U.S. Department of Energy

National Energy Technology Laboratory
Carbon Management Project Review Meeting
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Enhanced CO_2 Storage and Injectivity

(FWP-1022403)

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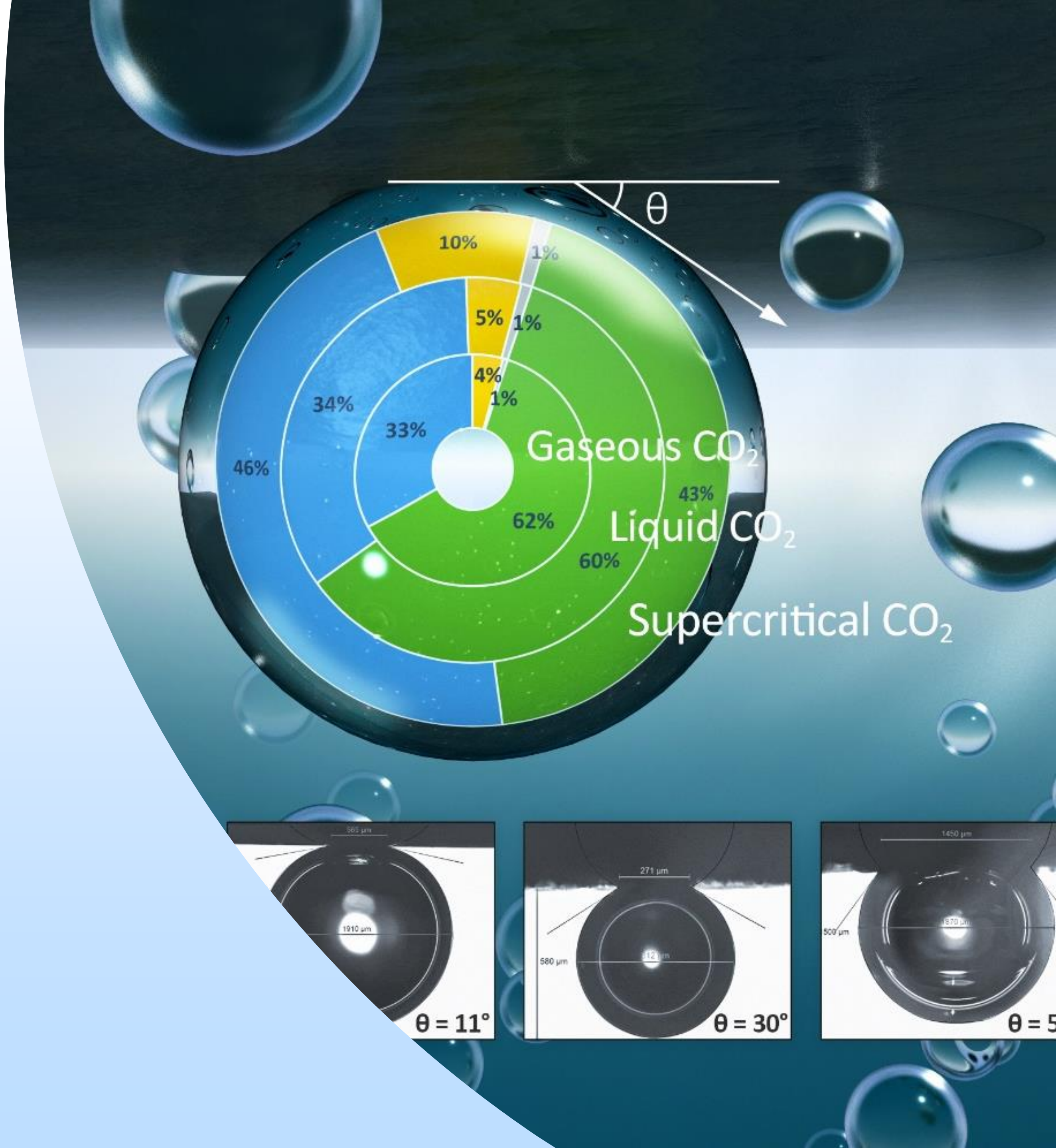
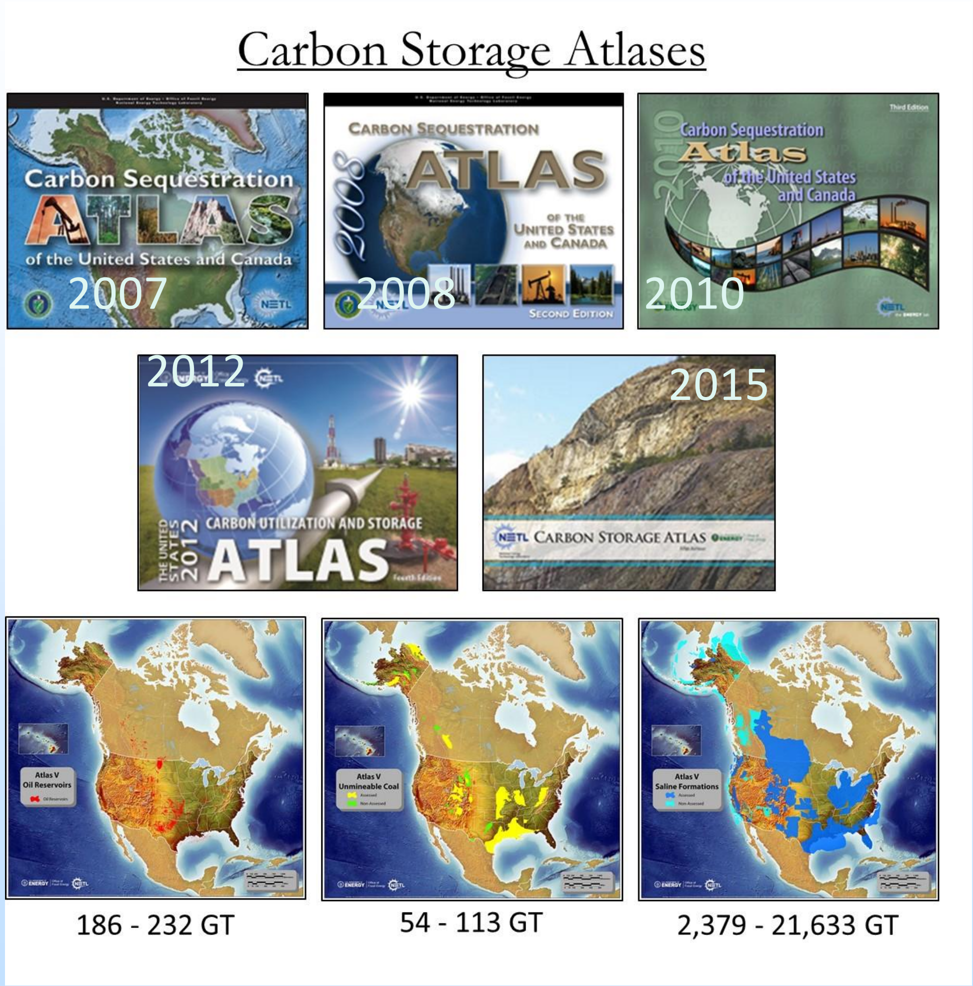


