Foam for mobility control of miscible CO_2 EOR

George J. Hirasaki

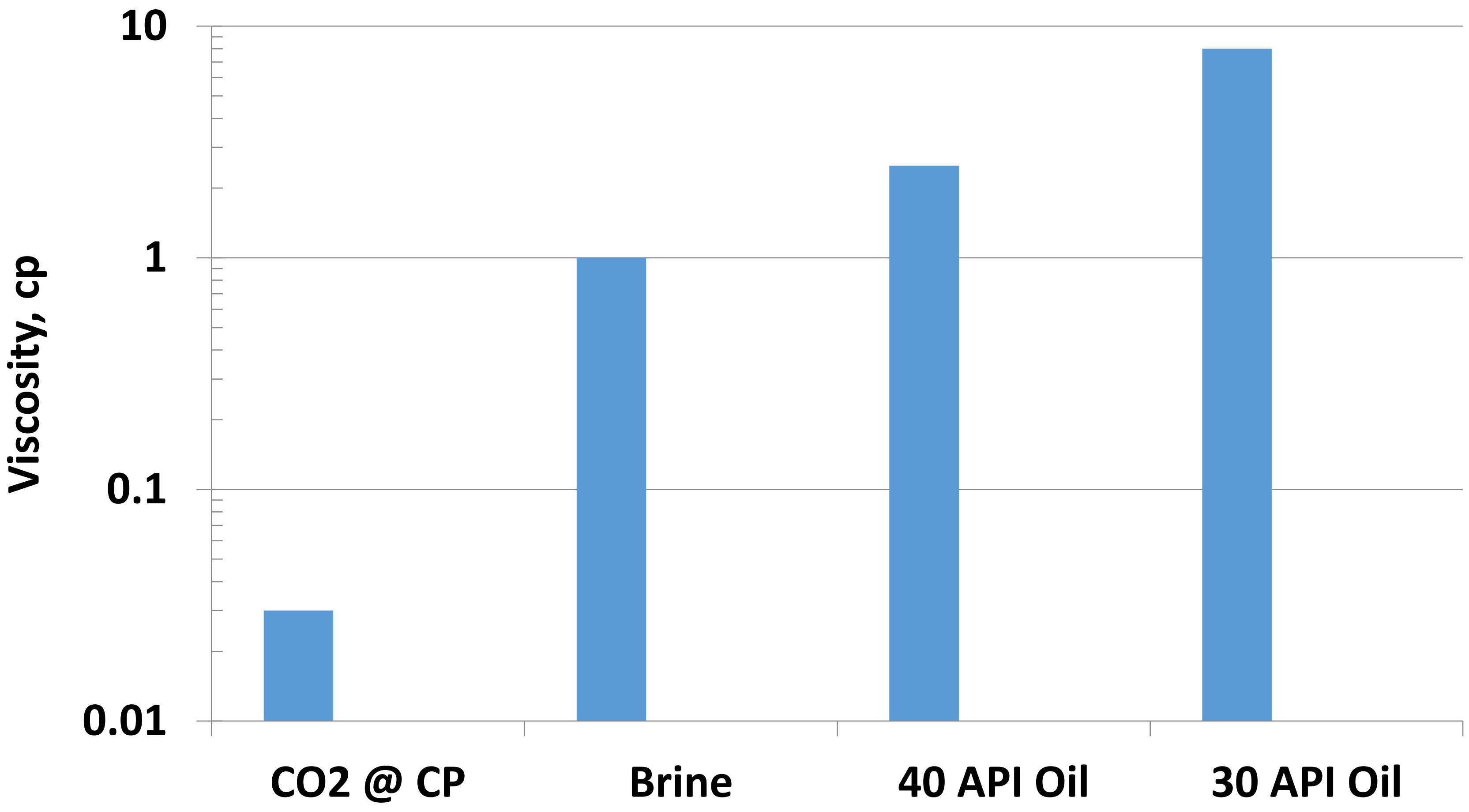
CCUS Student Week

Golden, Colorado

October, 2018

Why does CO_2 EOR need mobility control?

Viscosity of CO_2 and Reservoir Fluids



Displacement Fronts for Different Mobility Ratios and Injected Pore Volumes

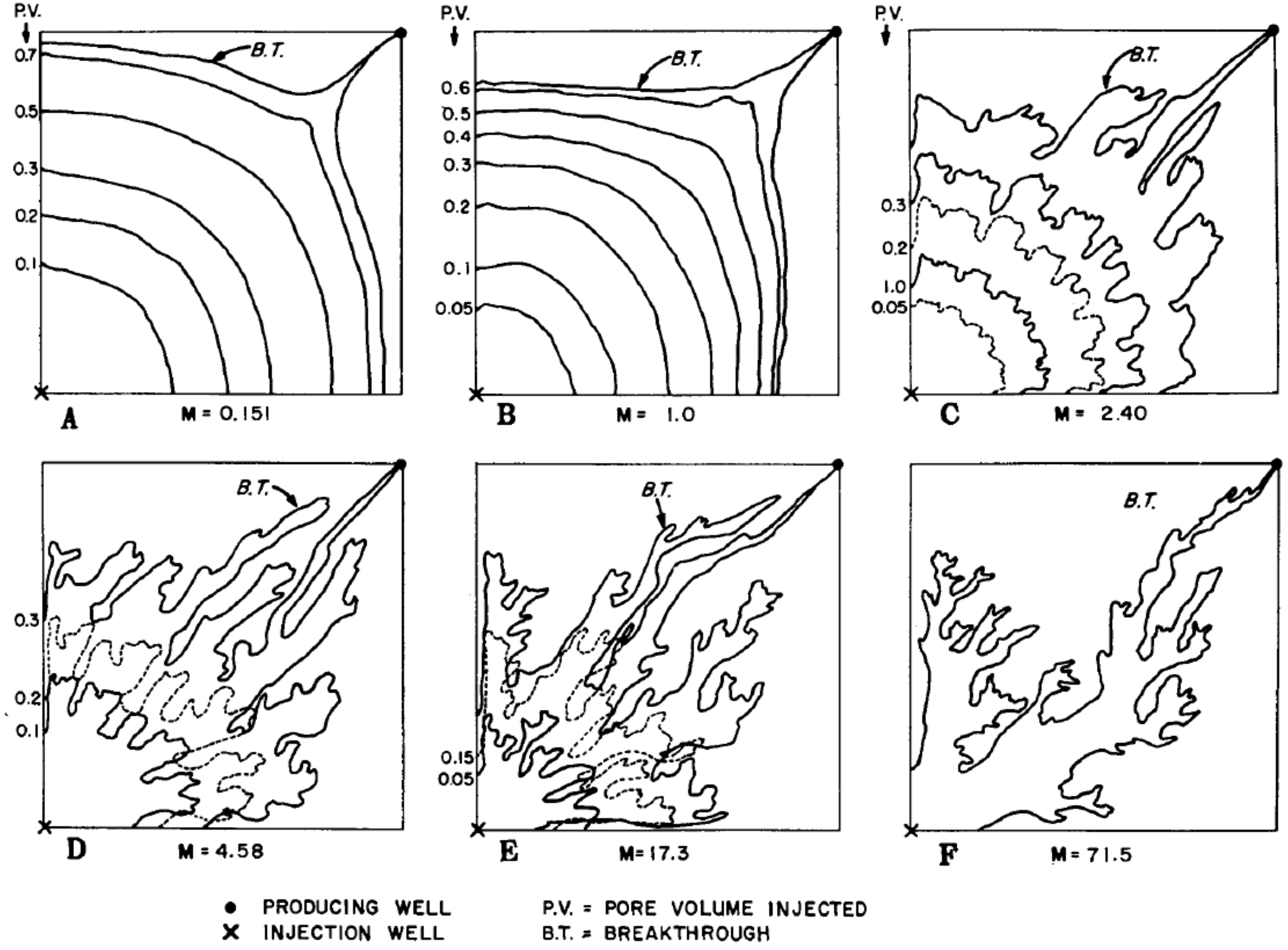


Fig. 5—Displacement Fronts for Different Mobility Ratios and Injected Pore Volumes until Breakthrough, Quarter of a Five-Spot.

Habermann, B., 1960

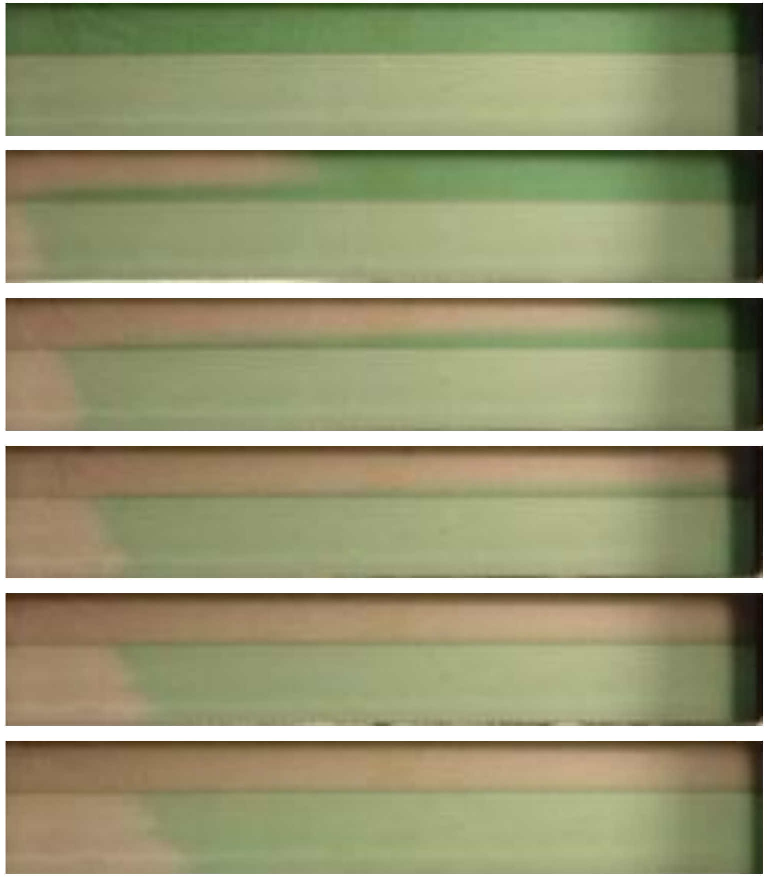
What is the effect of geological heterogeneity on EOR?

