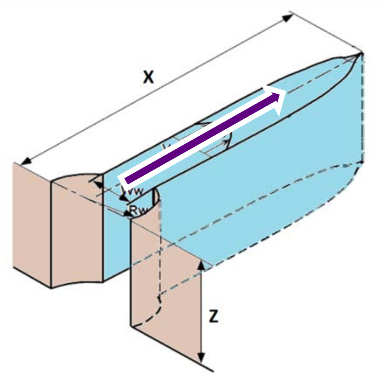


Water

Viscous frac pad

CO_2

Larger Foam Viscosity Generated Wider Fractures with Smaller Fracture Half-length

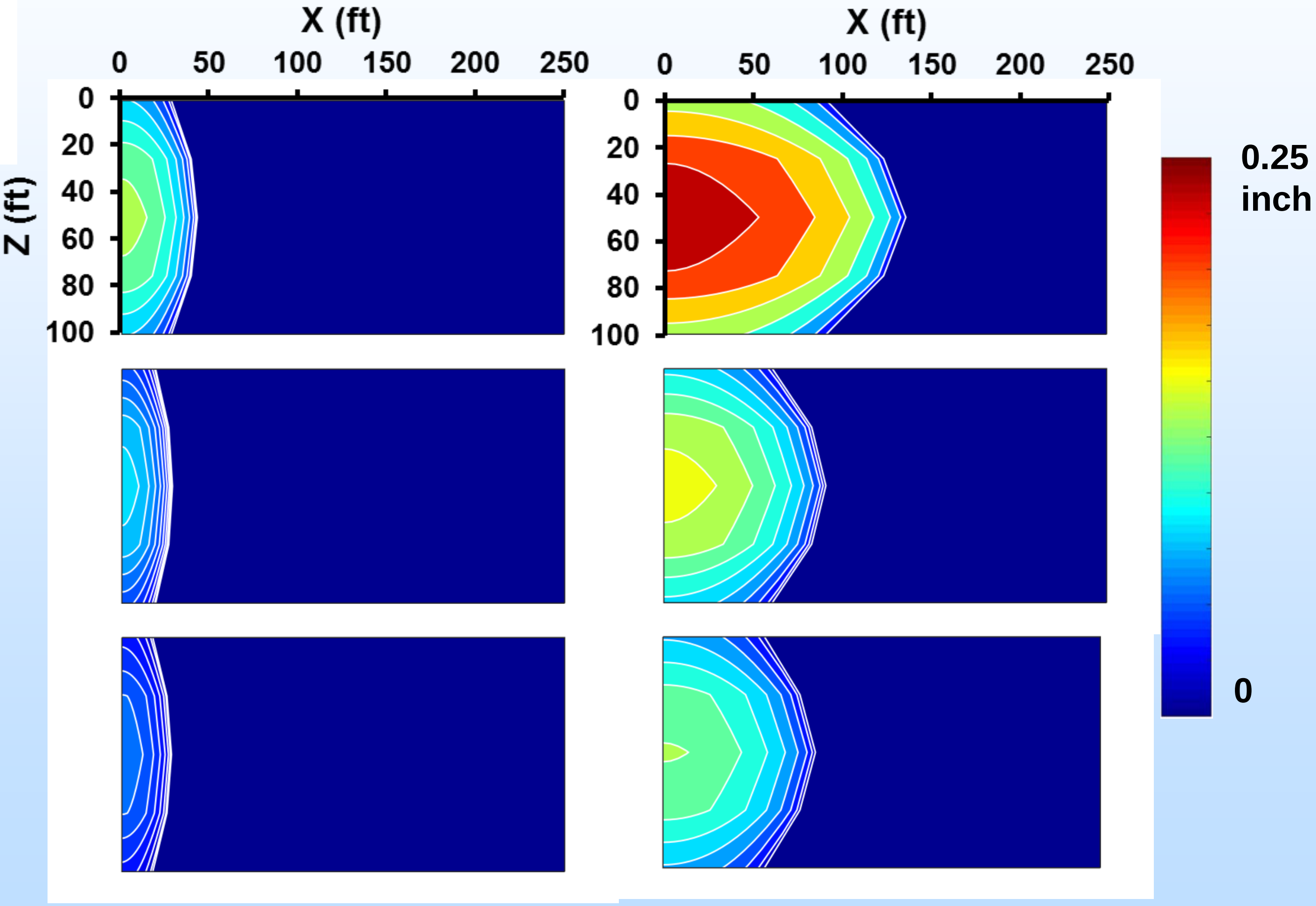