Prospective CO_2 Storage in the United States

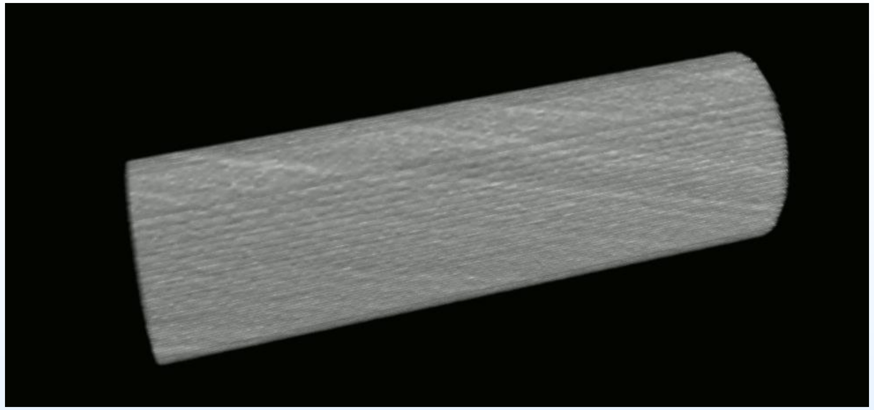


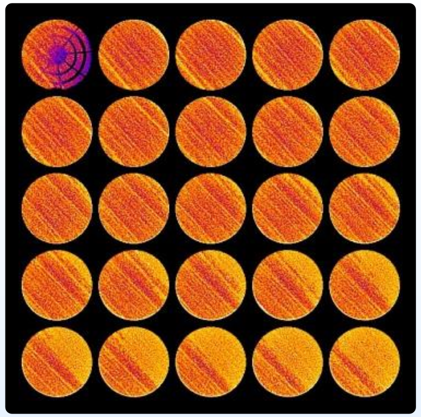
The United States has at least 2,400 billion metric tons of CO_2 storage capacity in saline formations, oil and gas reservoirs, and unmineable coal seams

Improving CO_2 sweep efficiency with additives?

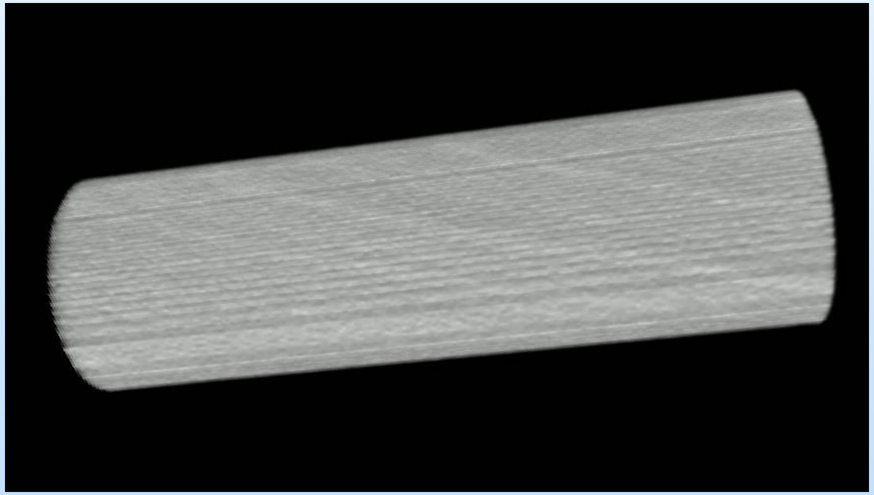
Enhanced CO_2 Storage

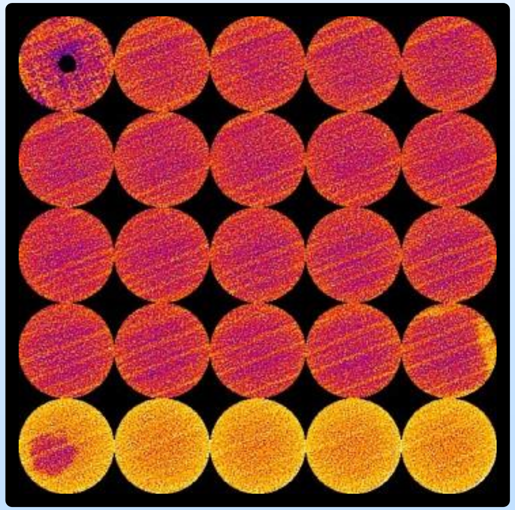
- **Initial tests 10 years ago showed change in CO_2 migration using surfactants**





CO_2 displacing brine



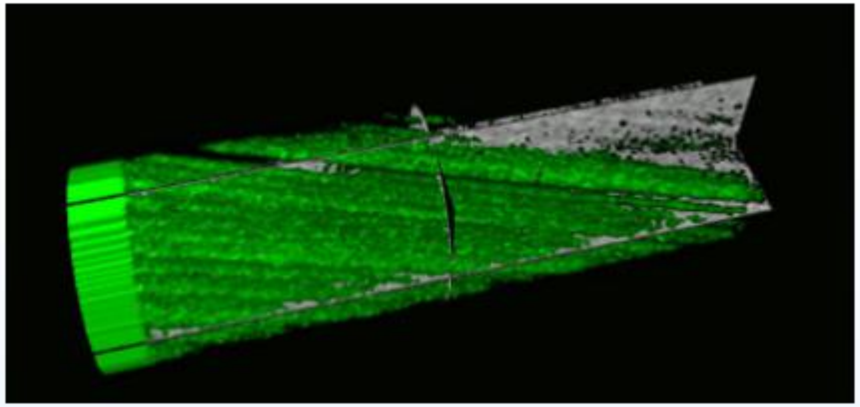


CO_2 displacing brine with surfactant

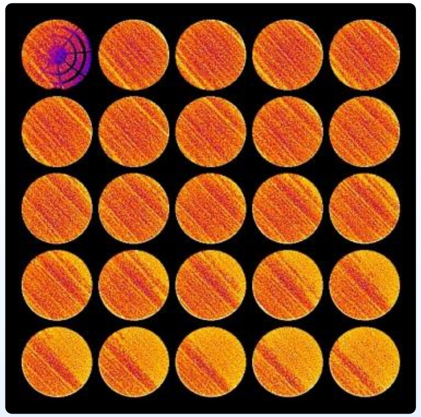
Improving CO_2 sweep efficiency with additives?

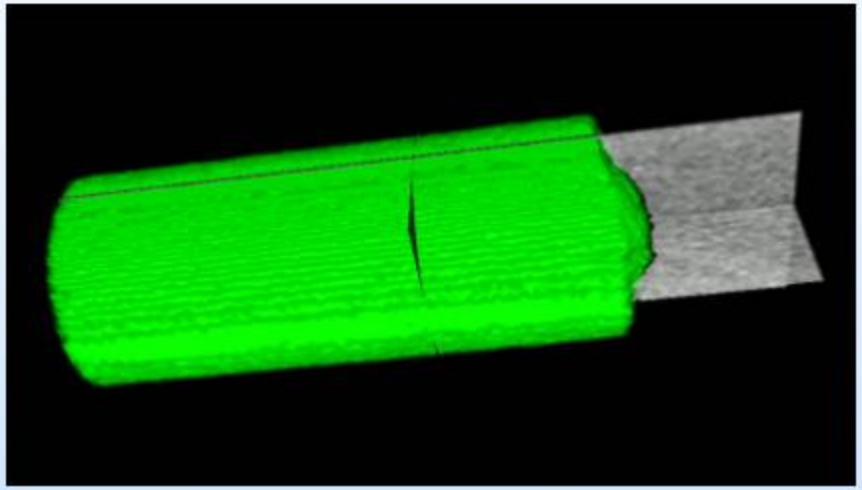
Enhanced CO_2 Storage

- **Initial tests 10 years ago showed change in CO_2 migration using surfactants**