Layered sandpack model with 20:1 permeability Contrast

Li, et al, SPEJ, 2010

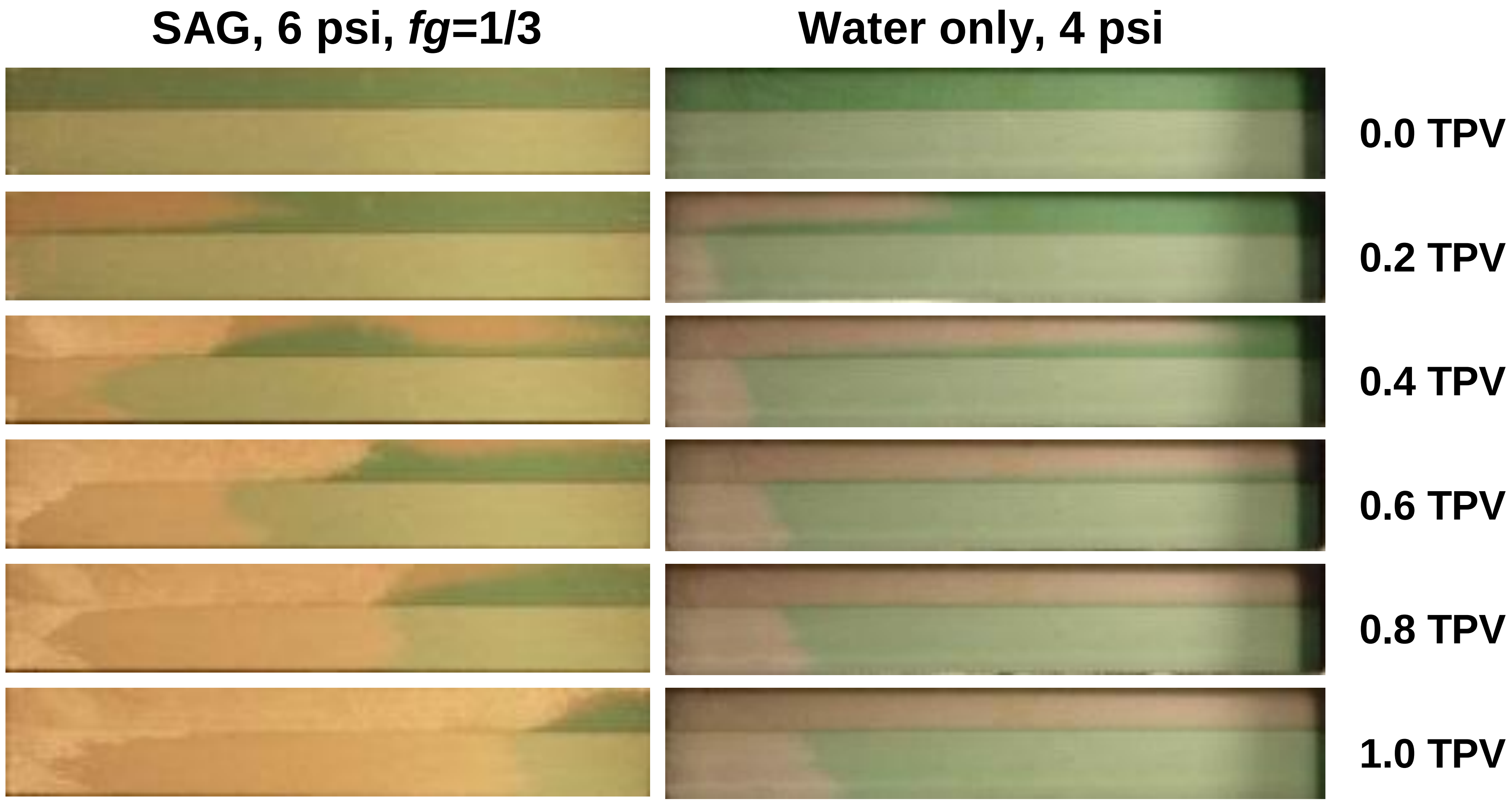
Layered sandpack with 19:1 permeability contrast about half-swept with only water but about completely swept with surfactant-alternated-gas (SAG)

Water only, 4 psi



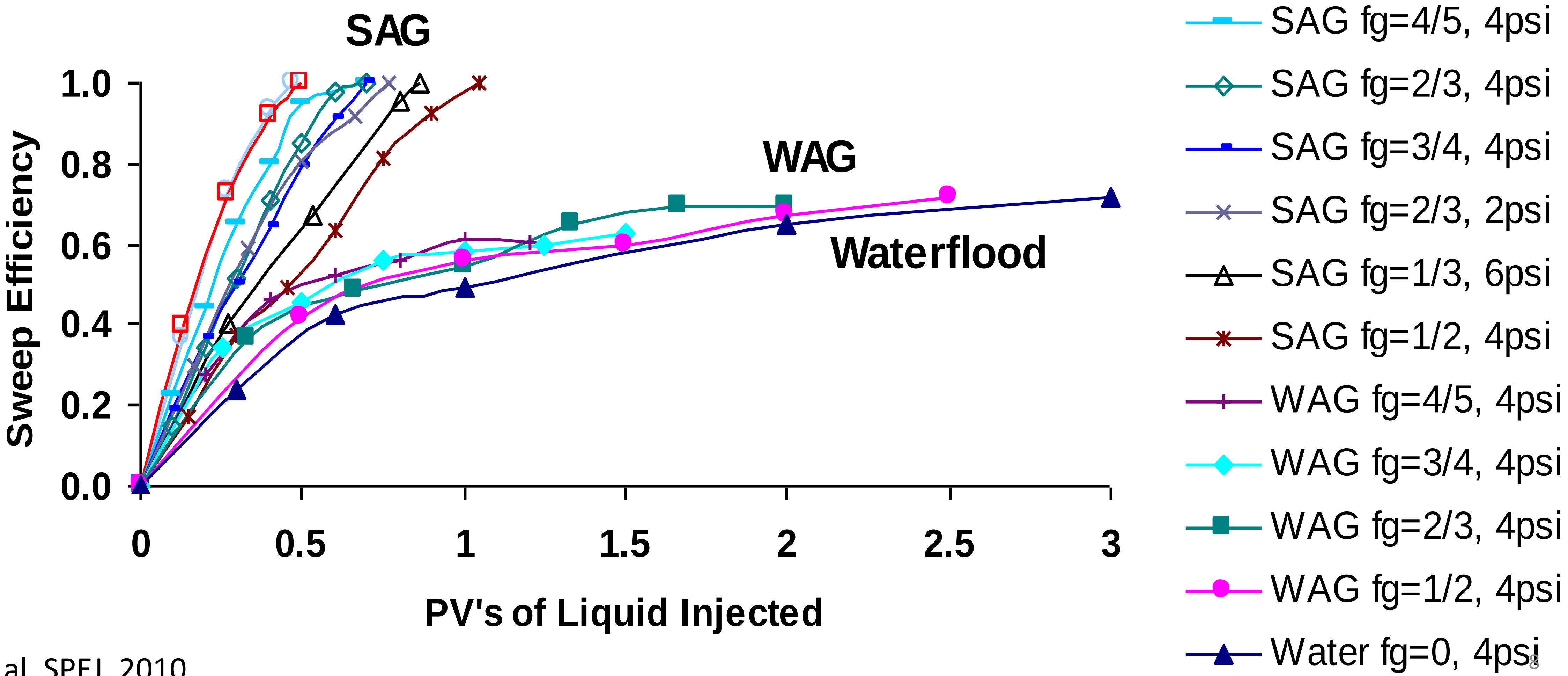
Li, et al, SPEJ, 2010

Layered sandpack with 19:1 permeability contrast about half-swept with only water but about completely swept with surfactant-alternated-gas (SAG)



Li, et al, SPEJ, 2010

Sweep Efficiency



Li, et al, SPEJ, 2010

Adsorption of Surfactant

- **Type of Formation**
  - **Sandstone – Mostly negatively charged, hydrogen bonding**
  - **Carbonate – Mostly positively charged**
- **Type of Surfactant**
  - **Anionic – Negatively charged**
  - **Cationic – Positively charged**
  - **Nonionic – Hydrogen bonding**

Reservoir Environment

- **Salinity**
  - **Low salinity – no problem**
  - **High Salinity – surfactant may precipitate**

- **Temperature**
  - **Low temperature – no problem**
  - **High temperature**
    - **Nonionic has cloud point**
    - **Surfactant may degrade**

Two carbonate reservoirs

- East Seminole, West Texas
  - 43 °C, 34,180 ppm TDS
- Middle East
  - 120 °C, 220,000 ppm TDS

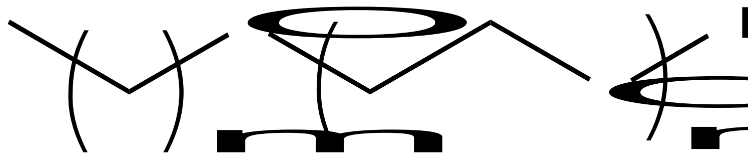
East Seminole miscible CO_2 pilot

- Composition of brine of East Seminole reservoir (TDS=34,180 ppm)

Na_2SO_4 (mg/l)	KCl (mg/l)	$CaCl_2 \cdot 2\,H_2O$ (mg/l)	$MgCl_2 \cdot 6H_2O$ (mg/l)	NaCl (mg/l)
5,236	458	5,825	2,760	22,796

- Surfactant

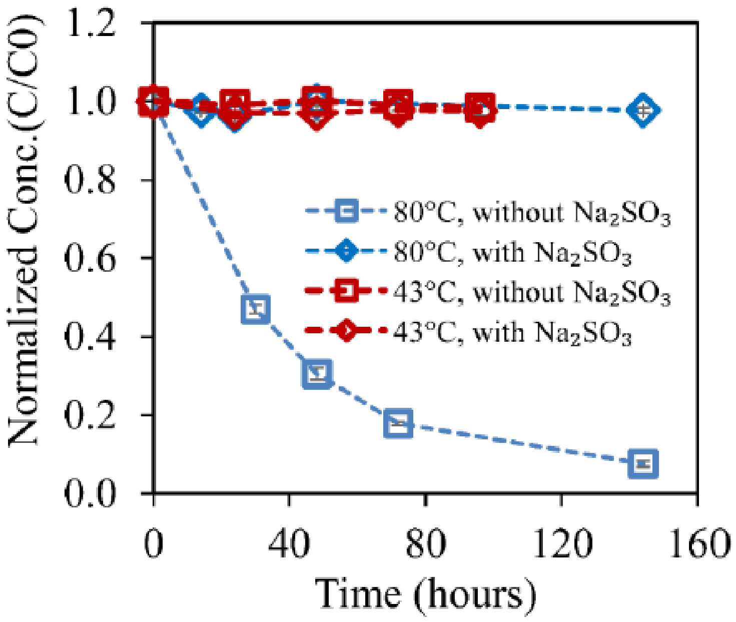
Linear alcohol ethoxylates SURFONIC®L24-22

