Enhanced CO$_2$ Storage and Injectivity
(FWP-1022403)

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Prospective CO₂ Storage in the United States

The United States has at least 2,400 billion metric tons of CO₂ storage capacity in saline formations, oil and gas reservoirs, and unmineable coal seams.
Enhanced CO₂ Storage

- Initial tests 10 years ago showed change in CO₂ migration using surfactants
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](image1.png)

![CO$_2$ displacing brine with surfactant](image2.png)
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) \[ C = \frac{v_{CO2} \cdot \mu_{CO2}}{\gamma \cdot \cos \theta} \]

\( C \) = capillary number
\( \mu_{CO2} \) = viscosity of CO2
\( \gamma \) = interfacial tension (IFT)
\( v_{CO2} \) = velocity of CO2 injection
\( \theta \) = contact angle

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

\( M \) = viscosity ratio
\( \mu_{CO2} \) = viscosity of CO2
\( \mu_{brine} \) = viscosity of brine

Typical parameters at supercritical conditions

\( \mu_{brine} = 0.7 \, cp \)
\( \mu_{CO2} = 0.03 \, cp \)
\( \sigma = 30 \, \frac{mN}{m} \)
\( v_{CO2} = 2.4 \, \frac{m}{d} \)
\( \theta = 20^{\circ} \)

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

Typical conditions:

1. Typical conditions
2. \( \theta = 20^{\circ} \rightarrow 70^{\circ} \)
3. \( \sigma = 30 \, \frac{mN}{m} \rightarrow 5 \, \frac{mN}{m} \)
4. \( \mu_{CO2} = 0.03 \, cp \rightarrow 16 \, cp \)
5. All 3 parameters
6. \( v_{CO2} = 2.4 \, \frac{m}{d} \rightarrow 24 \, \frac{m}{d} \)
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

Project Goal:
Optimize utilization of the available pore space for CO$_2$ storage by improving CO$_2$ displacement

Diagram:
- Yellow = supercritical CO$_2$
- Gray = brine-saturated porous rock
Enhancing CO$_2$ storage with additives

**Approach:** 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 ($\theta$) to more CO$_2$-wet

**B** Reduce CO$_2$-brine IFT ($\gamma$)

**C** Increase viscosity ($\mu_{CO2}$) by stabilizing CO$_2$-in-water foams

![Sandstone surface](image1)

![CO$_2$](image2)

![Brine](image3)
Previous experimental work with surfactants

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

(B) Increase in contact angle ($\theta$) with surfactant.

(C) Decrease in IFT ($\gamma$) 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 CO$_2$-water IFT
- Increased sweep efficiency in microfluidic glass chip

Our work:
- Dissolve surfactant in CO$_2$ phase
- Test using natural rock samples
- Measure sweep efficiency in rock core using CT

Our experimental approach

**Surfactant Selection**
- CO₂-soluble
- MORE water soluble
- Inexpensive
- Environmentally benign

**Wettability Alteration**
High pressure, high temperature contact angles

**Interfacial Tension (IFT)**
High pressure, high temperature CO₂-brine IFT

**Viscosity Increase**
High pressure high temperature CO₂-brine foaming

**Sweep Efficiency**
- Sandstone cores
- Measure by CT

**Simulations**
Measure field-scale improvement in sweep efficiency using TOUGH and CO₂-SCREEN

**Target experimental conditions:** 46 C, 20MPa (2900 psi)
**CO₂ 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 CO₂
- “**Switchable Nonionic**” in that it is made as a nonionic, and remains nonionic in CO₂, but becomes a cationic surfactant in H₂O 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)
Ionic surfactants are usually better foamers than nonionics; but ionics are insoluble in CO₂. A “switchable” surfactant gets around this by having the surfactant start out as a nonionic that dissolves in CO₂, but then “switch” into an ionic surfactant once it partitions into the brine.

Note that when high pressure CO₂ is in contact with water or brine, a portion of the CO₂ 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.%
H₂O – 92 wt.%

Brine with pH 3
KI – 5 wt.%
KCl – 3 wt.%
H₂O – 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

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>NETL Brine</th>
<th>NETL brine with pH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1wt% TDA - 11</td>
<td>74.5 C</td>
<td>75C</td>
</tr>
<tr>
<td>1wt% TDA - 18</td>
<td>&gt;100 C</td>
<td>&gt;100C</td>
</tr>
<tr>
<td>0.1wt% T - 5</td>
<td>34.8C</td>
<td>35C</td>
</tr>
</tbody>
</table>

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

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<th>NETL Brine with pH3</th>
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<tbody>
<tr>
<td>TDA 11</td>
<td>Completely Miscible</td>
<td>Completely Miscible</td>
</tr>
<tr>
<td>TDA 18</td>
<td>Completely Miscible</td>
<td>Completely Miscible</td>
</tr>
<tr>
<td>T-5</td>
<td>Miscible until 1wt%</td>
<td>Miscible until 1wt%</td>
</tr>
</tbody>
</table>

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

Foam stability test of T-5 in brine dissolved in CO₂ at 46 C and 2900 psia (20 MPa)

T-5 yields a “good” result, all of the CO₂ is initially consumed in the foam, the foam collapses slowly, the excess CO₂ 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 CO₂ 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 CO₂ does not appear after 24 hours, the foam is still stable until after 24 hours.
Foam stability TDA-11 at 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 0.1 wt% 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 (CO₂-5% brine-surfactant)
IFT: 26 mN/m (CO₂-5% brine)

Contact Angle

- 25°, 776 μm
- 27°, 1050 μm
- 21°, 1291 μm
Future Work

- Complete cloud point, solubility, and viscosity measurements (T-5, TDA-11, TDA-18)
- Complete Contact angle and IFT (T-5, TDA-11, TDA-18)
- Select two surfactants to measure sweep efficiency
- Conduct simulations to estimate improvement of sweep efficiency

**Viscosity Increase**
- High pressure, high temperature CO$_2$-brine foaming

**Wettability Alteration**
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