2 min | **20 min**

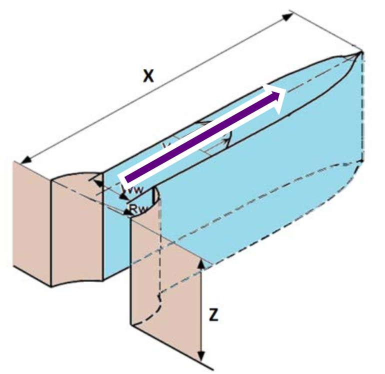
Foam 70% High Vis.

Foam 90% High Vis.

Foam 95% High Vis.



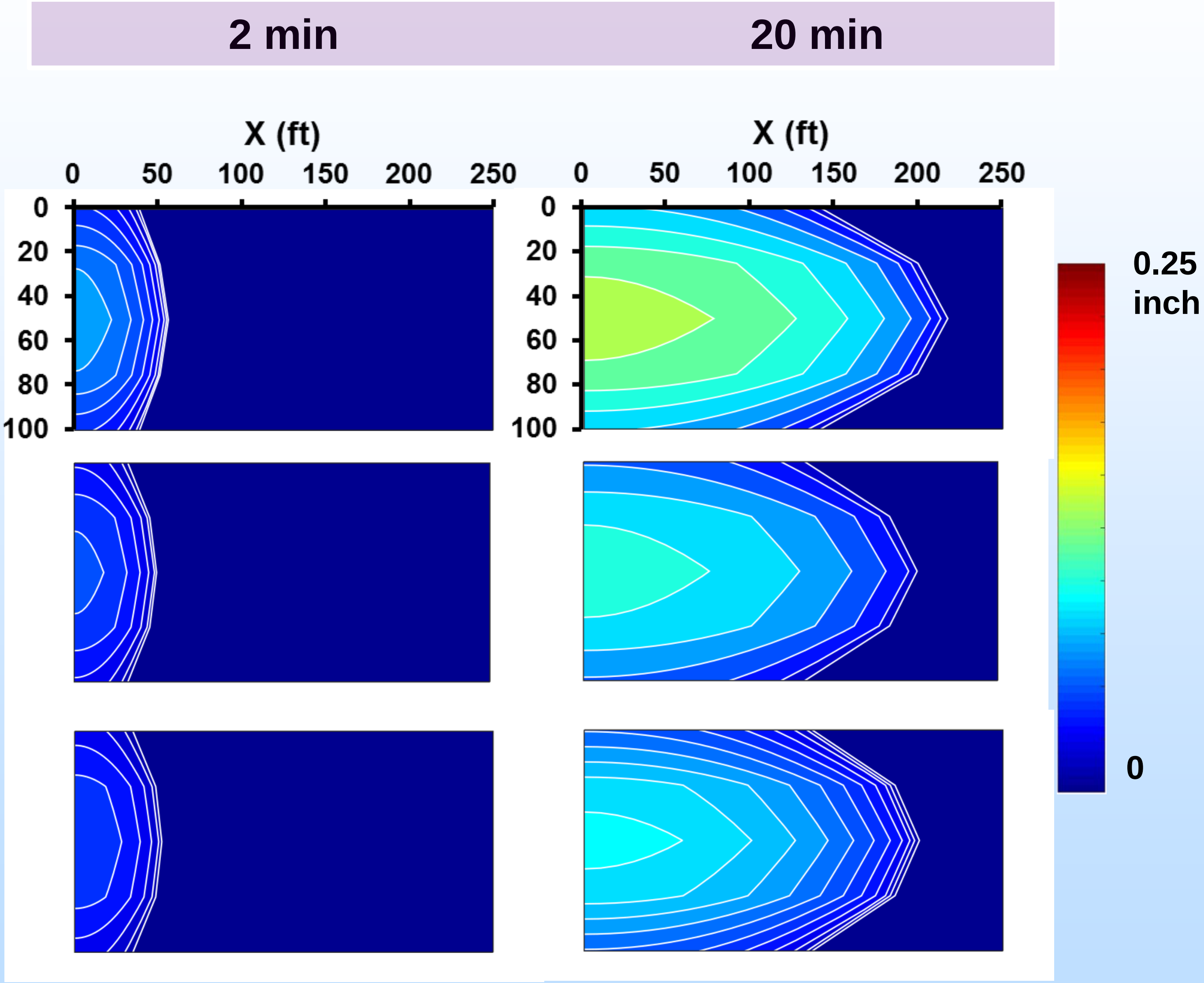
Fracture Geometry is Tunable Based on Viscosity