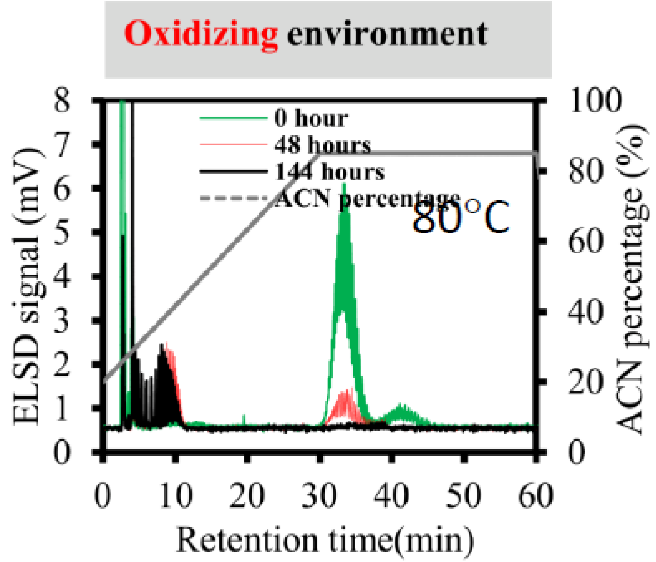


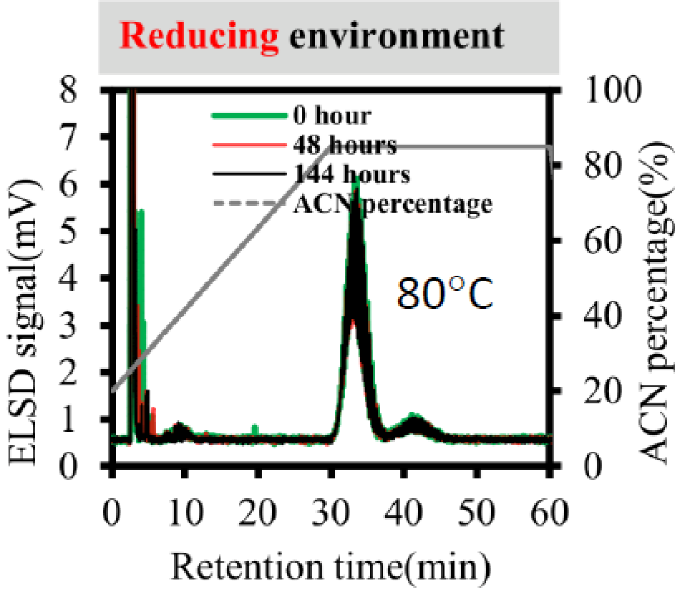
m=11~13;
n=22

SURFONIC®L24-22, Huntsman Corporation

Thermal stability of surfactant





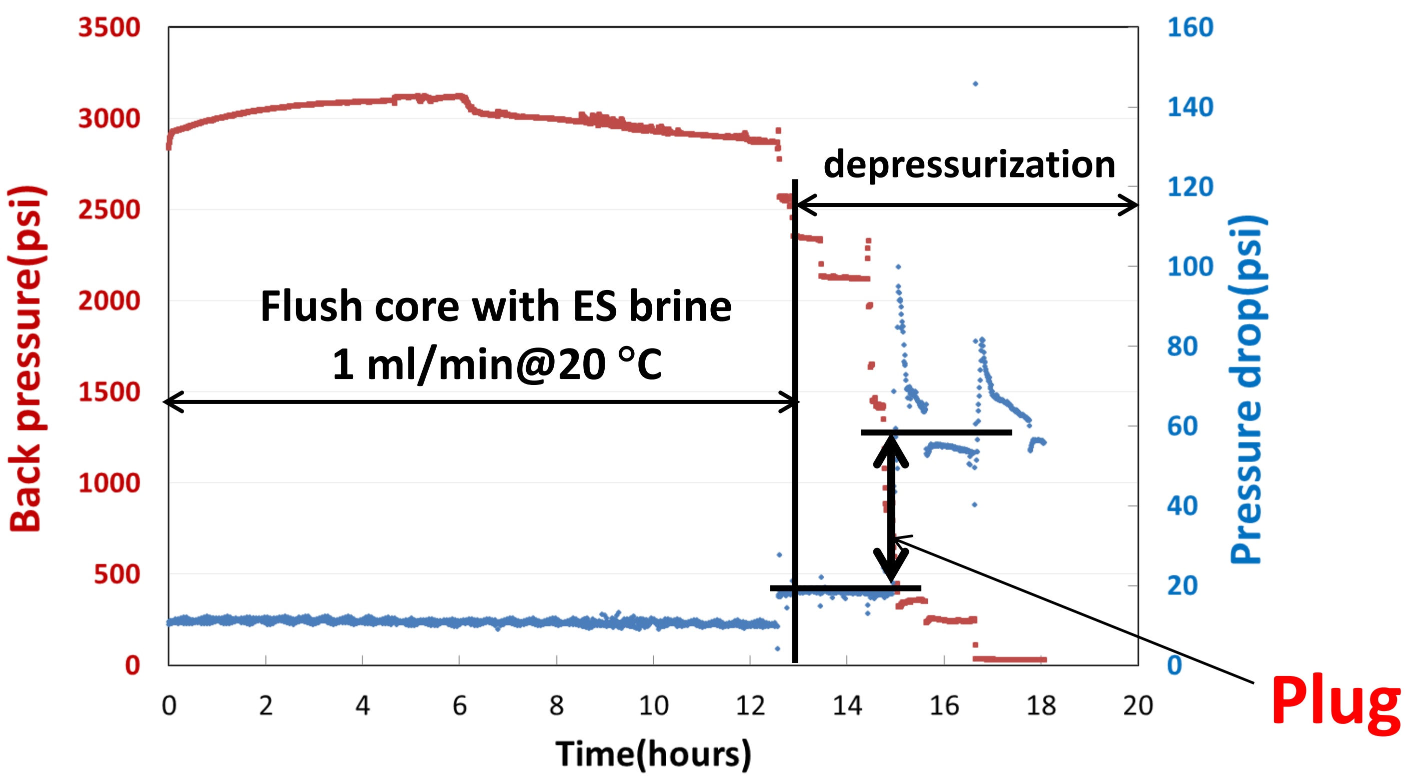


- L24-22 Surfactant degradation at temperature of 80°C, could be inhibited using oxygen scavenger
- Suggestion for field injection: for any process where surfactant solution heating is applied, oxygen scavenger must be added

Core Flood at 43 °C, 2600 psi

- Core
  - Diameter: 1.50 inch
  - Length: 2.97 inch
  - Pore volume: 14.4 cm^3
  - Lithology: Silurian dolomite core from Kocurek Industries
  - Porosity=16.7%
  - Permeability=91 mD

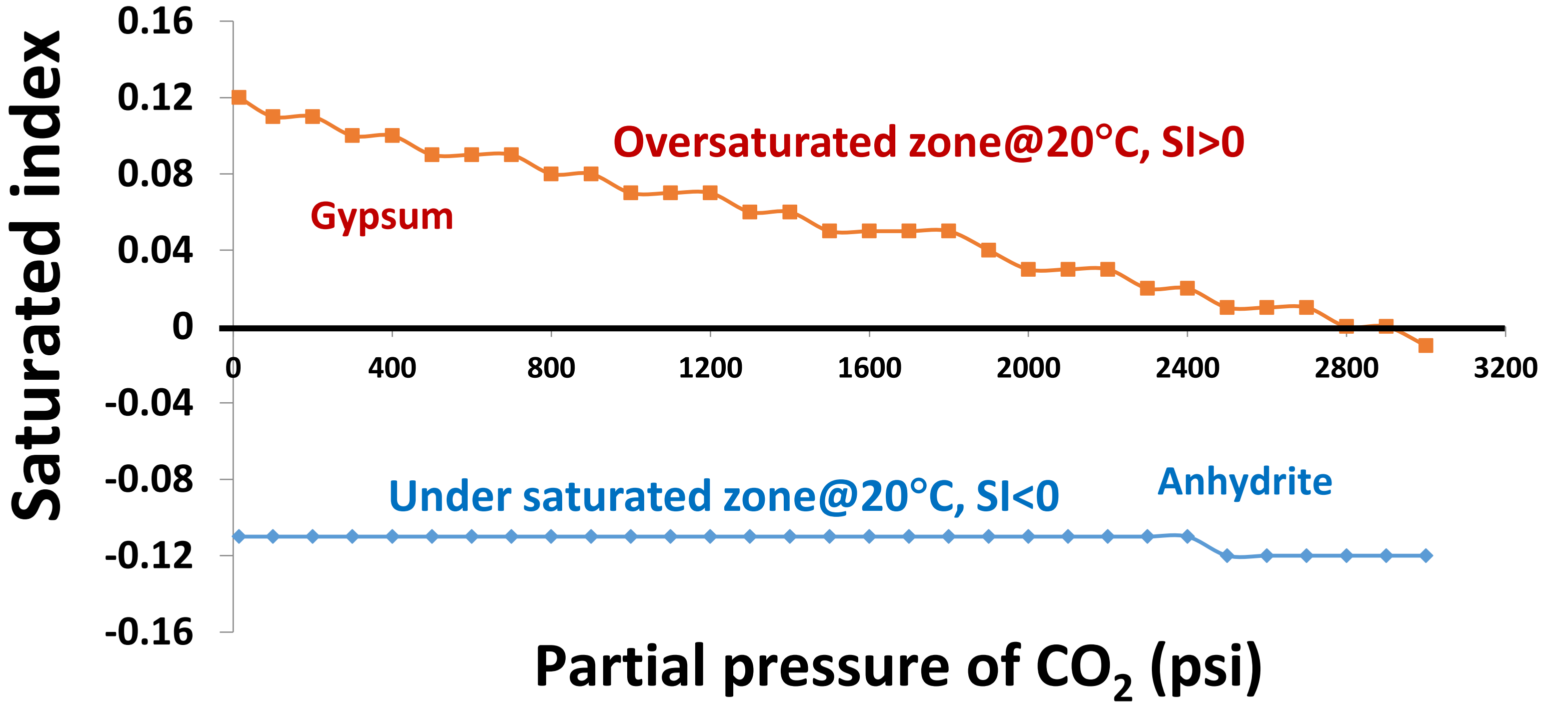
Depressurization



- Depressurization from 1500 psi to 800 psi and then to 200 psi(at 20 °C), we saw a sudden increase of pressure drop(from 20 psi to 60 psi)
- Does the pressure drop indicate core plug?

Interpretation of Core Plugging

- Saturated Index* of anhydrite and gypsum was simulated by PHREEQC Software
- Negative Saturated index(SI) means under saturated and positive SI means oversaturated



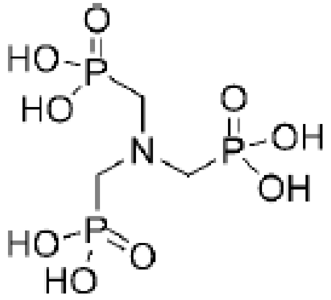
- Anhydrite is under saturated from 14.7 psi to 3000 psi
- Gypsum is over saturated from 14.7 psi to 2800 psi, which indicates that depressurization is favorable for gypsum formation

*Lopez-Salinas, Jose Luis, George J. Hirasaki, and Clarence A. Miller. *SPE141420*