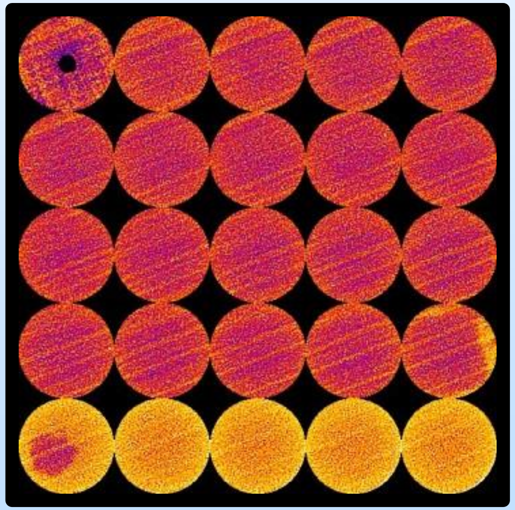


CO_2 displacing brine

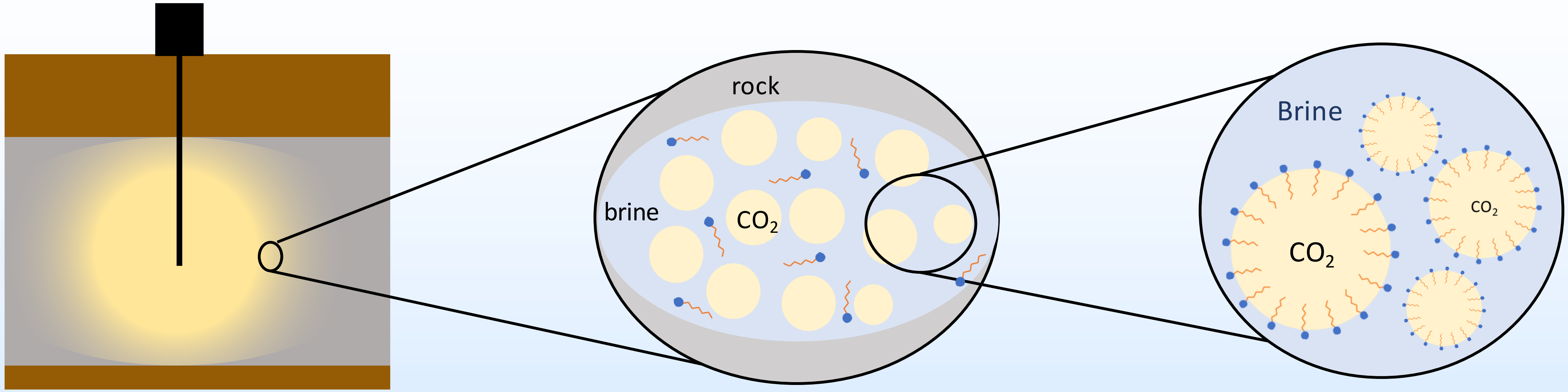




CO_2 displacing brine with surfactant



Surfactant partitioning and foam generation



Surfactant injected in CO_2 Phase

Avoids injection of additional water

Surfactant Partitions into the Brine

The surfactant will be designed to be more soluble in brine than CO_2

Stabilizes CO_2-in-brine Foam

Generating foams is the best way to increase CO_2 viscosity

Bancroft's Rule: The phase in which the surfactant is more soluble will constitute the continuous phase

Mathematical basis for surfactant-enhanced CCS.

Equations governing flow through porous materials

(1) $$C = \frac{v_{CO2}\,.\,\mu_{CO2}}{\gamma \cdot cos\theta}$$

C = capillary number
μ_{CO2} = viscosity of CO_2
γ = interfacial tension (IFT)
v_{CO2} = velocity of CO_2 injection
ϑ = contact angle

(2) $$M = \frac{\mu_{CO2}}{\mu_{brine}}$$

M = viscosity ratio
μ_{CO2} = viscosity of CO_2
μ_{brine} = viscosity of brine

Typical parameters at supercritical conditions

$\mu_{brine} = 0.7\ cp$

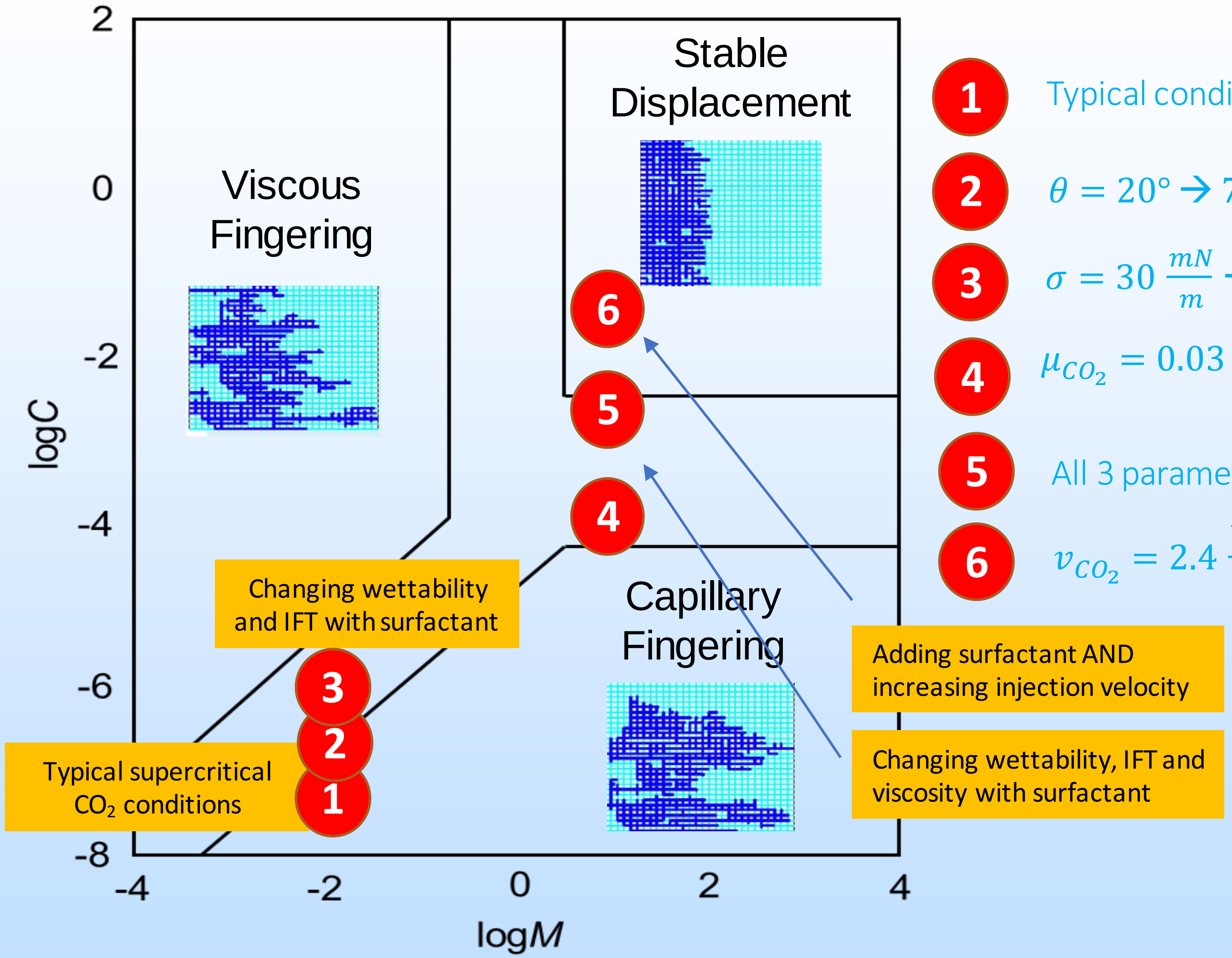
$\mu_{CO_2} = 0.03\ cp$

$\sigma = 30\ \frac{mN}{m}$

$\theta = 20°$

$v_{CO_2} = 2.4\ \frac{m}{d}$

While all three parameters (wettability, IFT, viscosity) contribute to displacement, viscosity is expected to have the most significant effect