Foam 70%
Low Vis.

Foam 90%
Low Vis.

Foam 95%
Low Vis.



Fracture Cleanup / Water Saturation

1 day | 2 days | 7 days

Water

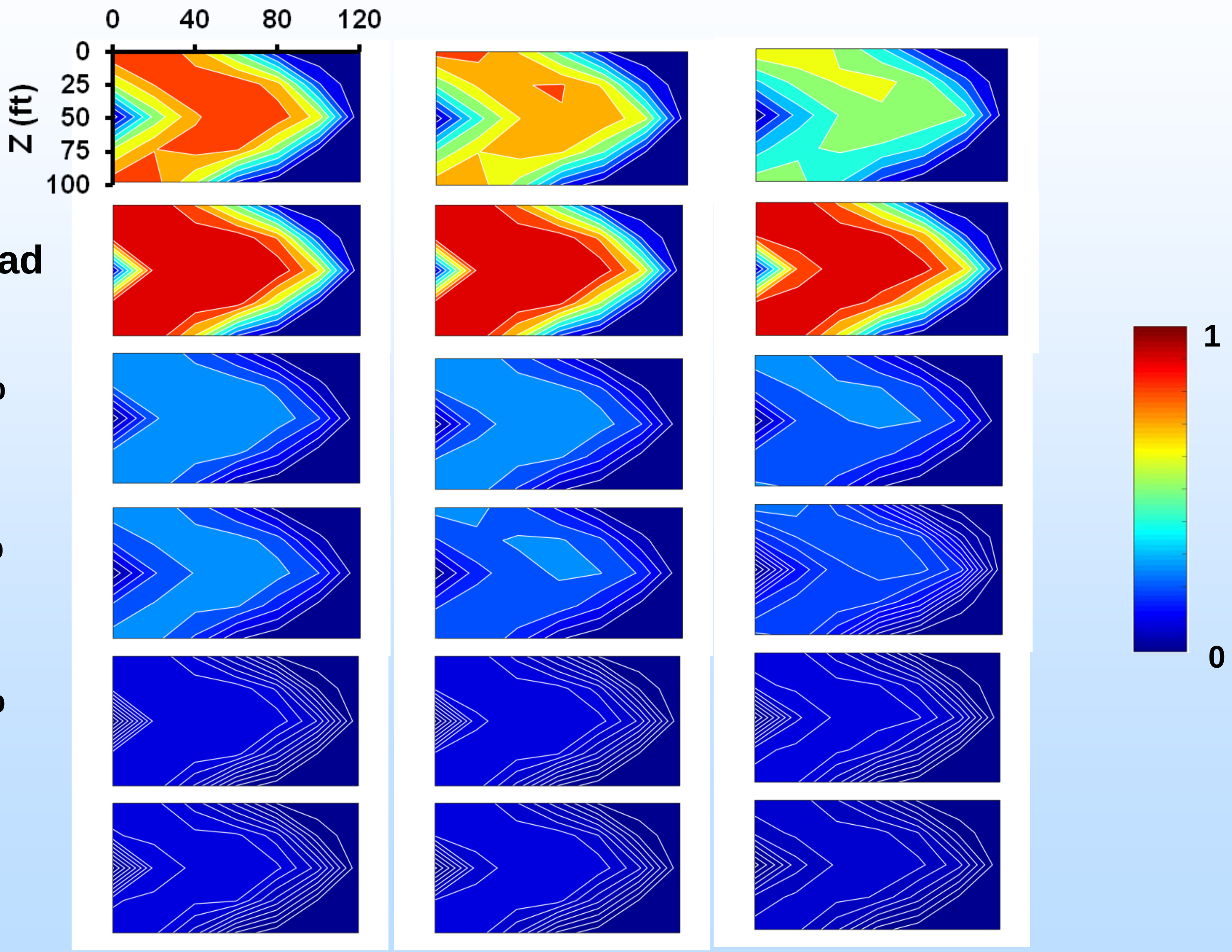