Add scale inhibitor & change oxygen scavanger

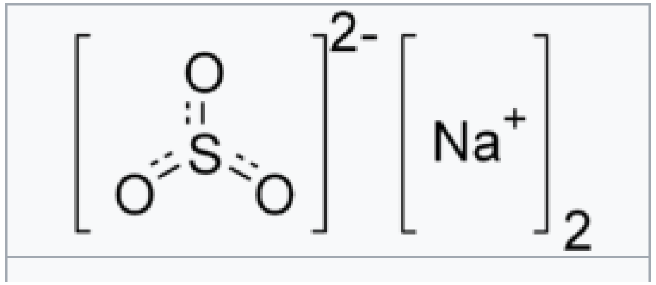
Add
Scale inhibitor

B106



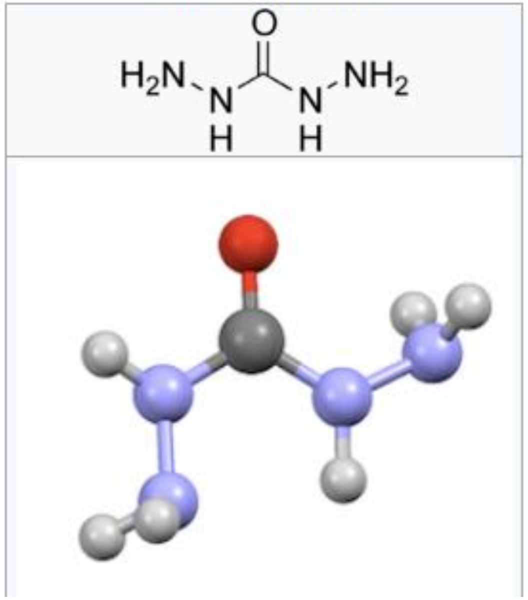
Replace

Sodium sulphite

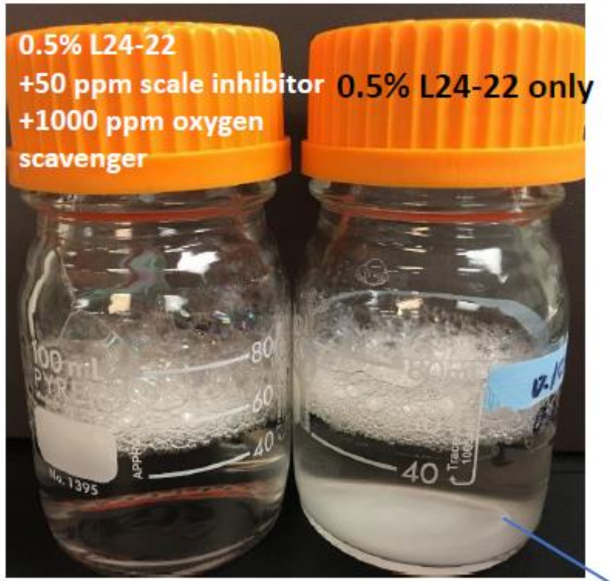


with

Carbohydrazide



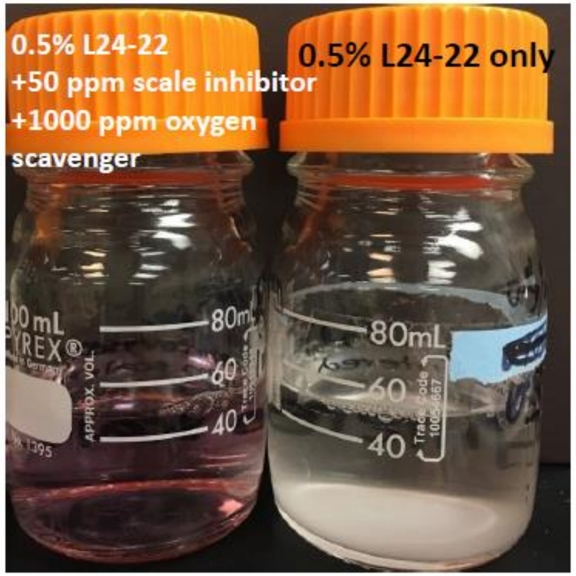
Stability of surfactant solution



L24-22 in filtered ES field brine

after 3~4hrs

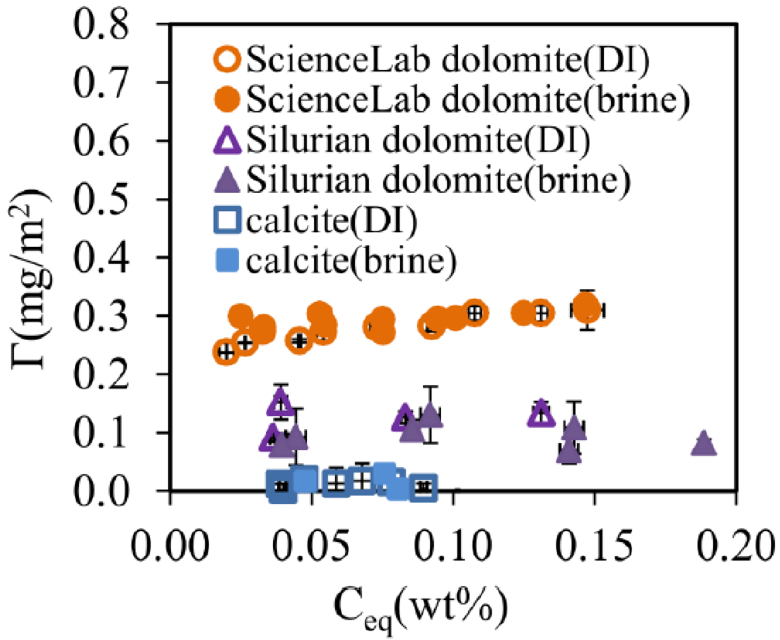
precipitation

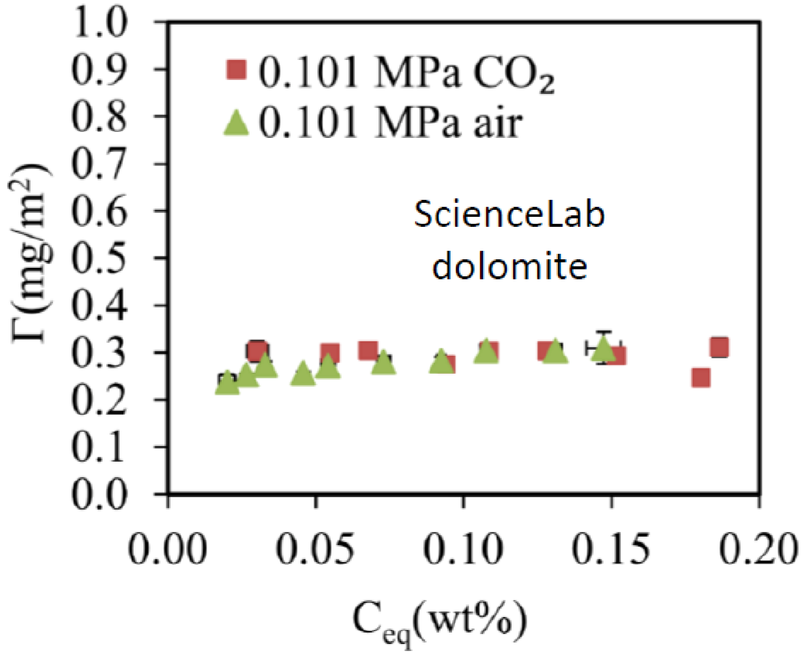


after 2 weeks

- Surfactant solution with 50 ppm scale inhibitor is clear after 2 weeks;
- The surfactant solution with 50 ppm scale inhibitor and 1000 ppm oxygen scavenger become pink

Adsorption of surfactant





Composition of synthetic brine for adsorption

NaCl (g/L)	MgCl2·6H2O (g/L)	CaCl2·2H2O (g/L)	KCl (g/L)
29.26	2.76	5.82	0.46

BET surface area

CaCO3	2.12m²/g
Silurian dolomite	0.73m²/g
ScienceLab dolomite	0.85m²/g

- Adsorption of L24-22 on Silurian dolomite in brine is as low as 0.1mg/m2(0.13mg/g)
- CO_2 has no effect on adsorption of L24-22 surfactant on dolomite

Core flooding: Apparent Viscosity

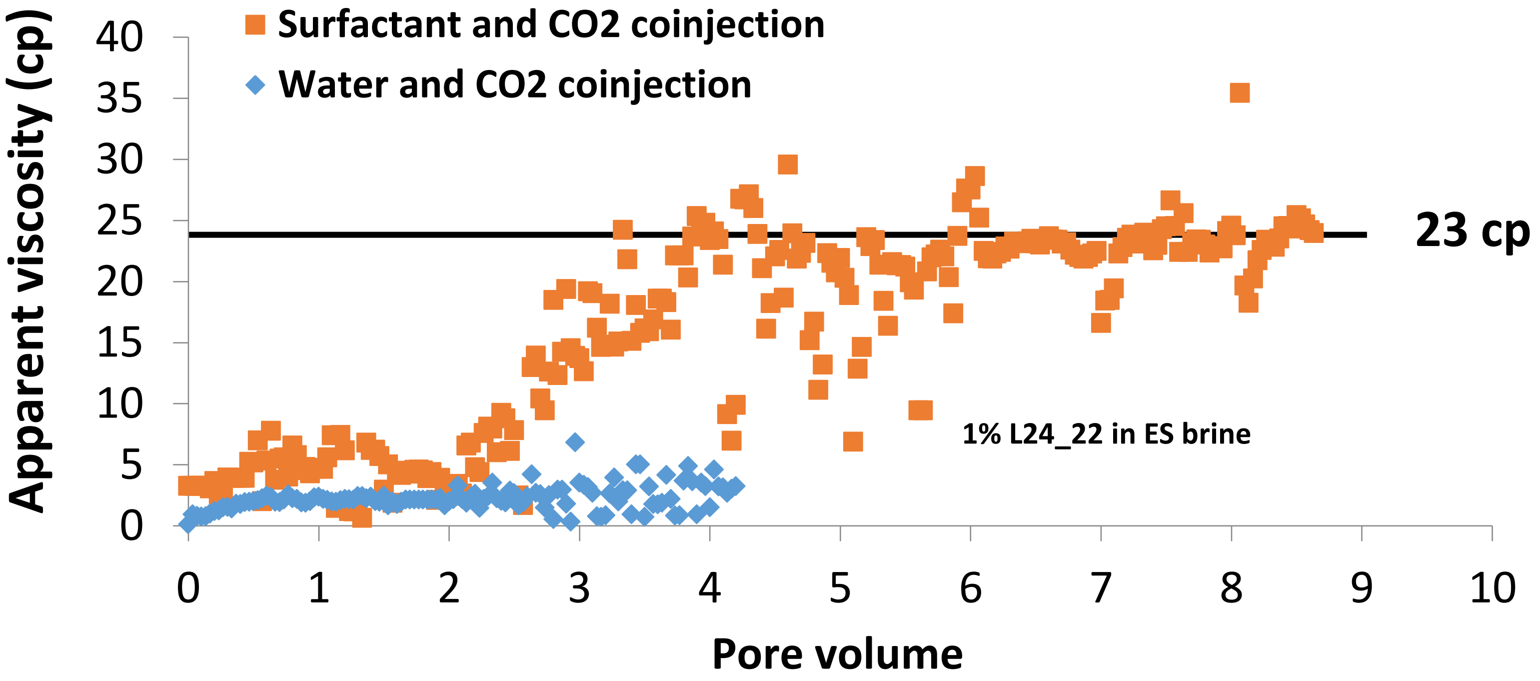
- Apparent viscosity is used to describe the foam strength, which is calculated by **Darcy's law**:

$$\mu_{app} = -\frac{k}{u_t} \cdot \nabla p$$

where μ_{app} is foam apparent viscosity, k is core permeability, u_t is the total superficial velocity and ∇p is the pressure gradient.

Core flooding

80% foam quality, Injection rate=4 ft/day, T=110 °F(43.3 °C), Injection pressure=2600 psi.



- **Equilibrium average apparent viscosity by co-injection of surfactant and CO_2 is 23 cp**

Conclusions for East Seminole

- Using 1wt% L24_22 nonionic surfactant, Foam with apparent viscosity of 23 cp can be generated in Silurian dolomite core(80% foam quality, 4 ft/day injection rate, 110°F(43.3°C), pressure of 2600psi, reservoir brine)
- Gypsum can precipitate during depressurization at 20°C which was observed by experiment and simulation results from PHREEQC
- Adsorption on Silurian dolomite is as low as 0.08 mg/g
- Oxygen scavenger and scale inhibitor should be used

Reservoir Conditions for Middle East

- Carbonate formations
- High temperature, 120 °C
- High salinity, 22% TDS
- High MMP, 3,400 psi

Task 1: Selection and Optimization of Surfactant

K. Johnston, Chen, Y. , Elhag, A., Da, C., et al.

- **Anionic surfactants cannot withstand high temperature and/or high divalent ion concentrations of Middle East reservoirs**
- **Nonionic surfactants that work for West Texas will phase separate (cloud point temperature exceeded) at Middle East temperatures**
- **Zwitterionic, betaine surfactants have large adsorption on carbonates**
- **Cationic amine surfactants can result in CO_2 foam with apparent viscosity**

Evaluation Procedure of Surfactant Formulations for Foam EOR

Can CO_2 foam be generated and applied at reservoir conditions for mobility control?

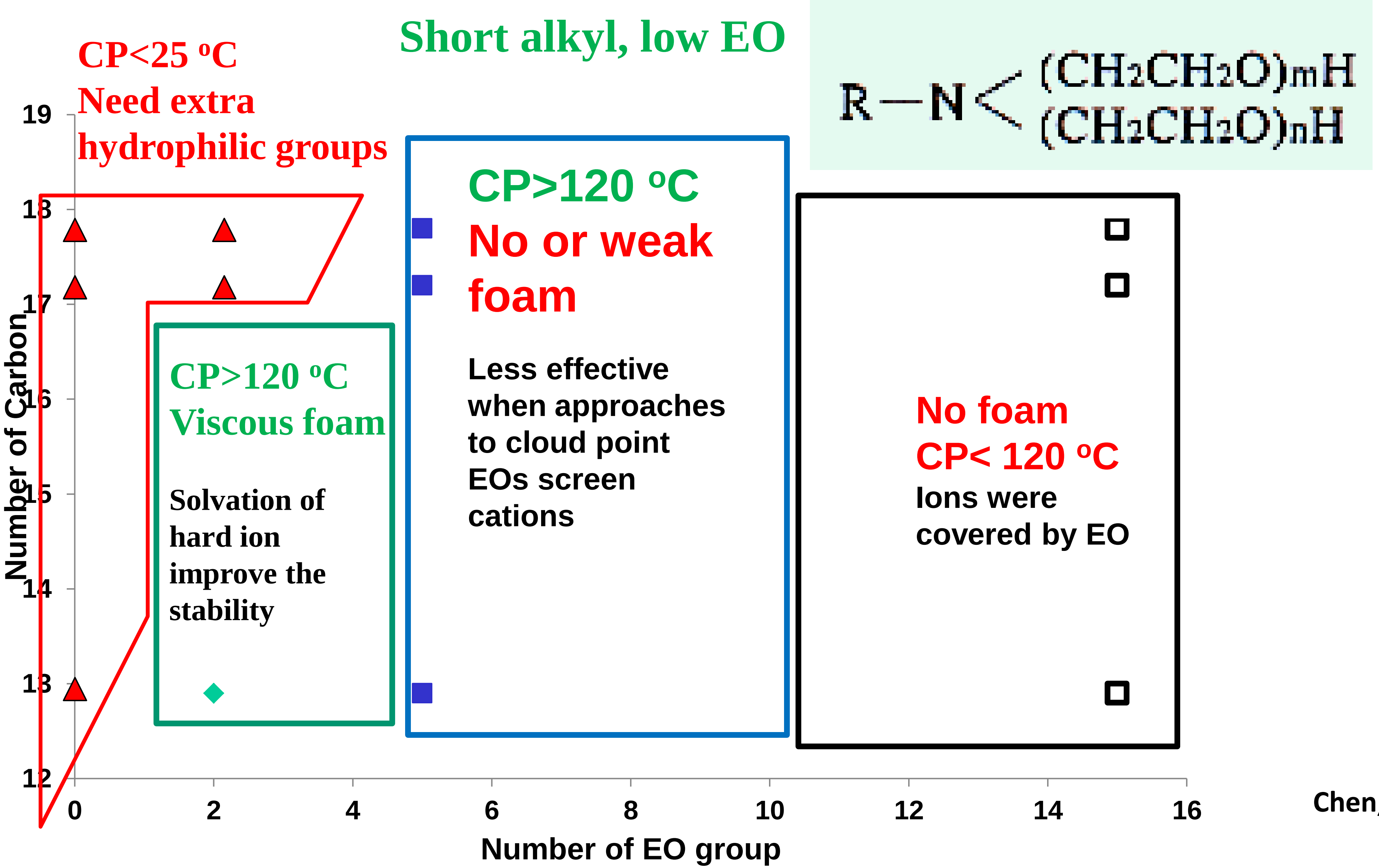
A systematic procedure should be used to evaluate the foam process:

- Evaluation of Surfactant Properties:
  1. Solubility
  2. Thermal Stability
  3. Adsorption
  4. *Partitioning Coefficient for CO_2-soluble surfactant; **Interfacial tension (IFT) for immiscible foam

- Investigation of Foam Mobility Control
  1. *Pre-Screening of Foaming Agents in Sandpack
  2. Foam Flooding at Reservoir Conditions

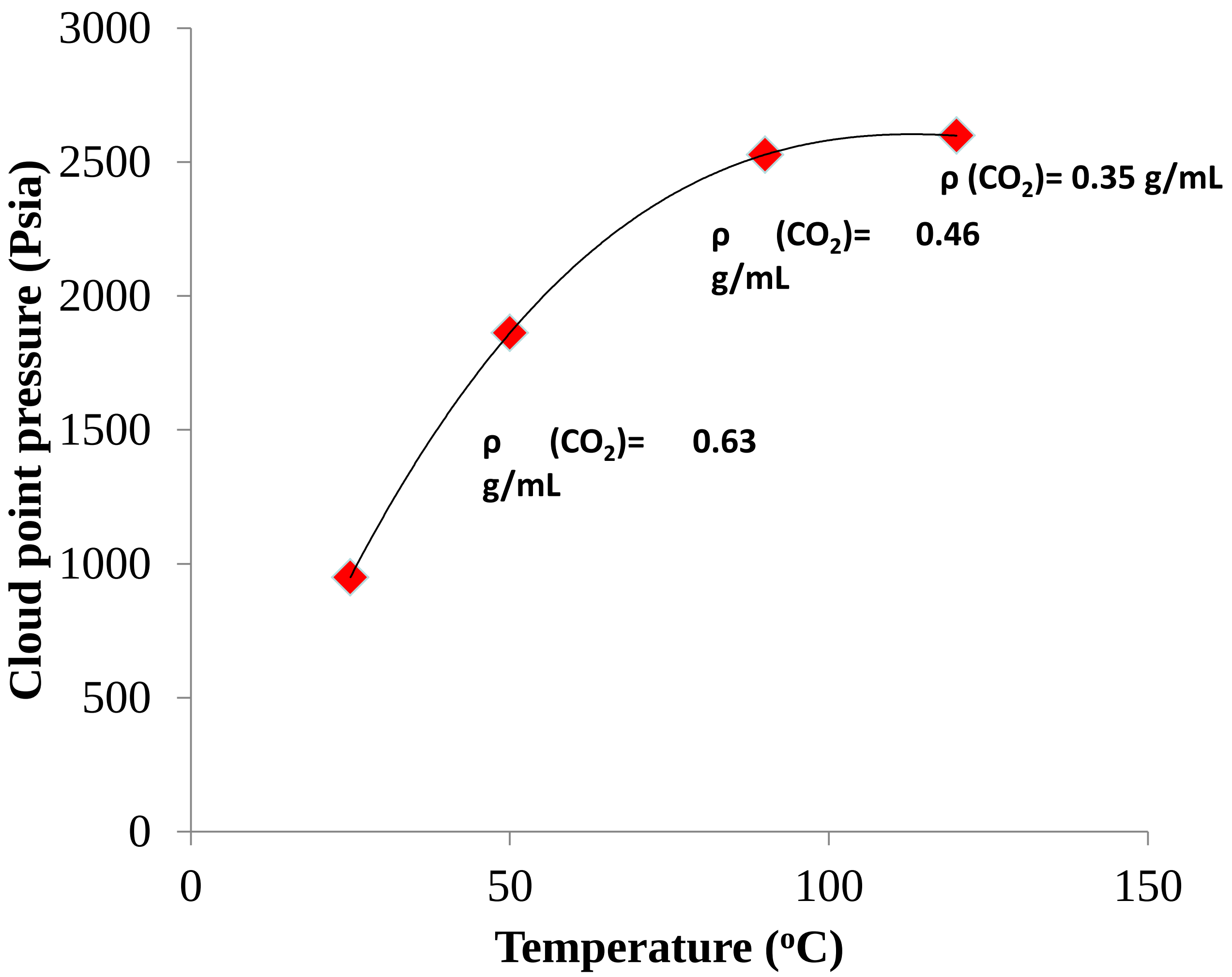
***Chen, Y. et al., 2013. SPE-154222**
****Wang, et al., 2001. SPE-72147**

Effect of EO number and Tail length on foam formation: injected in pH 4, 22% TDS brine, 120°C



Chen, Y. et al., 2014

Solubility of ETHOMEEN C/12 in CO_2

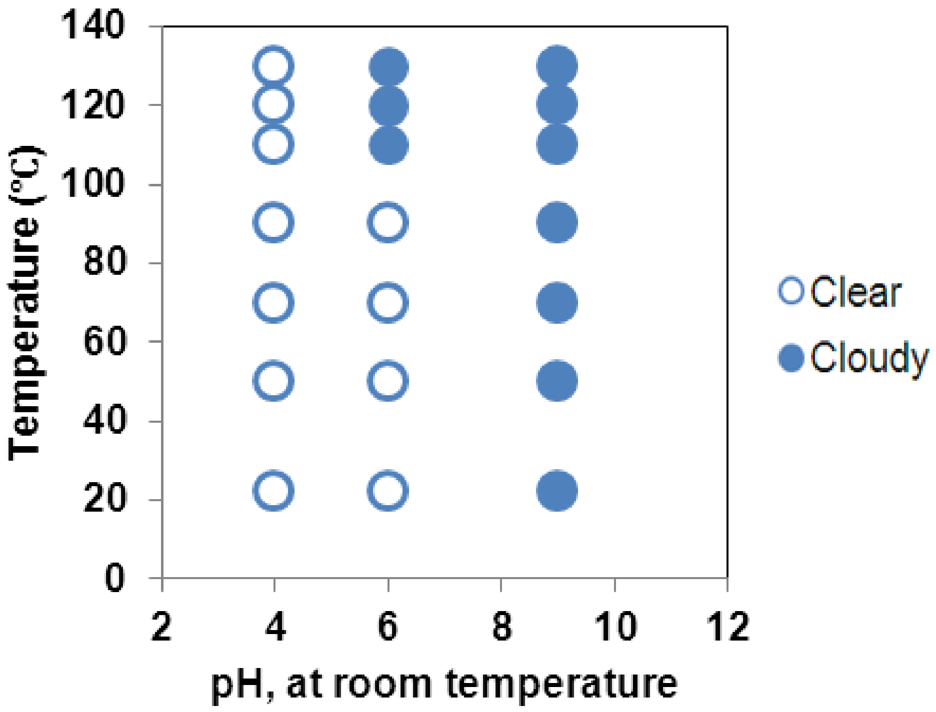


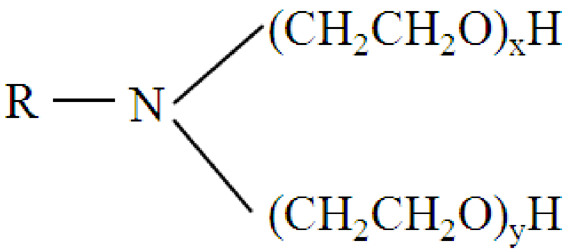
Density decreases with an increase in temperature

Chen, Elhag, et al., 2014

Solubility of Ethomeen C12 in Brine

- **CO_2 phase**: C12 is **CO_2-soluble** (**SPE-154222**)
- **Aqueous phase**: the **cloud point** of C12 is lower than room temperature at original pH (9.24), and is enhanced with decreasing pH due to the protonation of C12.





1% C12 in brine (22% TDS):

Na^+: 71720 ppm

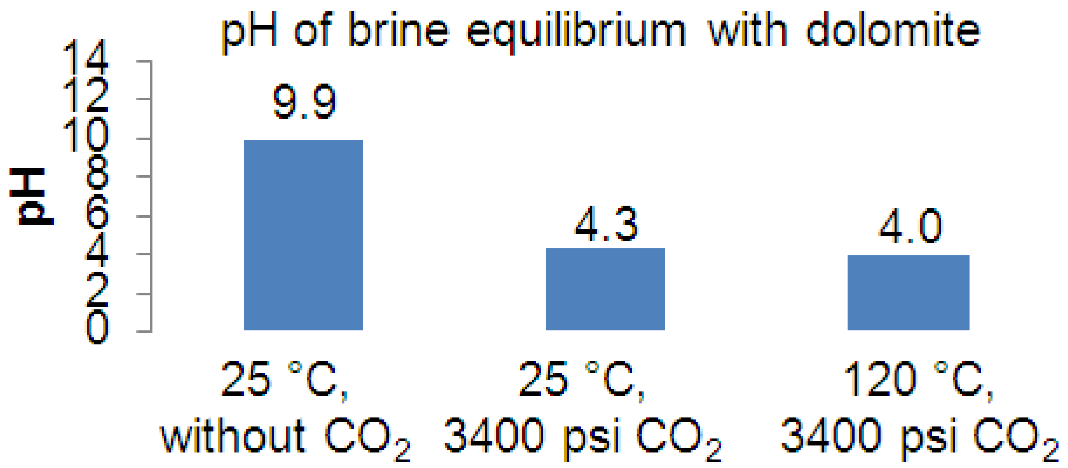
Ca^{2+}: 21060 ppm

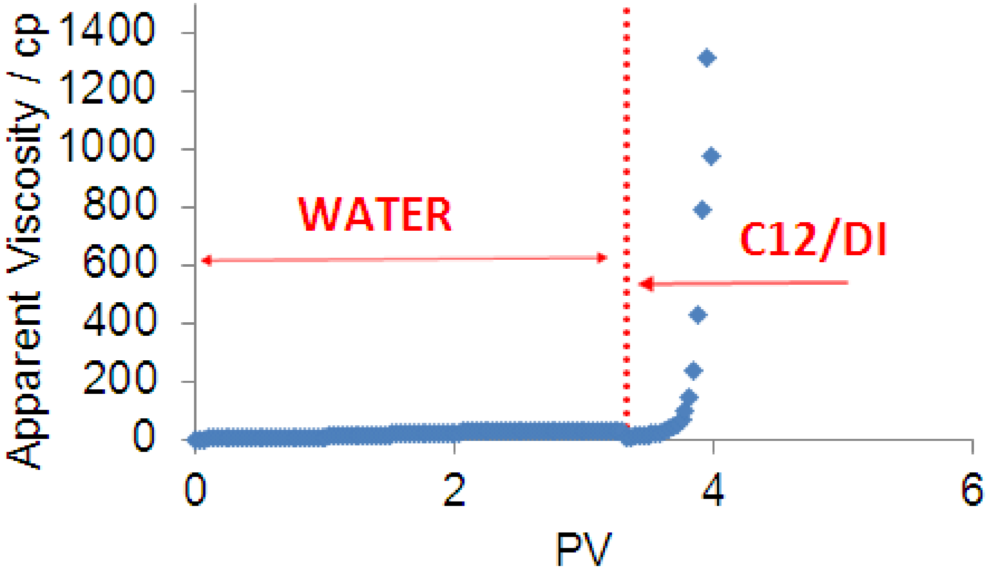
Mg^{2+}: 3063 ppm

Cl^-: 156777 ppm

Core Plug by Poor Solubility at pH 9

- The equilibrium pH of dolomite-water without CO_2 is up to **9.9**.
- C12 is **not water-soluble** at such high pH.
- The core was **plugged** by C12 during core flooding.
- A slug of **CO_2 is required** to reduce the system pH.