1 Typical conditions

2 $\theta = 20° \rightarrow 70°$

3 $\sigma = 30\ \frac{mN}{m} \rightarrow 5\ \frac{mN}{m}$

4 $\mu_{CO_2} = 0.03\ cp \rightarrow 16\ cp$

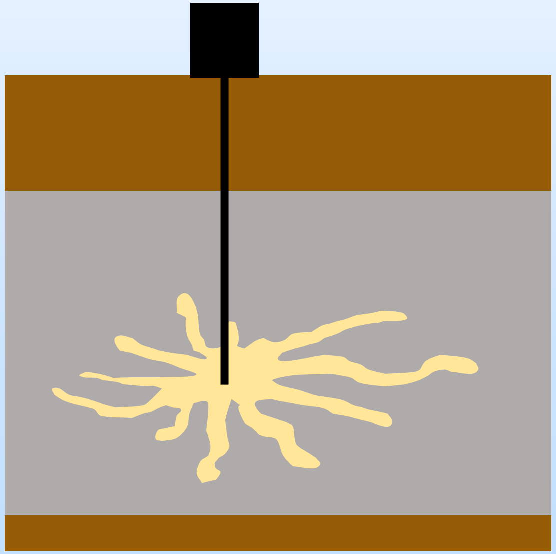
5 All 3 parameters

6 $v_{CO_2} = 2.4\ \frac{m}{d} \rightarrow 24\ \frac{m}{d}$

Pore Space Utilization

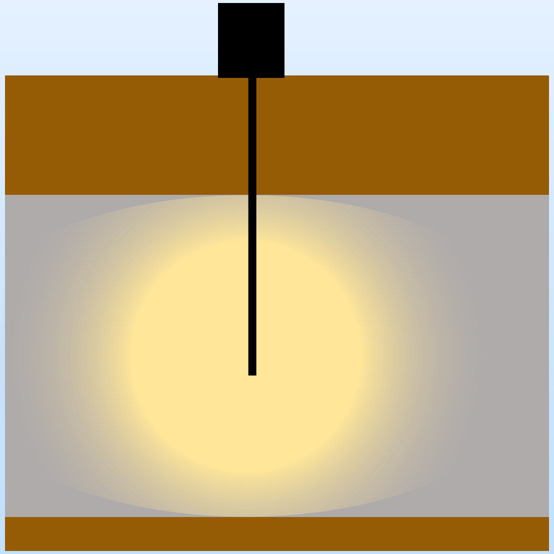
Capillary Fingering

- Low viscosity of CO_2 causes it to move quickly through the path of least resistance
- Causes low pore utilization



Stable Displacement

- Uniform sweep of CO_2
- High pore utilization



<u>Project Goal:</u>
Optimize utilization of the available pore space for CO_2 storage by improving CO_2 displacement

= supercritical CO_2

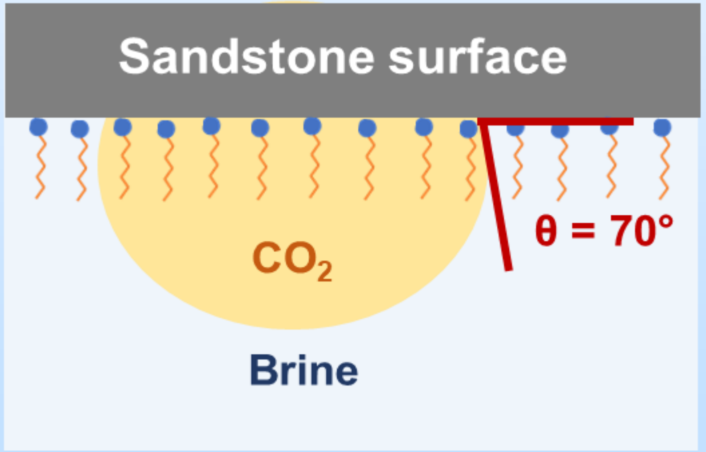
= brine-saturated porous rock

Enhancing CO_2 storage with additives

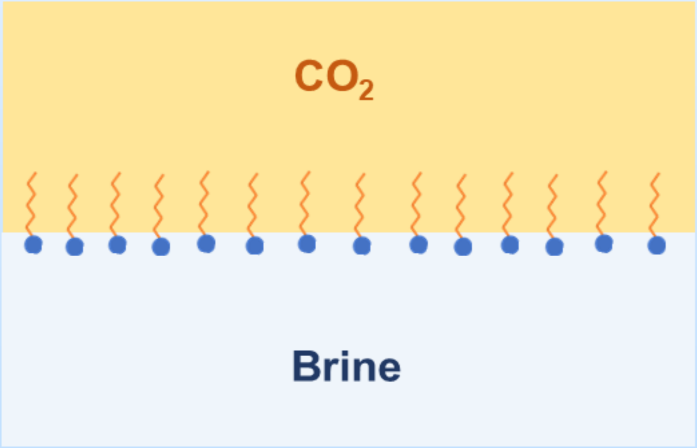
<u>Approach:</u> Add dilute concentrations of inexpensive, environmentally benign surfactants to the injected CO_2

Surfactants will improve both CO_2 injectivity and sweep efficiency by:

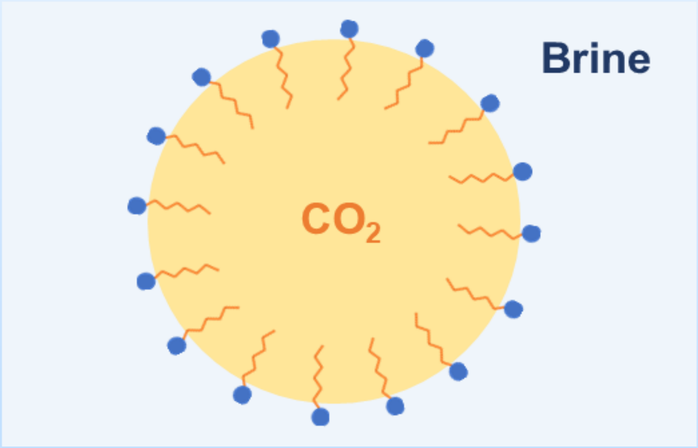
(A) Change wettability (θ) to more CO_2-wet



(B) Reduce CO_2-brine IFT (γ)

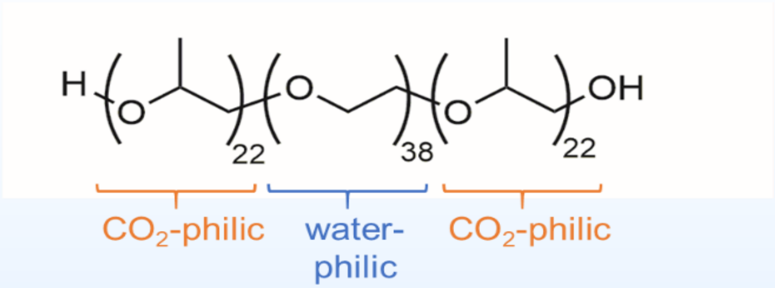


(C) Increase viscosity (μ_{CO2}) by stabilizing CO_2-in-water foams

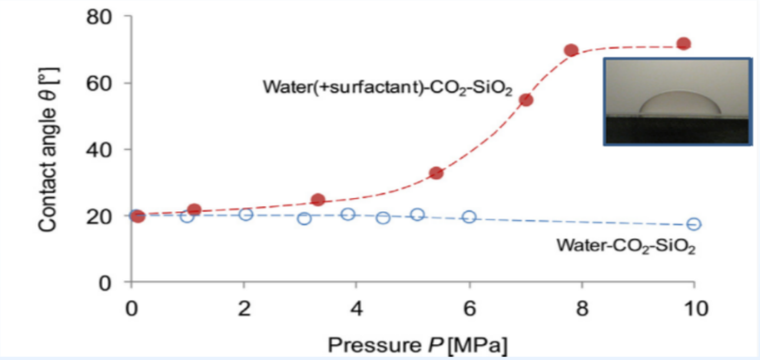


Previous experimental work with surfactants

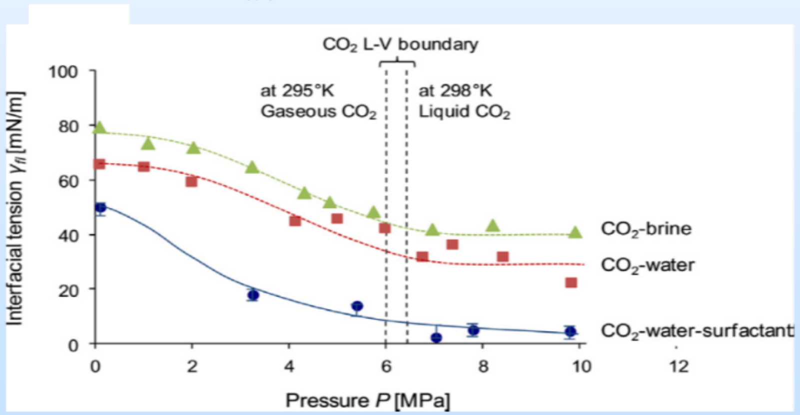
(A) Surfactant employed by Kim et al. in water phase.