Vis Fracpad

Foam 70%
High Vis.

Foam 70%
Low Vis.

Foam 90%
High Vis.

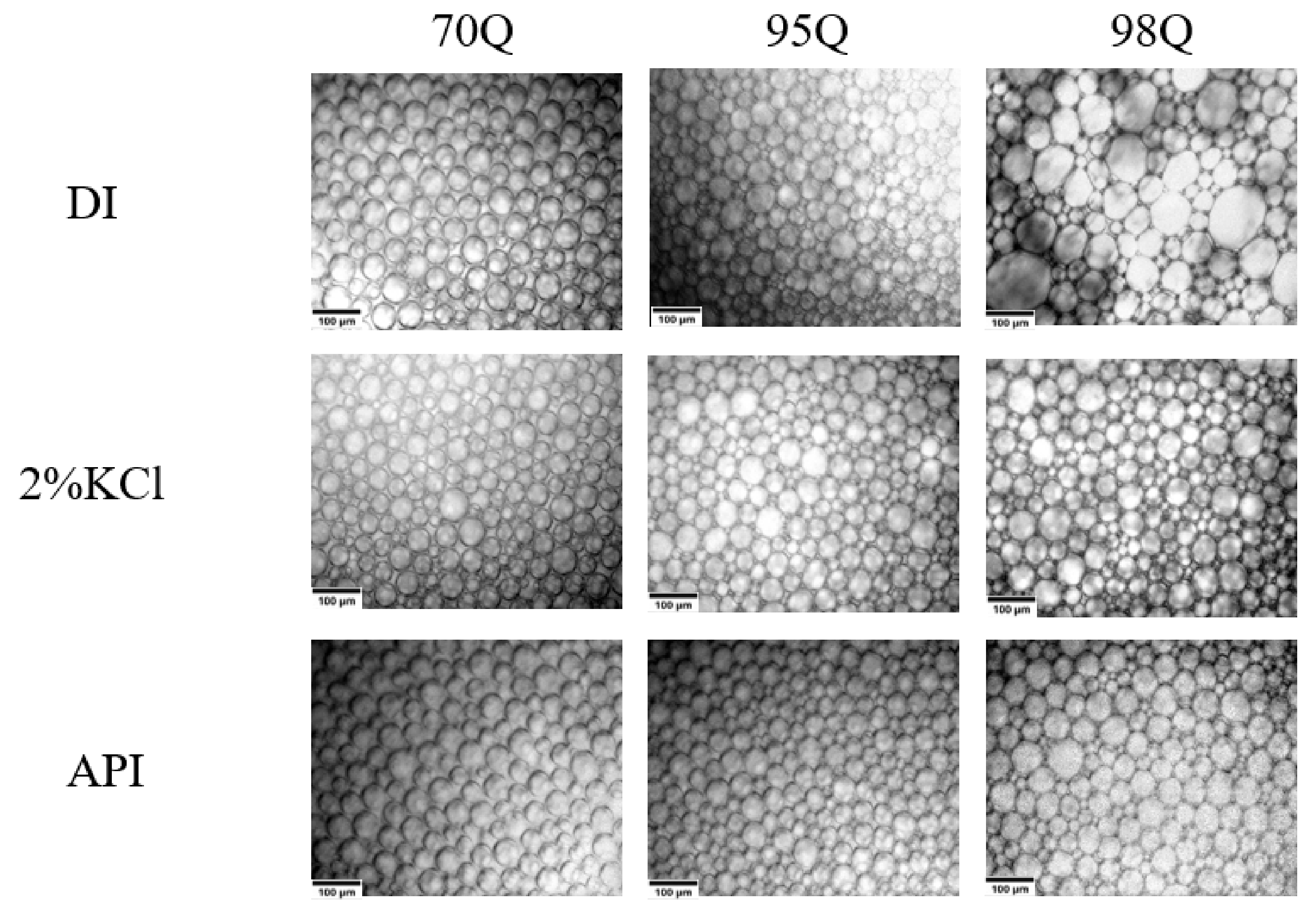
Foam 90%
Low Vis.