Cationic at pH<7 for low O/W and C/W partition coefficients

$$\text{Partition coefficient} = \frac{\text{mass fraction in nonaqs. phase}}{\text{mass fraction in brine}}$$

O/W partition coefficients at 90 °C, 1 atm

Surfactant	pH	30 g/L NaCl	182 g/L NaCl	22% TDS
$C_{12-14}N(EO)_2$	4	0.02*	0*	0.04
	5			0.05
	6	0*	0.02*	0.03
	7			0.21
	8	7.13*	15.96*	
	9			7.59

- Cationic form (pH<7) for low O/W partition coefficients (<0.25) to minimize loss towards oil
- Nonionic form (pH >7): hydrophobic and prefers oil –switchable concept

* published in Chen et al. SPE J 2014 preprint

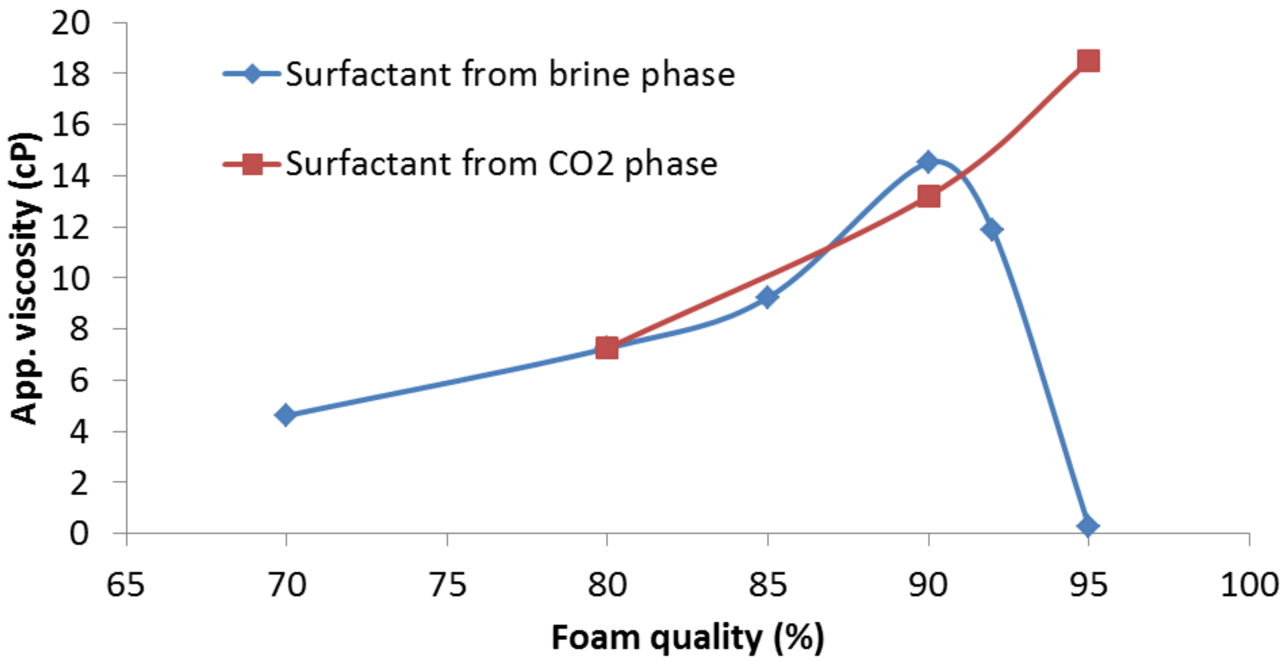
- CO_2 acidified brine at high pressure for low C/W partition coefficients
- Lower C/W partition coefficients for diamine

C/W partition coefficients at 3400 psia

Surfactant	Salinity	25 °C		60 °C		90 °C	
		Avg.	Standard dev.	Avg.	Standard dev.	Avg.	Standard dev.
$C_{12-14}N(EO)_2$	182 g/L NaCl	0.030	0	0.030	0.001	0.032	0.001
	22% TDS	0.026	0.004	-		0.028	0.002

Foam at 120 ^oC, 3400 psia (22% TDS), 938 ft/day (total) in crushed limestone pack

Co-injecting 1% (w/w) $C_{12-14}N(EO)_2$ 22%TDS brine pH 6 solution with CO_2 or by co-injecting 0.2% (w/w) $C_{12-14}N(EO)_2$ CO_2 solution with 22%TDS brine in 76 Darcy limestone pack

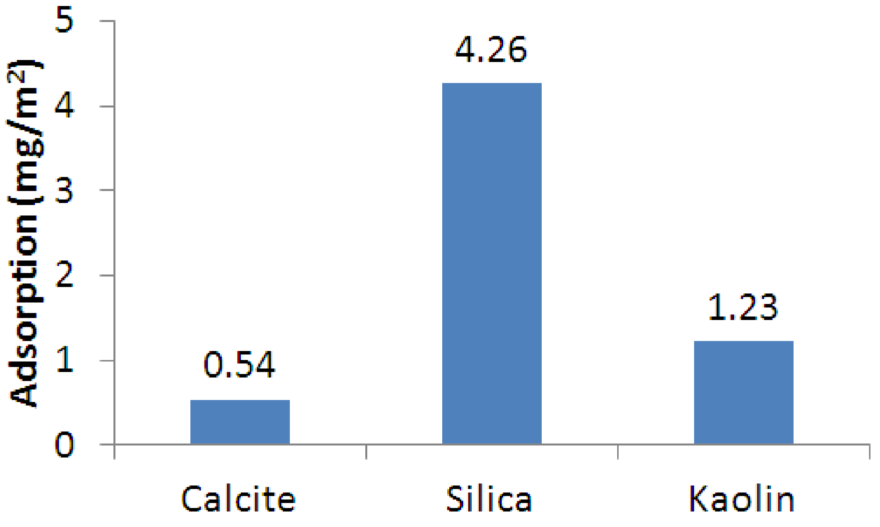


- Highest viscosity at 90% foam quality (surfactant injected from brine)
- Foam at 95% foam quality when injected from CO_2 (higher surfactant conc. in total fluid than injecting surfactant from brine)

Chen, Elhag, et al., 2014

Adsorption of C12 on Pure Minerals

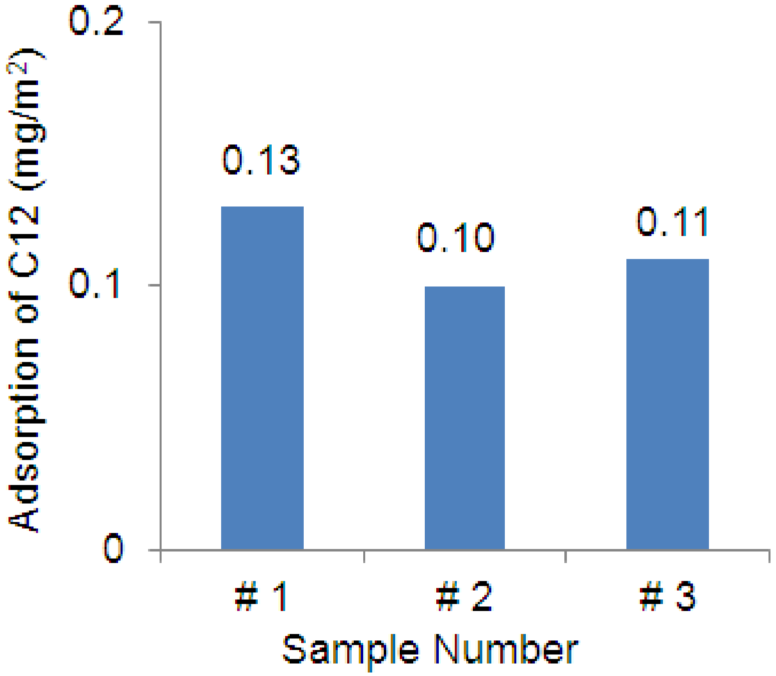
(Cui, et al., 2014, SPE-169040)



- Adsorption was measured in brine at 2 atm CO_2 and room temperature.
- C12 is partially protonated to cationic surfactant at test conditions. The zeta potential of the minerals dominates the adsorption.
- Carbonate minerals (calcite) carry positive zeta potential which results in the least adsorption.
- Silica minerals carry negative zeta potential which results in the highest adsorption.
- The silicon content in carbonate reservoir determines the retardation and loss of C12 due to adsorption.

Adsorption of C12 on Potential Formation Minerals

(Cui, et al., 2014, SPE-169040)



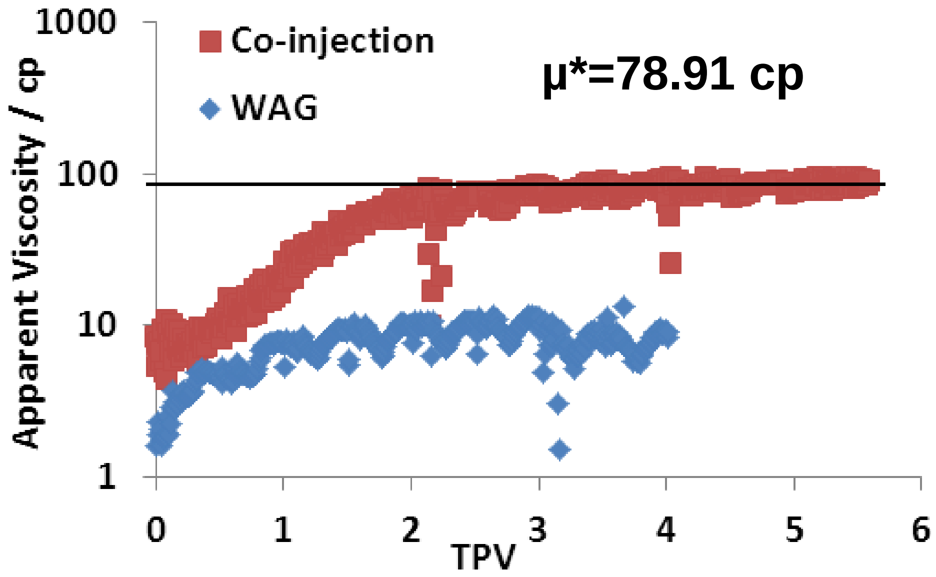
BET surface area of the cores samples is 4.00 m^2/g.