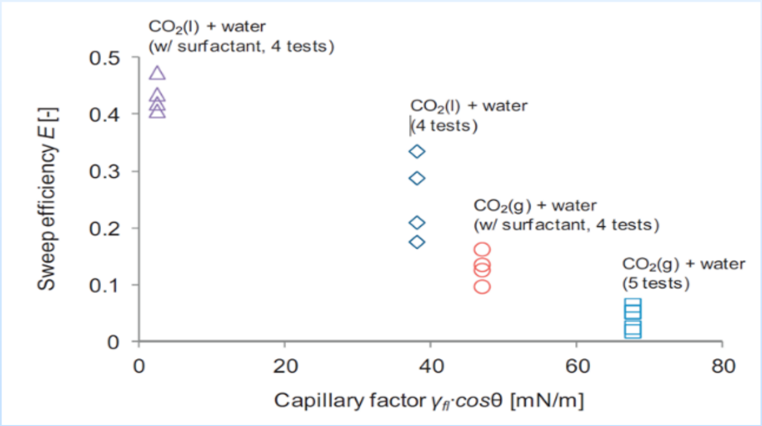
(B) Increase in contact angle (θ) with surfactant.



(C) Decrease in IFT (γ) with surfactant.



(D) Increase in Sweep Efficiency (E) with surfactant.



- Surfactant dissolved in water phase
- Changed wettability of SiO_2 to more CO_2-wet
- Reduced CO2-water IFT
- Increased sweep efficiency in microfluidic glass chip

<u>Our work:</u>

- Dissolve surfactant in CO_2 phase
- Test using natural rock samples
- Measure sweep efficiency in rock core using CT

Kim, S.; Santamarina, J. C., Engineered CO_2 injection: The use of surfactants for enhanced sweep efficiency. *International Journal of Greenhouse Gas Control* **2014**, *20*, 324-332.

Our experimental approach

Surfactant Selection

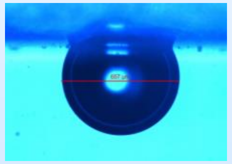
- ✓ CO_2-soluble
- ✓ MORE water soluble
- ✓ Inexpensive
- ✓ Environmentally benign

Hydrophilic “head”

Hydrophobic “tail”

Wettability Alteration

High pressure,
high temperature
contact angles

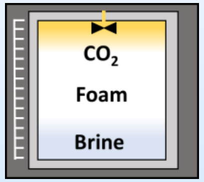


Interfacial Tension (IFT)

High pressure,
high temperature
CO_2-brine IFT

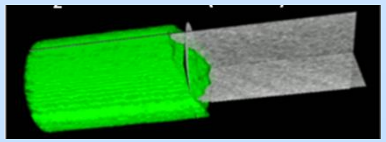
Viscosity Increase

High pressure
high temperature
CO_2-brine foaming



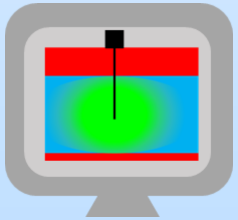
Sweep Efficiency

- Sandstone cores
- Measure by CT



Simulations

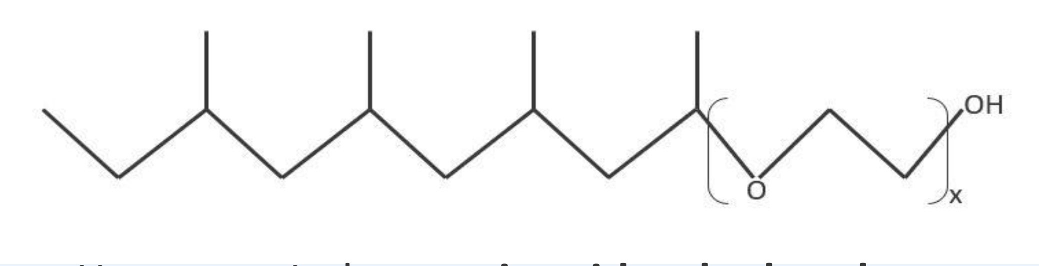
Measure field-scale improvement in sweep efficiency using TOUGH and CO_2-SCREEN



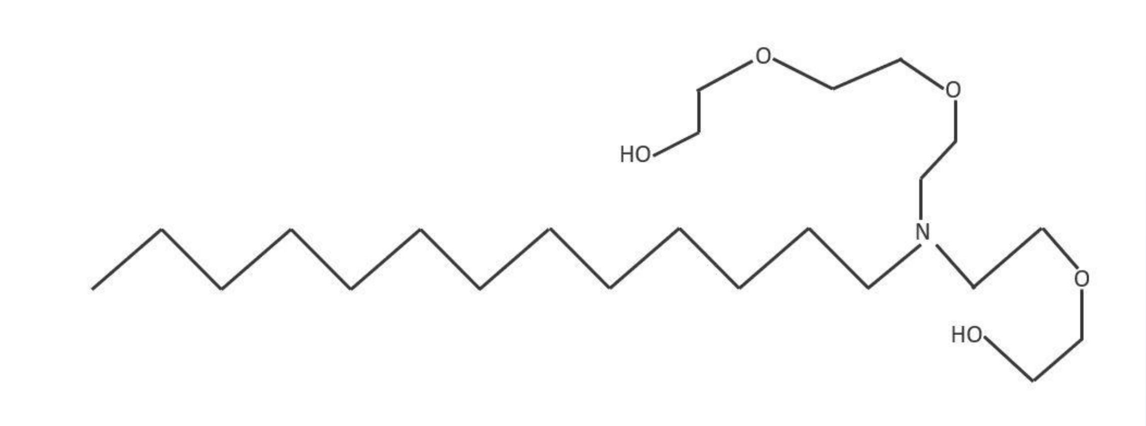
Target experimental conditions: 46 C, 20MPa (2900 psi)