Work in Progress

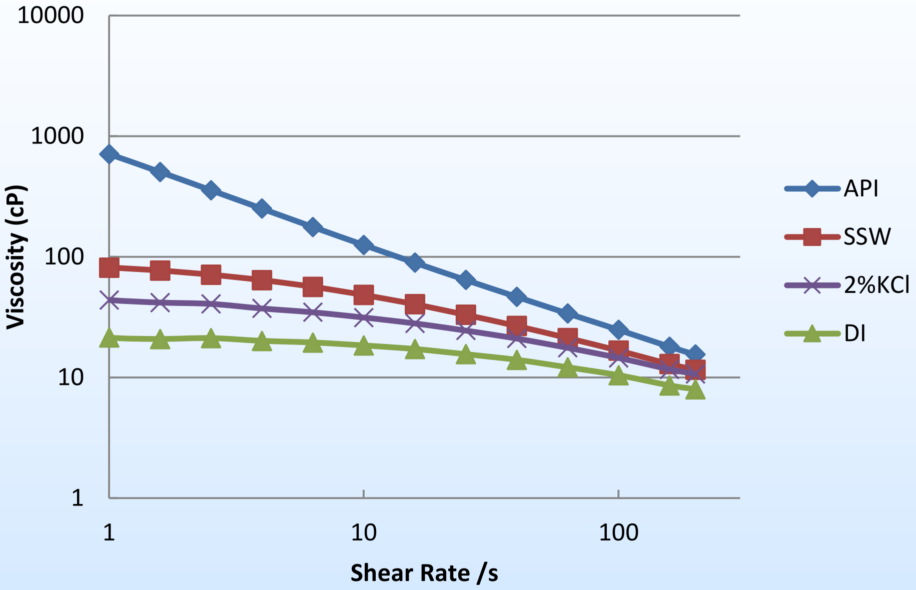
- Results replicated with N_2 foams
  - Foam quality, stability and texture very similar
  - **Hypothesis to be tested:** depressurization triggers foam destabilization due to compressibility
- Results replicated at 90°C
- Environmentally responsible surfactants

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

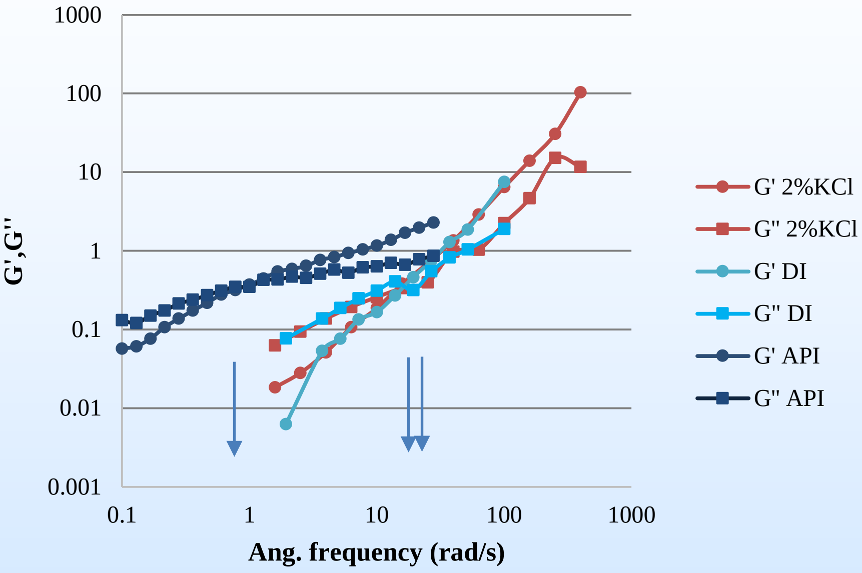


- Increasing salt concentration increases the aqueous phase viscosity, which in turn helps decreasing the initial bubble sizes especially at very high qualities.
- Smaller bubble sizes give rise to higher foam viscosity.