- Quantitative analysis of XRD revealed that the three core plugs were composed of:
  Calcite: 95.4 - 98.6%,
  Dolomite: 0.5 - 4.1%,
  Quartz: 0.4 - 0.9% .
- the adsorption of C12 in synthetic brine is **low** on the formation material which has low quartz content

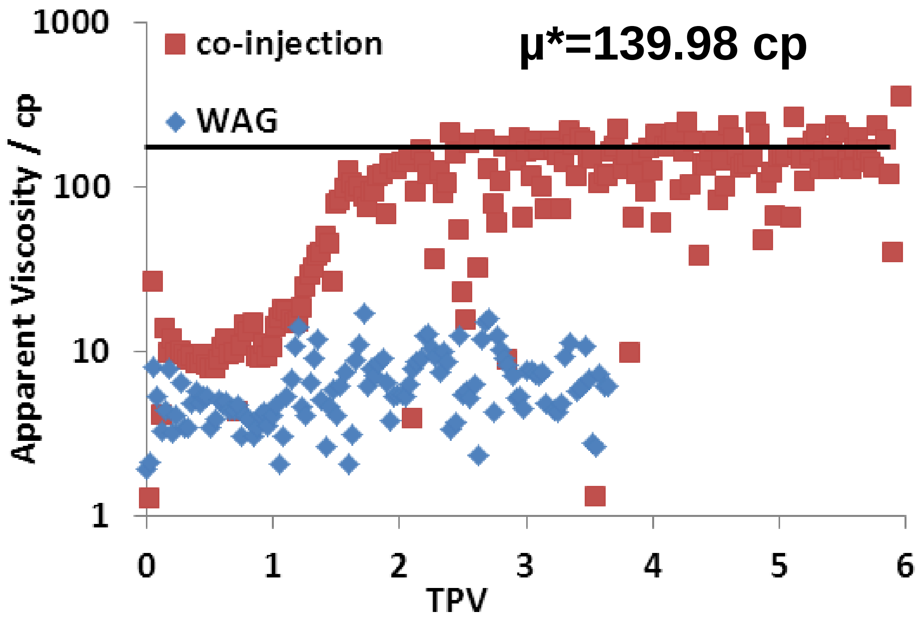
C12/DI and CO_2 Foam at 20 °C

- C12/DI and CO_2 were **co-injected** into a Silurian dolomite core at **room temperature, 3400 psi and various foam qualities (gas fraction)**, following the water alternating CO_2 (**WAG**).
- The foam is **strong** compared to WAG

30% Foam Quality



70% Foam Quality



Influence of Foam Quality

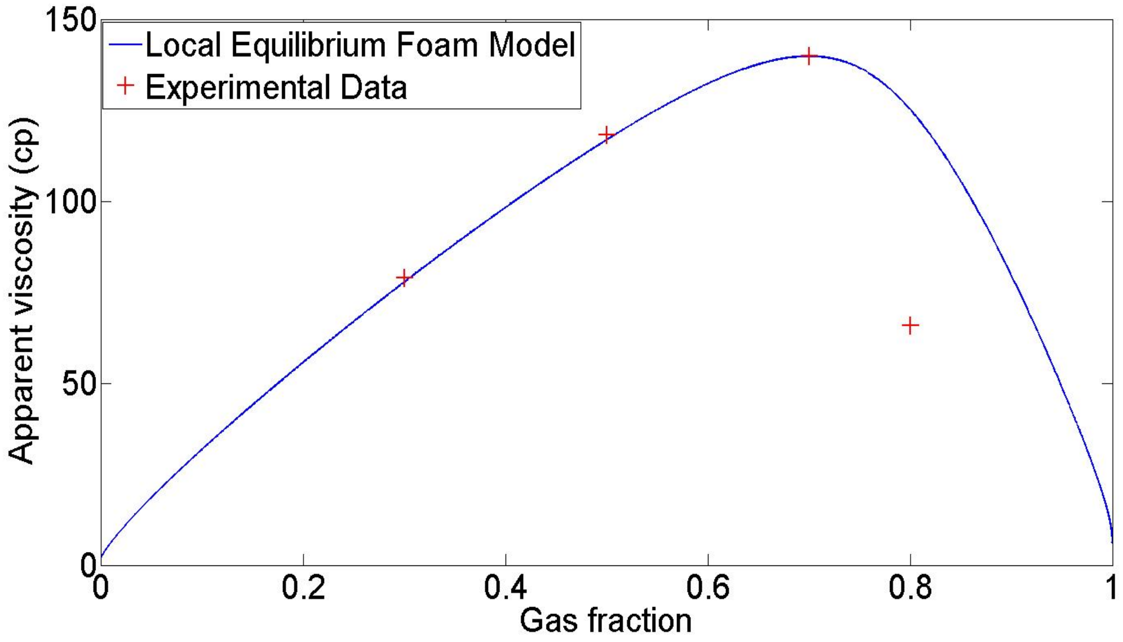
- *Local equilibrium foam model is the "dry-out" **foam model**, used in **CMG-STARS**.
- The change of foam strength with foam quality can be divided into:

"Low Quality" regime,

transition foam quality,

"High Quality" regime.

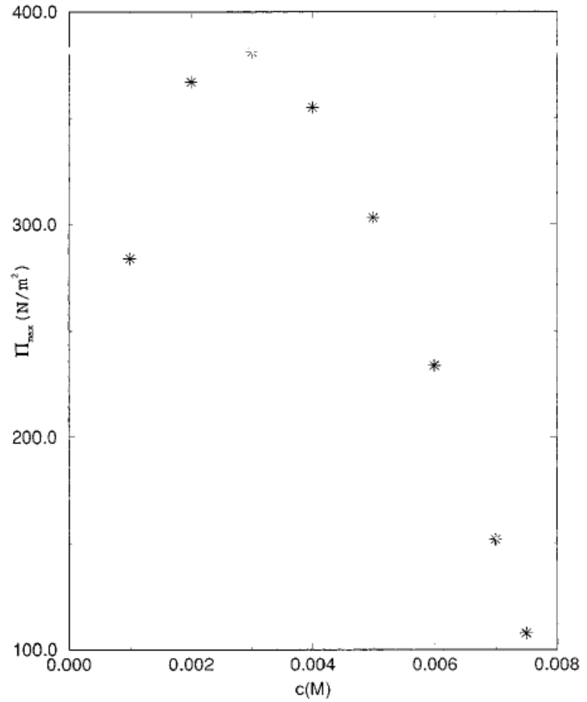
A slug of water is necessary to maintain the foam apparent viscosity



*Ma, K., Lopez-Salinas, J. L., Puerto, M. C., Miller, C. A., Biswal, S. L., & Hirasaki, G. J. (2013). *Energy Fuels, 27*(5), 2363–2375.

Influence of Salinity

- Salinity can **stabilize** foam by **increasing the packing density** of surfactants on water-gas interface and **destabilize** foam by **decreasing the electric repulsion** of double layers in film plateau.
- **Disjoining pressure** can be utilized to explain the salinity influence.
- The Π_{max} increases with electrolyte (NaCl) concentration, reaches a maximum at a **"optimal" salinity**, and decreases with electrolyte concentration.
- The change of **foam strength and stability** should be consistent with that of disjoining pressure.



(Bhakta and Ruckenstein, 1996)

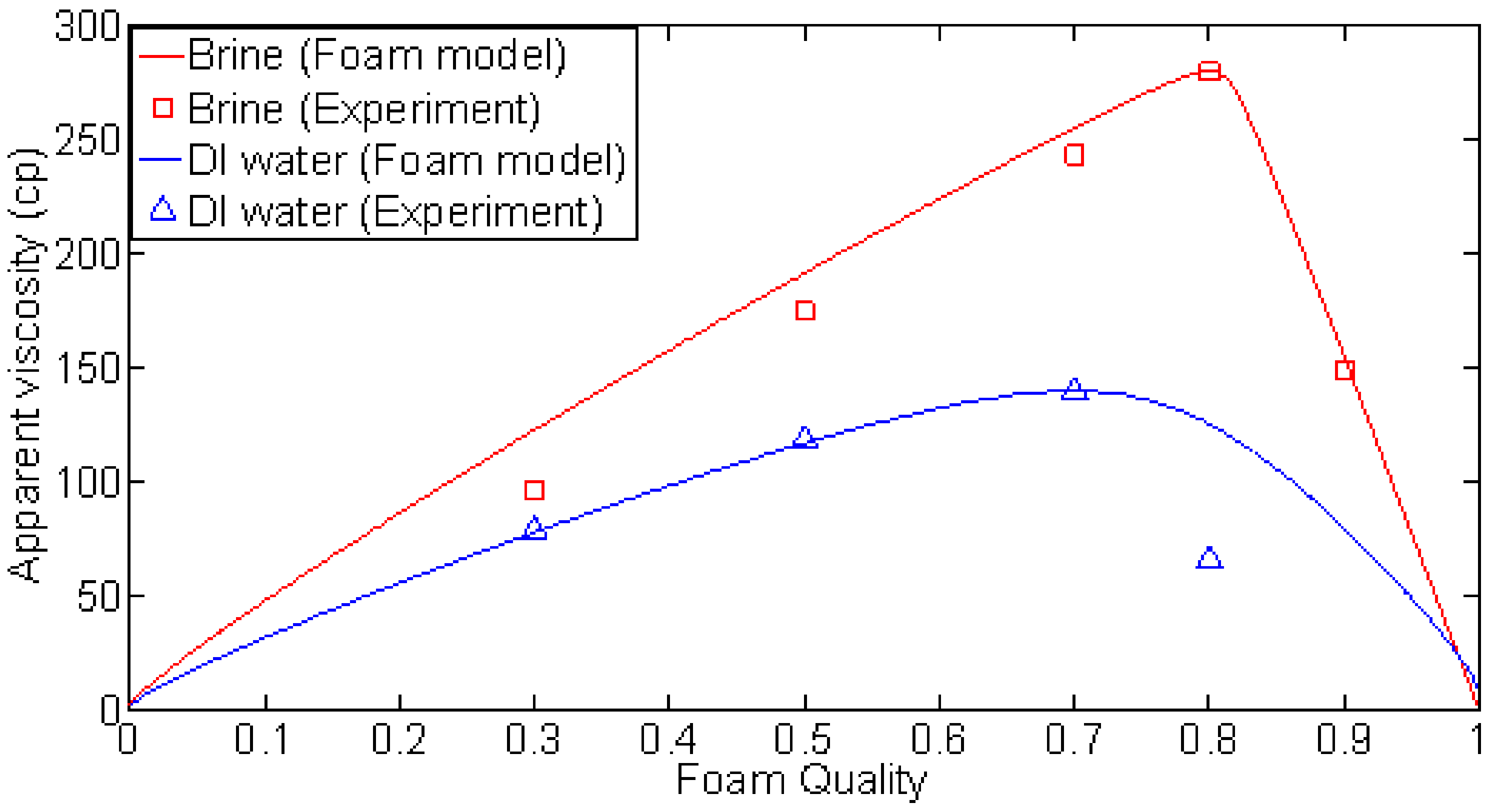
Mineral Dissolution

- The carbonate mineral was dissolved in DI water and CO_2 at elevated T.
- The **sufficient divalent cations**, *i.e.*, Ca^{2+} and Mg^{2+}, are suggested to be added in brine.

Cui, et al., 2016

Salinity: Stabilization

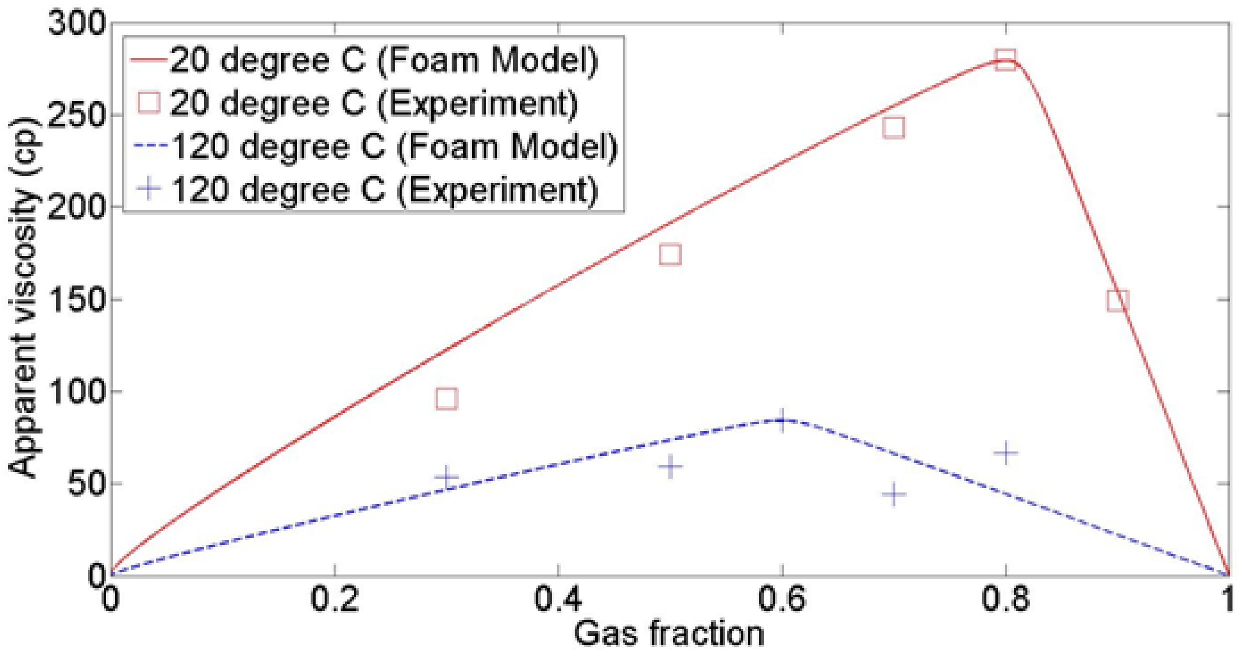
- Salinity in synthetic brine is **favorable** for C12 and CO_2 foam strength.
- Salinity in synthetic brine is around the **“optimal” salinity**