CO_2 Soluble Surfactants

- Price $2-3 per pound
- Pumpable liquid above its pour point temperature



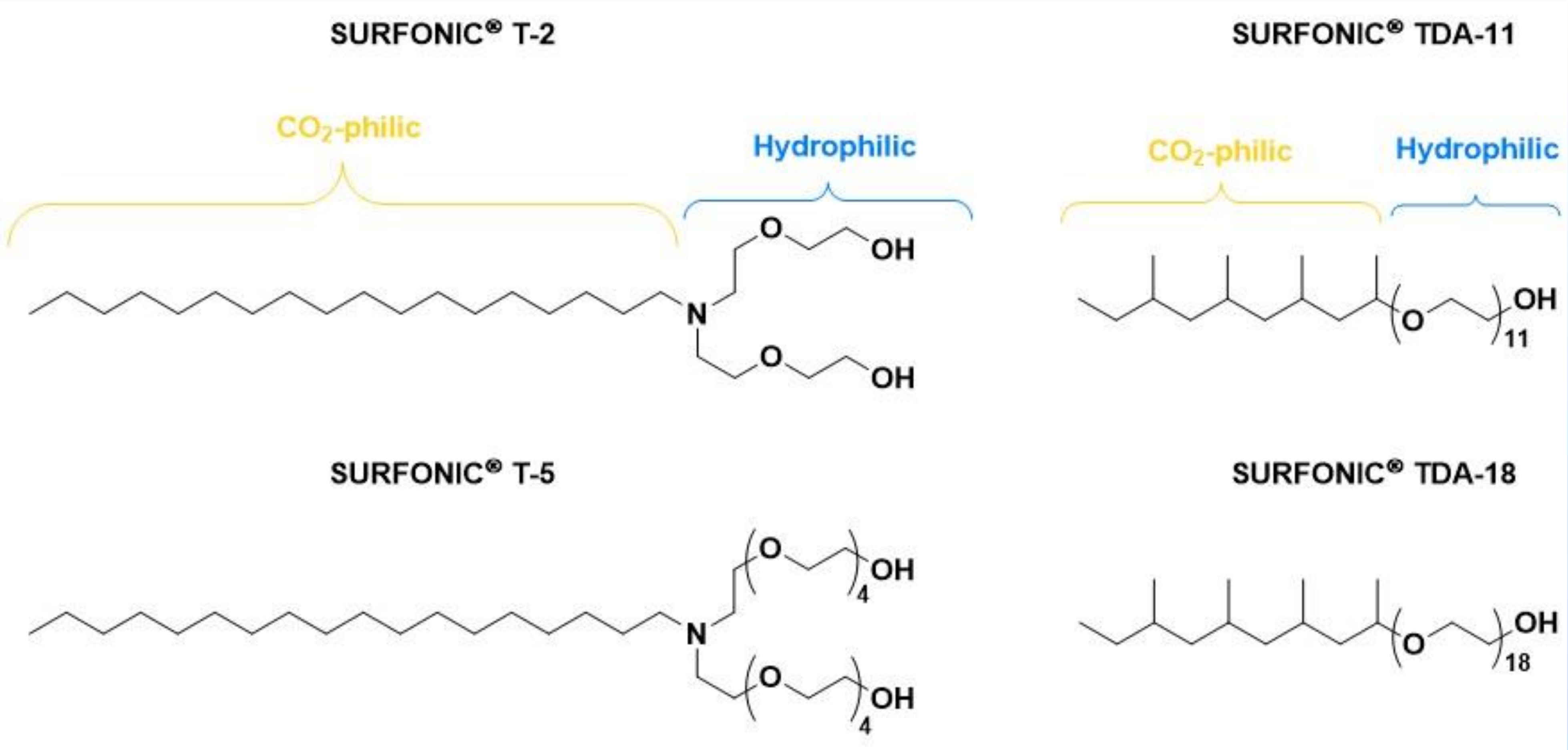
- Huntsman Indorama **isotridecyl ethoxylate**
- **“Conventional Nonionic”** that remains nonionic
- TDA – 9 (x=9)
- TDA – 11 (x=11)
- TDA – 18 (x=18)
- Pour Points
- TDA – 9 (x=9) 18 C
- TDA – 11 (x=11) 15 C
- TDA – 18 (x=18) >25C (solid at typical ambient T; would require heating to pump)



- Huntsman Indorama **polyoxyethylene cocoalkylamine**
- T – 5
- Nonionic; remains nonionic in CO_2
- **“Switchable Nonionic”** in that it is made as a nonionic, and remains nonionic in CO_2, but becomes a cationic surfactant in H_2O or brine when it reacts with carbonic acid
- Pour point -5 C
- **Low pour point or T-5 is favorable for pumping the surfactant in cold weather**

Surfactants used in this study

All surfactants are commercially-available and inexpensive ($2-3 per pound)

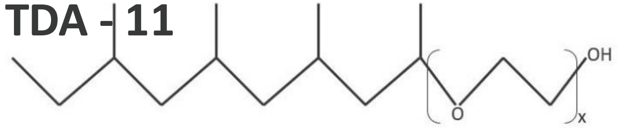


Composition in Brine and CO_2

Conventional Nonionic

Nonionic in CO_2

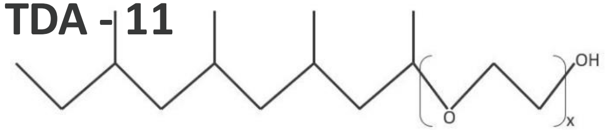
TDA - 11



CO_2

Nonionic in Brine

TDA - 11



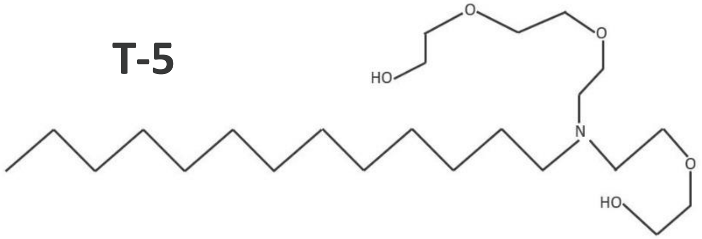
pH 3 Brine

Switchable Nonionic

CO_2

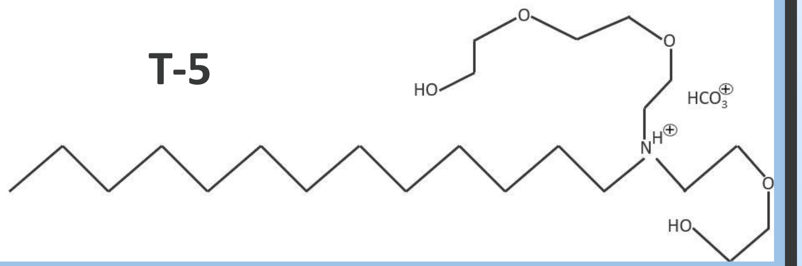
Nonionic in CO_2

T-5



Cationic in Brine

T-5



pH 3 Brine

Ionic surfactants are usually better foamers than nonionics; but ionics are insoluble in CO_2. A "switchable" surfactant gets around this by having the surfactant start out as a nonionic that dissolves in CO_2, but then "switch" into an ionic surfactant once it partitions into the brine.

Note that when high pressure CO_2 is in contact with water or brine, a portion of the CO_2 that dissolves in the aqueous phase forms carbonic acid, and the **pH drops to ~3**

Surfactant Solubility in Brine at Ambient P

Brine
KI – 5 wt.%
KCl – 3 wt.%
H_2O – 92 wt.%

Brine with pH 3
KI – 5 wt.%
KCl – 3 wt.%
H_2O – 92 wt.%
Required Addition of HCl to attain pH 3 (to simulate high pressure carbonic acid pH)

Cloud point at 1 wt% surfactant in brine

and at atmospheric pressure are as follows

Surfactants	NETL Brine	NETL brine with pH3
1wt% TDA - 11	74.5 C	75C
1wt% TDA - 18	>100 C	>100C
0.1wt% T - 5	34.8C	35C

Surfactants are at least 1 wt% soluble in brine at Temperature < Cloud Point Temperature

The cloud point must be greater than the aquifer temperature for the surfactant to be able to partition into aquifer brine

Brine Solubility of Surfactants at 46 C

Surfactants	NETL Brine	NETL Brine with pH3
TDA 11	Completely Miscible	Completely Miscible
TDA 18	Completely Miscible	Completely Miscible
T-5	Miscible until 1wt%	Miscible until 1wt%

Solubility of surfactants in brine observed in many mixtures of surfactant and brine from **0.1% surfactant 99.9% brine to 95% surfactant 5% brine**

T-5 is not soluble above 1 wt% and also the cloud point is low compared to our condition which Is 46C

All surfactants except T-5 are remarkably brine soluble; which is favorable for this application