Aqueous Phase Rheology with 1% w/v Single Surfactant that Makes Wormlike Micelles



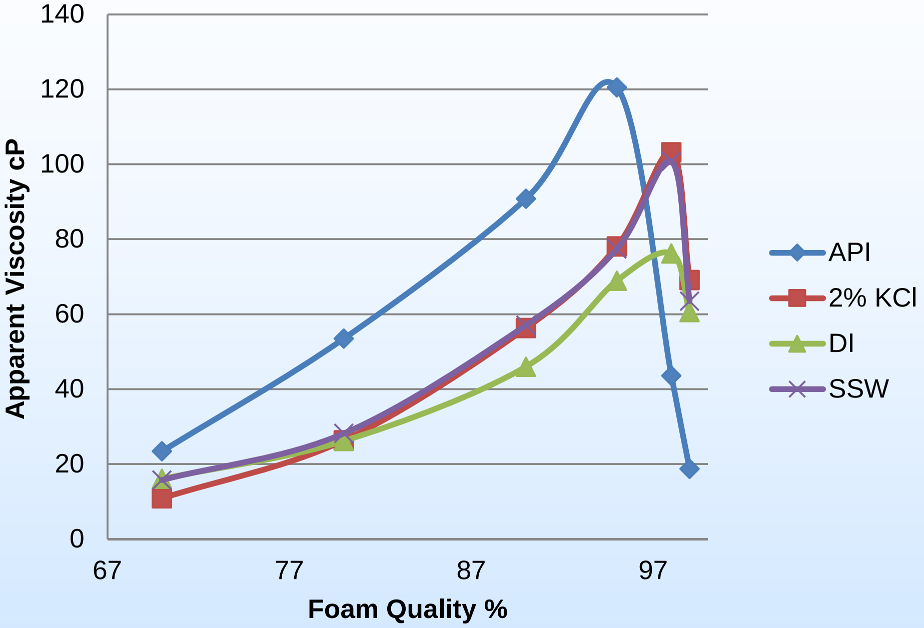
Aqueous rheology at 25°C and ambient pressure



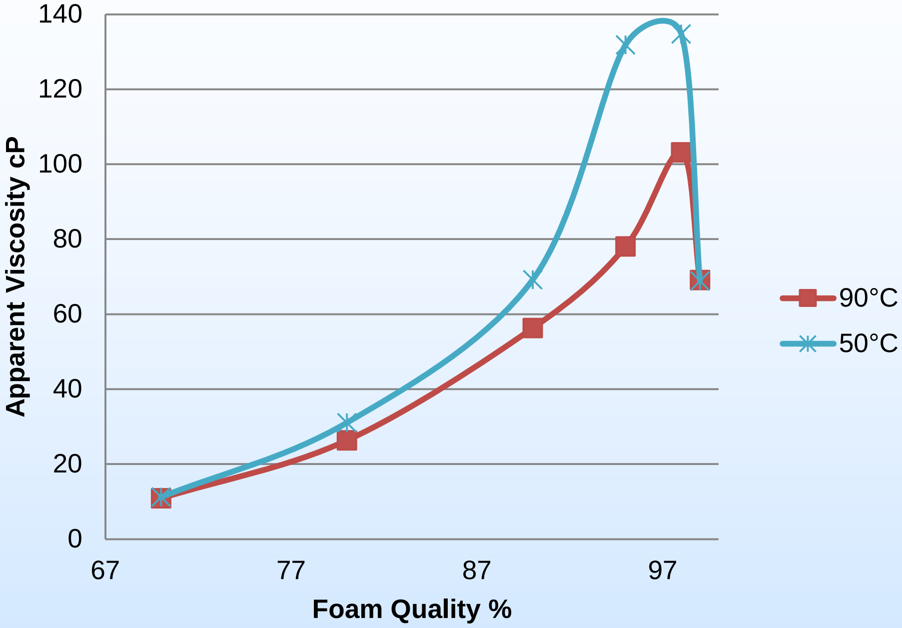
Complex rheology at 25°C and ambient pressure