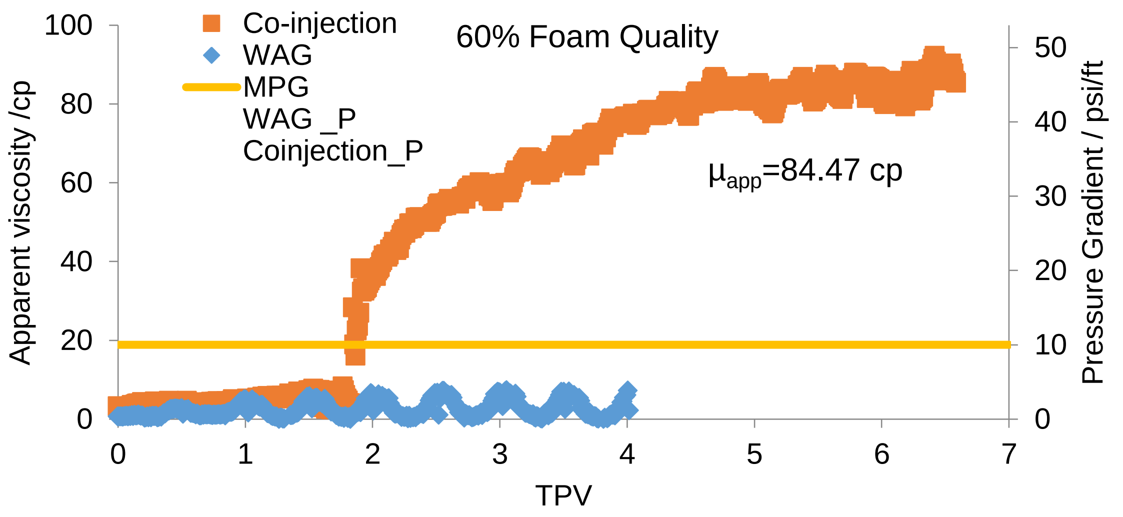
Influence of Elevated Temperature

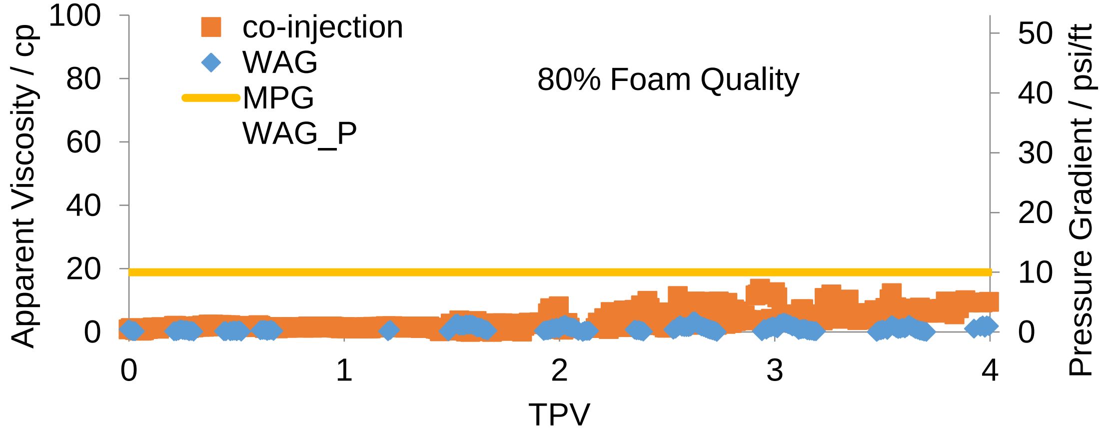
- **Dehydration** of EO and OH head groups at elevated temperature **reduces** the effective size of the polar head group, **increases** the packing density and **stabilizes** the foam.
- The enhancement of **thermal motion** of surfactant molecules decreases the packing density and **destabilize** the foam.

Elevated reservoir temperature (120 ℃) is **detrimental** for C12/brine and CO_2 foam strength due to the short length of EO group.



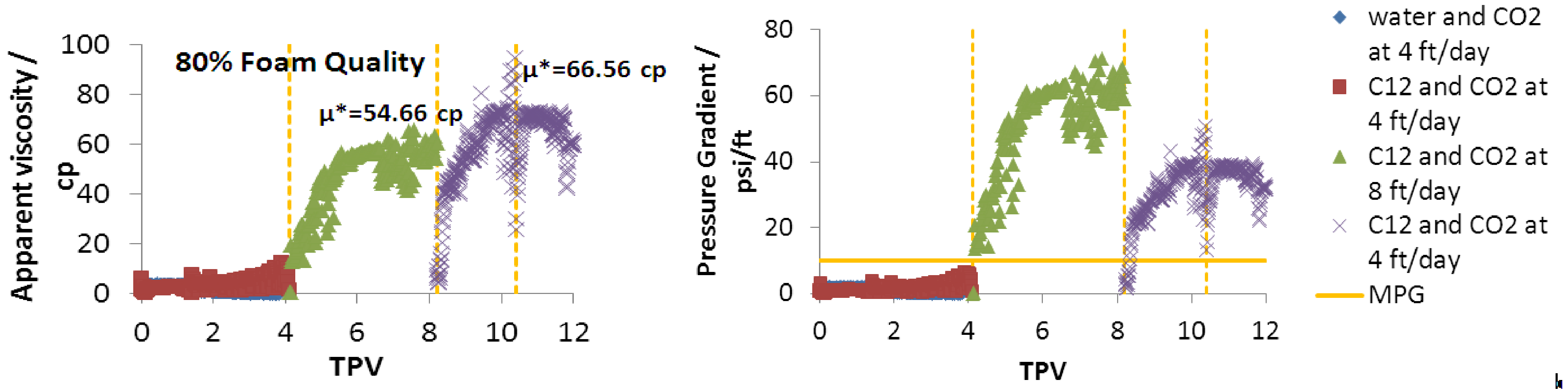
At 120 °C foam was not always generated





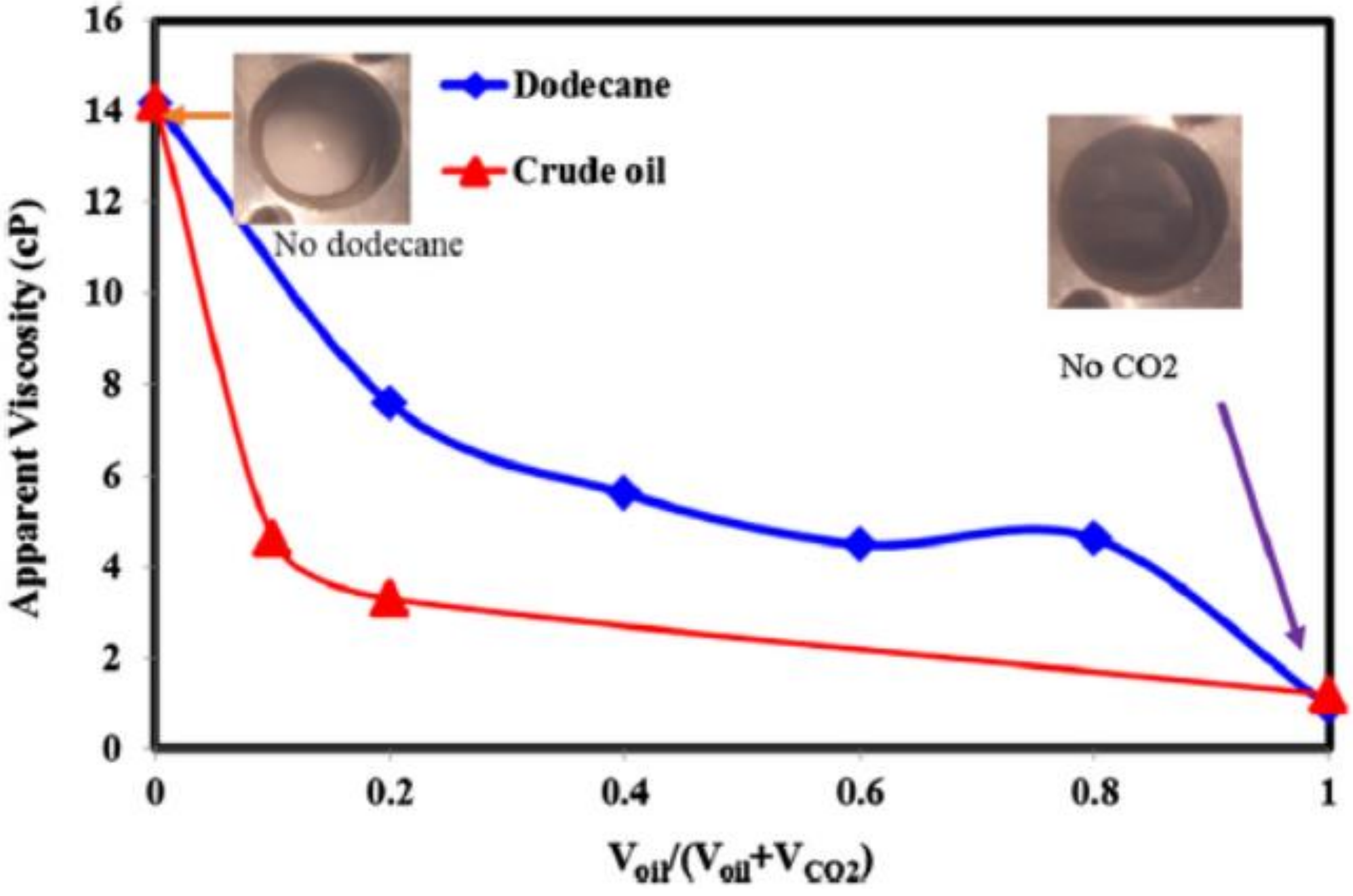
C12/Brine and CO_2 foam at 120 °C

- C12/brine and CO_2 can generate **strong** foam at high temperature
- **Minimum Pressure Gradient (MPG)** exists. High flow rate is required to reach the MPG to onset the foam generation at high foam quality.



C12/Brine and CO_2 foam strength history at 80% foam quality and 120 °C. Start at 4 ft/day total superficial velocity, no foam. Switch to 8 ft/day, foam is generated. Switch back to 4 ft/day, foam is still stable

Effect of Oil



Recent developments

(a) N[1]-dodecyl-N[3], N[3]-dimethylpropane-1,3-diamine (noted as C12-DA)

(b) N[1]-tetradecyl-N[3], N[3]-dimethylpropane-1,3-diamine (noted as C14-DA)

(c) $C_{16-18}N(CH_3)C_3N(CH_3)_2$ (Duomeen TTM)

Cui, et al., (2018), SPE 190252
Da, et al., (2018), SPE 191479

Conclusions – Evaluation Results

- **The solubility of C12 depends on pH and temperature. C12 is water-soluble at 120 °C in CO_2 flooding processes.**
- **C12 was slowly degraded at 125 °C and pH=4. But oxygen was not eliminated and may have caused this degradation.**
- **The adsorption of C12 is low on relative pure carbonate surface.**
- **Ethomeen C12 and CO_2 can generate strong foam at reservoir conditions, *i.e.*, high temperature, high salinity and carbonate minerals.**

Conclusions – Field Application

- **Ethomeen C12 can be injected in CO_2 phase.**
- **A slug of water should be injected to maintain the CO_2 foam strength, even though Ethomeen C12 is a CO_2-soluble surfactant.**
- **The high minimum pressure gradient (10 psi/ft) for foam generation of Ethomeen C12 at reservoir conditions may result in the failure of foam generation in situ. This is not observed in Duomeen TTM.**
- **Sufficient divalent cations are needed to suppress the dissolution of carbonate mineral in CO_2 and water flooding.**

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