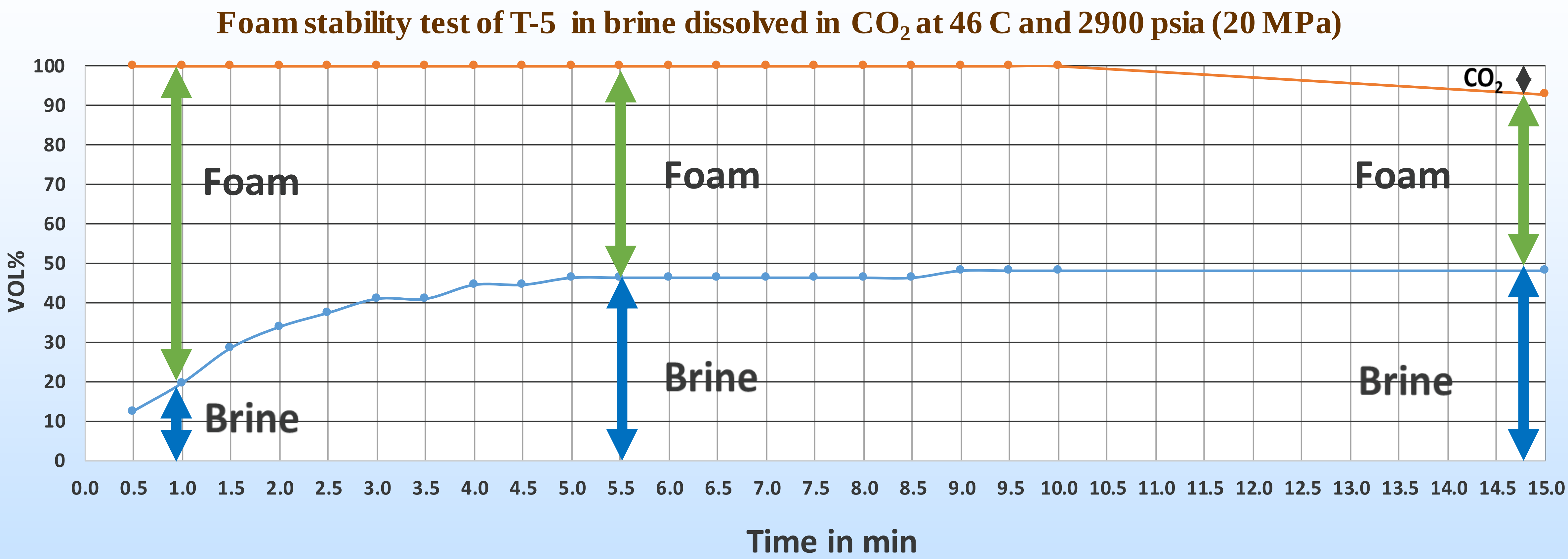
Foam Stability in a Windowed Vessel

- **This is a screening test, a "good foamer" in this test usually promotes the formation of high apparent viscosity foams within porous media**
  - Equal volumes of CO_2 and brine are mixed at reservoir T and high P
  - About 0.1wt% surfactant (based on CO_2 mass) is also added
  - The mixture is stirred at 2000 rpm for 10 minutes
  - Initially there will be some brine at the bottom, a CO_2-in-brine foam in the middle, and excess CO_2 on top
  - The positions of the brine-foam and foam-CO_2 interfaces are monitored with time

✓ **A "good" result is a large volume foam that lasts a long time (the foam may initially consume all of the CO_2)**

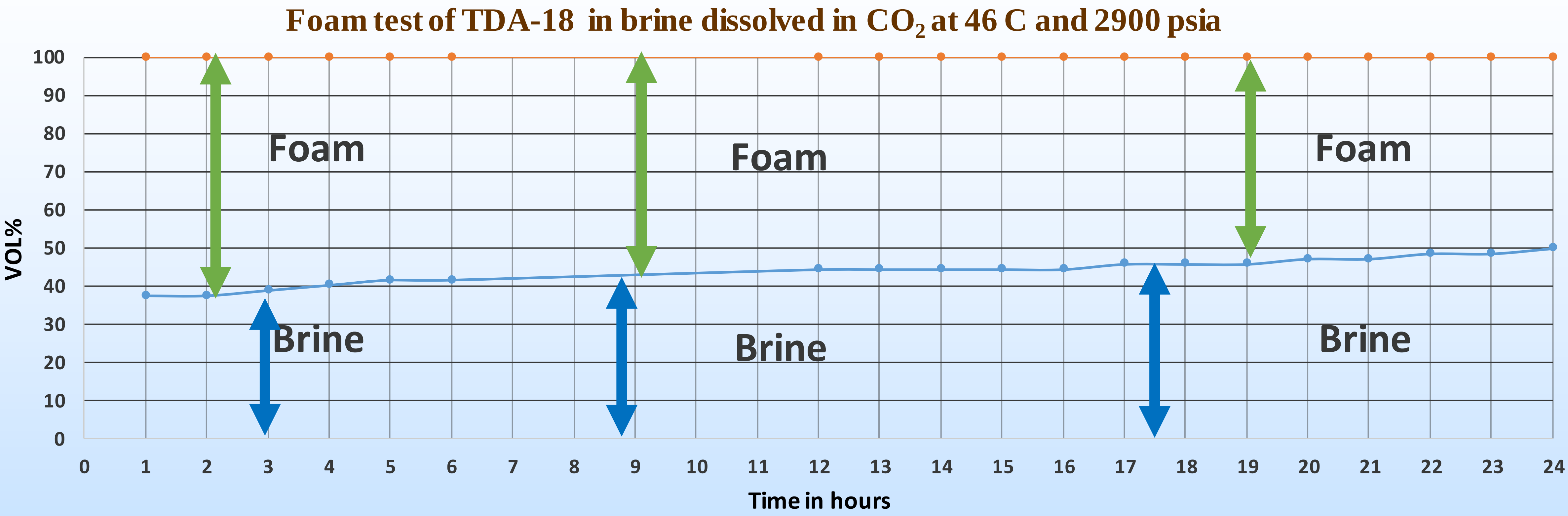
✓ **A "poor" result is a small amount of foam that collapses quickly**

Foam stability with T-5 at 46 C



T-5 yields a "good" result, all of the CO_2 is initially consumed in the foam, the foam collapses slowly, **the excess CO_2 first appears after 10+ minutes**, the foam is still **stable after 15 minutes**

Foam stability TDA-18 at 46 C



TDA -18 yields an "excellent" result, all of the CO_2 is initially consumed in the foam, the foam looks more opaque because the bubbles are smaller (< 1 mm) and the foam collapses slowly,

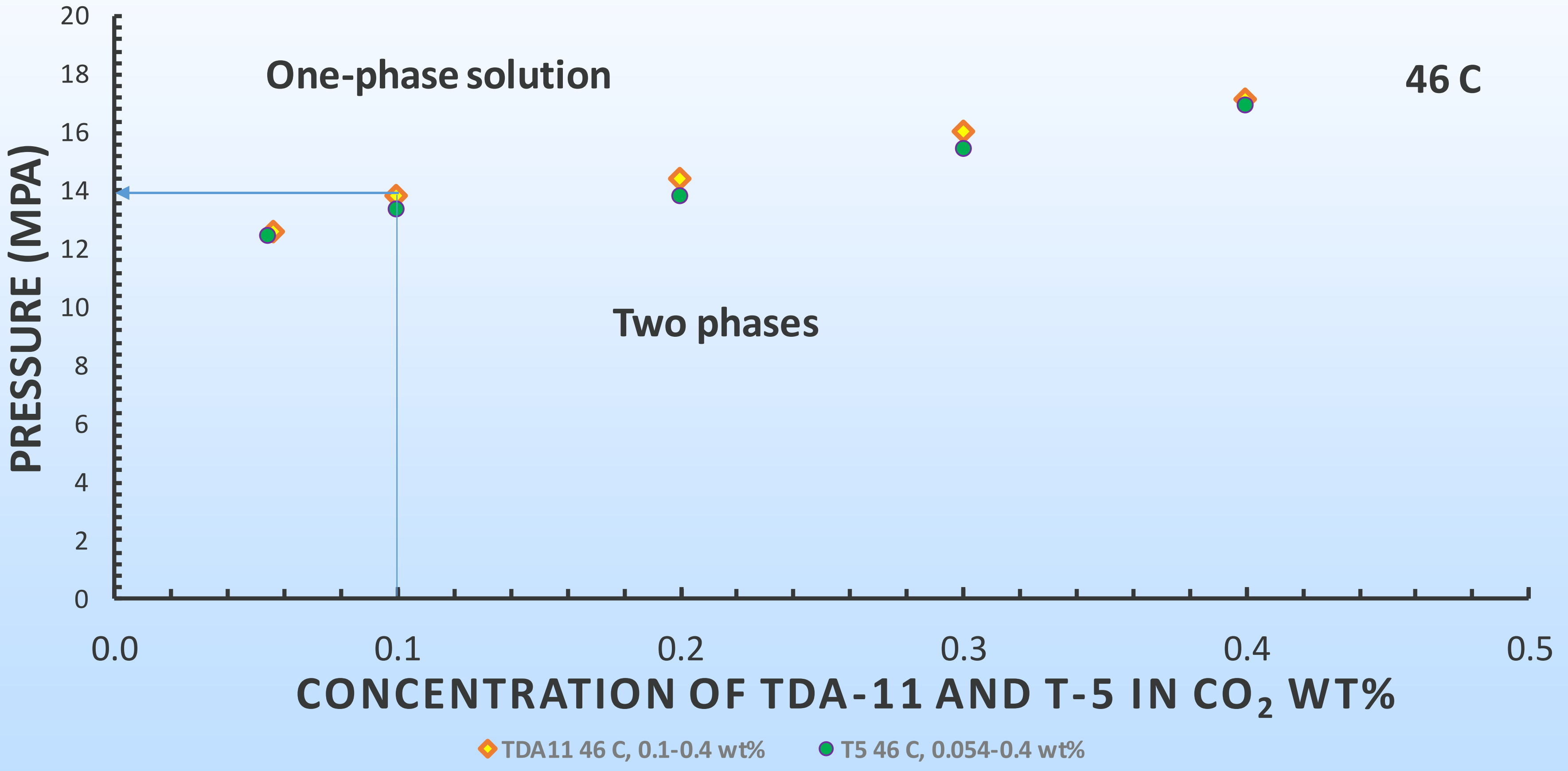
the excess CO_2 does not appear after 24 hours, the foam is still stable until after 24 hours