- 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



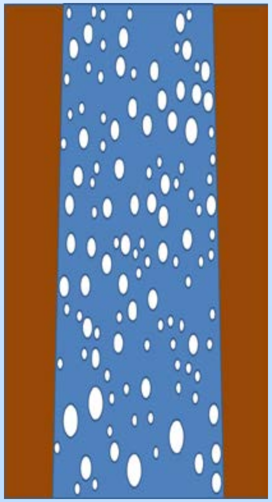
2% KCl foam viscosity and temperature effect

- 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

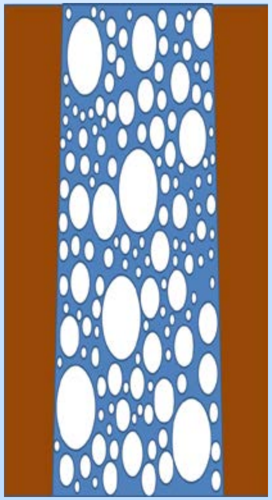
Accomplishments to Date

- 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

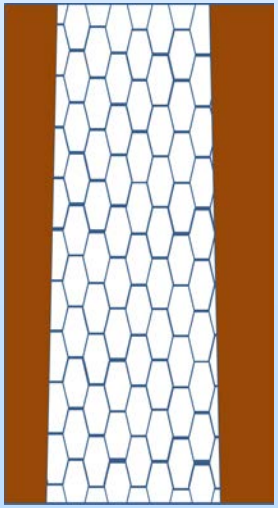
Energized Fluids (Q <40%)



High Quality Foam (Q>60%)



Ultry Dry Foam (Q>90%)



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

Key finding 1: ultra dry foams with NPs, surfactant and polymer

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Key finding 2: Ultra Dry Foams with Viscoelastic Aqueous Phases

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

- – 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.
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- 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
- Model combines:
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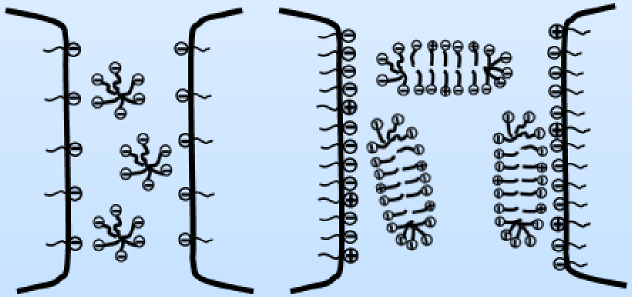
Lessons Learned: Technology basis for stabilizing and viscosifying foams

Most advanced ultra dry CO_2-in-water foams are stabilized with a viscoelastic aqueous phase

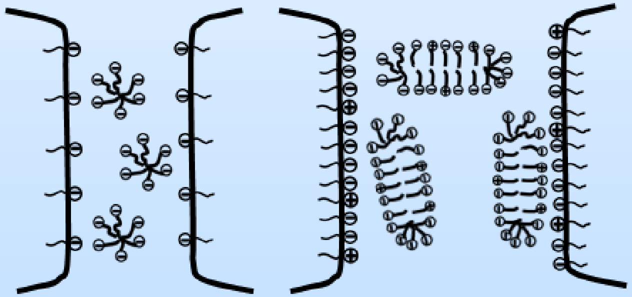
- Key finding 2: viscoelastic anionic wormlike micelles
- Key finding 1a: mixtures of anionic NPs and cationic surfactant
- Key finding 1b: mixtures of anionic NPs, anionic polyelectrolyte and low conc. cationic surfactant

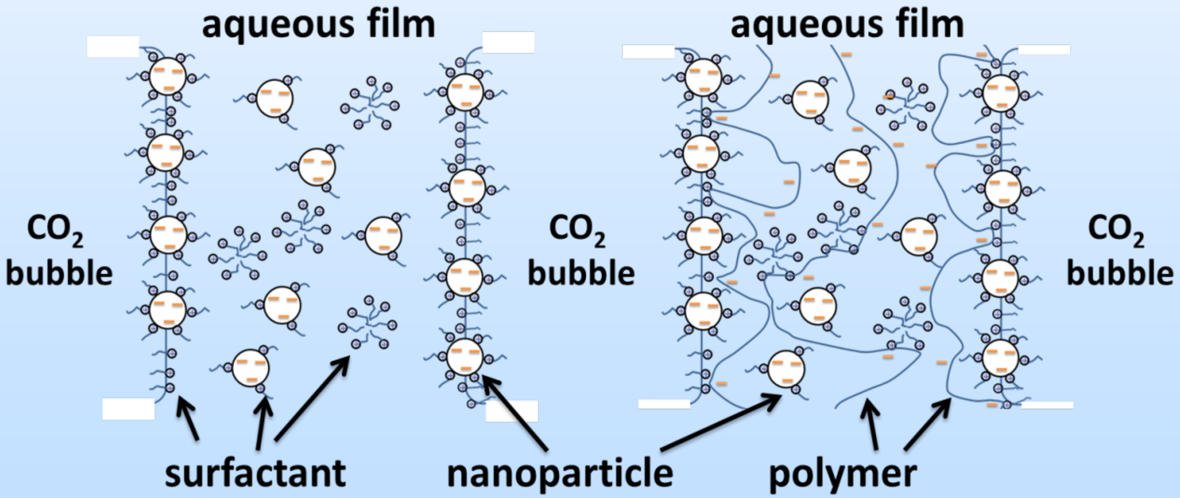


Lessons Learned: Technology basis for stabilizing and viscosifying foams

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





Work in progress

- Results replicated with N_2 foams
  - Foam quality, stability and texture very similar
  - Publication in preparation
  - **Hypothesis to be tested:** depressurization triggers foam destabilization due to compressibility
- Results replicated at 90^{o}C
  - Publication in preparation
- Environmentally responsible surfactants
  - Publication in preparation

Appendix

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

Organization Chart

- Maša Prodanović[1] (PI)
- Keith Johnston[2] (co-PI)
- Chun Huh[1] (co-PI)
- PhD Students: Shehab Alzobaidi[2], Chang Da[2]
- Graduated students: Zheng Xue[2], Andrew J. Worthen[2]
- Postdoctoral researcher: Ali Qajar[1]
- [1]Petroleum and Geosystems Engineering, UT Austin
- [2]Chemical Engineering, UT Austin

Project Schedule

GLOSSARY	
N/W	Nitrogen-in-water foam
C/W	CO_2-in-water foam
N/LHC	N_2-in-liquid-hydrocarbon foam

- *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:

- Z. Xue, A. Worthen, A. Qajar, I. Robert, S. L. Bryant, C. Huh, M. Prodanović, and K. P. Johnston, “Viscosity and stability of ultra-high internal phase CO2-in-water foams stabilized with surfactants and nanoparticles with or without polyelectrolytes,” *Journal of Colloid and Interface Science*, vol. 461, pp. 383–395, Jan. 2016.
- Z. Xue, A. J. Worthen, C. Da, A. Qajar, I. R. Ketchum, S. Alzobaidi, C. Huh, M. Prodanović, and K. P. Johnston, “Ultradry Carbon Dioxide-in-Water Foams with Viscoelastic Aqueous Phases,” *Langmuir*, vol. 32, no. 1, pp. 28–37, Jan. 2016.
- A. Qajar, Z. Xue, A. J. Worthen, K. P. Johnston, C. Huh, S. L. Bryant, and M. Prodanović, “Modeling fracture propagation and cleanup for dry nanoparticle-stabilized-foam fracturing fluids,” *Journal of Petroleum Science and Engineering*, vol. 146, pp. 210–221, Oct. 2016.

Conference paper:

- C. Da, Z. Xue, A. J. Worthen, A. Qajar, C. Huh, M. Prodanovic, and K. P. Johnston, “Viscosity and Stability of Dry CO2 Foams for Improved Oil Recovery,” in *SPE Improved Oil Recovery Conference Proceedings*, Tulsa, OK, 2016, p. Paper number 179690.