Foam stability TDA-11at 46 C

Experiments in progress

CO_2 Solubility of Surfactants TDA-11 and T-5 at 46 C

TDA-18 solubility is in progress



The CO_2-solution pressure must remain above the cloud point for the surfactant to dissolve in CO_2 at the desired concentration

To dissolve 0.1wt% of ether surfactant in CO_2 at 46C, the P must be 14 MPa or more

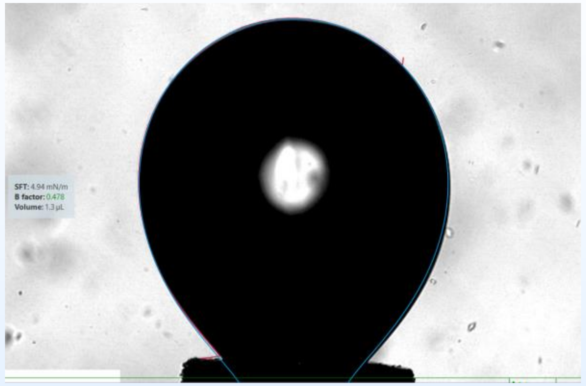
T-5, TDA-11 and TDA-18 are all promising candidates

- **T-5 has the lowest pour point , -5 C, which is favorable for use in winter**
- **TDA-18 is the best foamer, but is solid at 25 C and will be the least CO_2-soluble (in progress)**
- **TDA-11 is liquid at 25 C, is likely to be more soluble in CO_2 than TDA-18, but is very likely to be a poorer foamer than TDA-18**
- **The surfactants are inexpensive**
- Indorama Surfonic T-5 has a new different name **ULTROIL CI 2050:** $2.77/lb, Totes-FTL, EXW – Pasadena, TX; Valid July 2022
- Indorama TDA 11 or 12 **ALKOSYNT IT 120:** $2.33/lb, Totes-FTL, EXW – Pasadena, TX; Valid July 2022
- **The surfactants will likely be used at ~0.1wt% in CO_2; for example, 2 pounds T-5 per ton CO_2, or $5.54 T-5/ton CO_2.**
- **It is very unlikely that the surfactant can be effective at less than 0.01wt%,**

or ~$0.50 surfactant/ton CO_2

Contact Angle and Interfacial Tension at 47 C and 20 MPa

Interfacial Tension

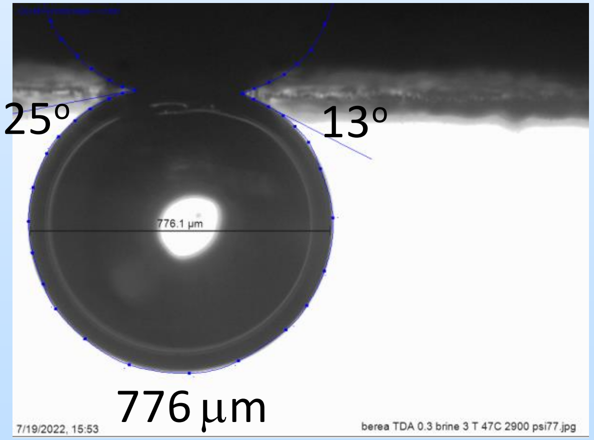


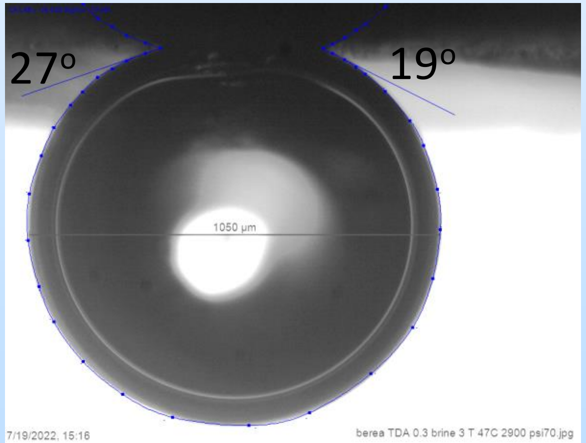
Berea Sandstone

47C, 2900 psi, TDA 18 (0.1%)

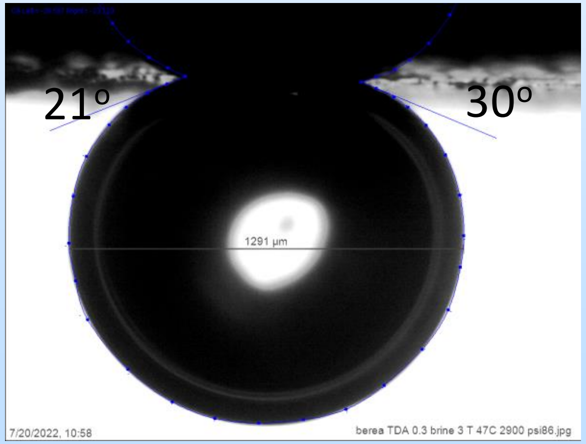
IFT: 4.9 mN/m (CO_2-5% brine-surfactant)
IFT: 26 mN/m (CO_2-5% brine)

Contact Angle





1050 µm



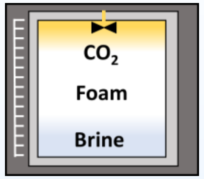
1291 µm

Future Work

❑Complete cloud point, solubility, and viscosity measurements (T-5, TDA-11, TDA-18)

Viscosity Increase

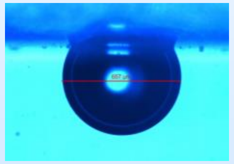
High pressure
high temperature
CO_2-brine foaming



❑Complete Contact angle and IFT (T-5, TDA-11, TDA-18)

Wettability Alteration

High pressure,
high temperature
contact angles



Interfacial Tension (IFT)

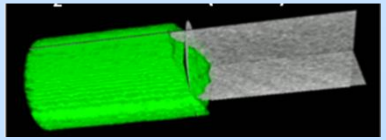
High pressure,
high temperature
CO_2-brine IFT

❑Select two surfactants to measure sweep efficiency

❑Conduct simulations to estimate improvement of sweep efficiency

Sweep Efficiency

- Sandstone cores
- Measure by CT



Simulations

Measure field-scale improvement in sweep efficiency using TOUGH and CO_2-SCREEN