FUNDAMENTAL RESEARCH PROJECT REVIEW MEETING

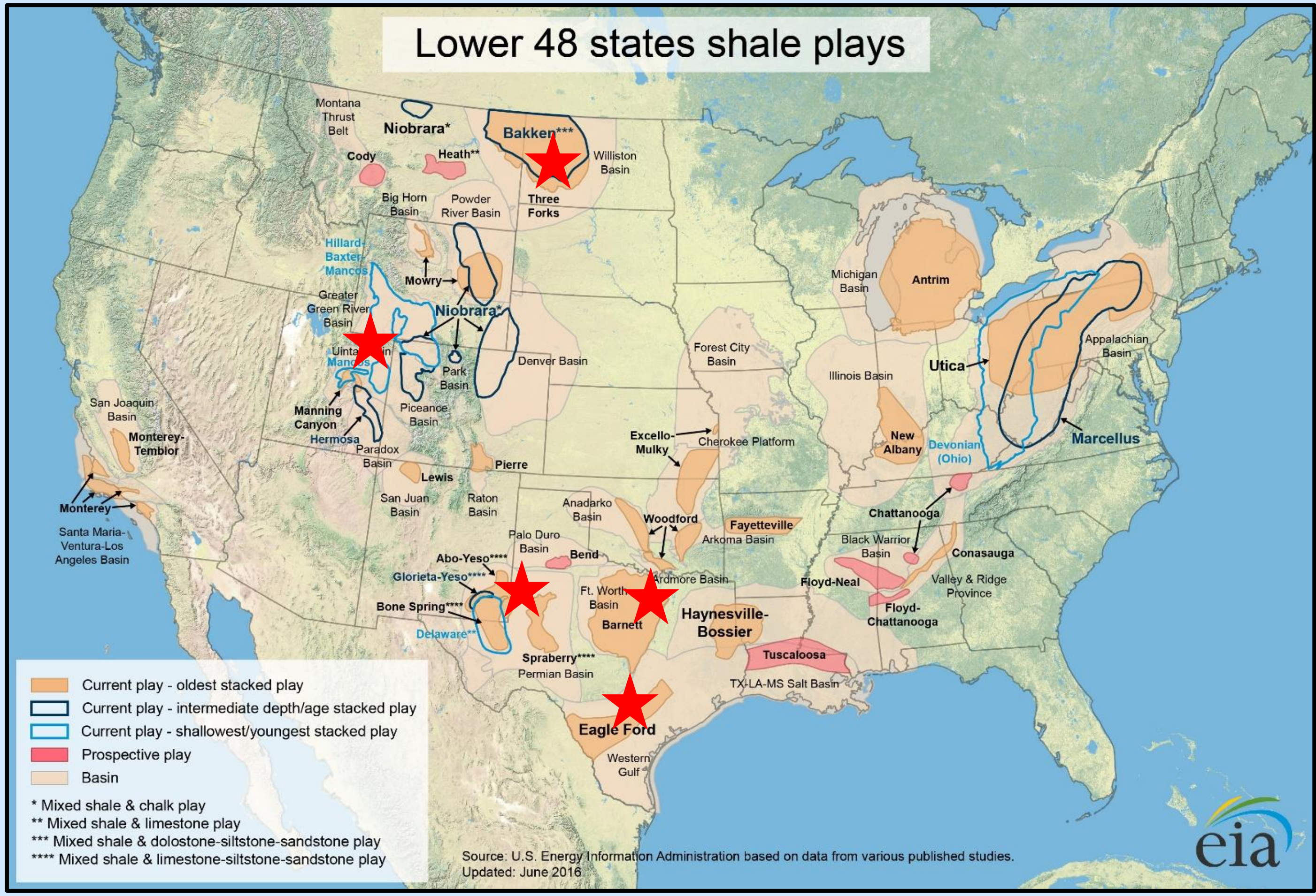
Virtual Agenda
October 16, 2020

Characterizing CO_2 as a Recovery Agent to Mobilize Hydrocarbons from Shale

Angela Goodman, Foad Haeri, Lauren C. Burrows, Parth G. Shah, Deepak Tapriyal, Robert M. Enick, Sean Sanguinito, Dustin Crandall

U.S. Department of Energy
National Energy Technology Laboratory

Oil & Natural Gas
2020 Integrated Review Webinar



U.S. DEPARTMENT OF ENERGY

Characterizing Application of CO_2 as a Recovery Agent to Mobilize Hydrocarbons from Shale

- **Objective:**
  - Determine viability of CO_2 as an enhanced recovery agent for unconventional oil
- **Challenges:**
  - Primary oil recovery from fractured unconventional formations **is typically less than 10%** - EOR is highly desired by industry
  - However, EOR in **shale is far more challenging** than conventional formations due to their extreme low permeability and mixed wettability
- **Approach:**
  - **Determine how CO_2 and in surfactants dissolved in CO_2 can be used to increase EOR** by simulating subsurface EOR conditions in the laboratory
    - Surfactants – identify CO_2-soluble surfactants to change wetting properties
    - Contact angle – observe change from oil-wet to water-wet
    - Confined Huff n' Puff core floods – relate to field tests
- **Value:**
  - Successful EOR in shales would lead to tremendous increases in domestic oil production

Characterizing Application of CO_2 as a Recovery Agent to Mobilize Hydrocarbons from Shale

Analysis of prior efforts for enhanced oil recovery from shales

- Critical review developed from literature study which defined laboratory R&D needs for EOR

Laboratory-based confined huff n' puff tests to relate to the field and are a primary focus of this project moving forward.

energy&fuels

"A Literature Review of CO_2, Natural Gas, and Water-Based Fluids for Enhanced Oil Recovery in Unconventional Reservoirs"

Energy & Fuels **2020** *34* (5), 5331-5380
DOI: 10.1021/acs.energyfuels.9b03658

Findings:

- CO_2 and natural gas are promising fluids for huff 'n puff EOR
- CO_2 EOR shale is a complex process that involves many mechanisms, especially miscibility and diffusion
- High pressure CO_2 and natural gas will recover much more oil than water. However, interest persists in the lower cost, water-based EOR
- CO_2 EOR reduces the carbon intensity of the oil produced by associated CO_2 storage
- Field cores "from depth" and reservoir crude oil (rather than outcrop cores and synthetic crude oil) are needed to improve the reliability of laboratory-scale results

Experimental approach: CO_2 EOR using shale cores

Oil-saturated cores
Taken from oil-producing shales, at depth. Weigh cores, no cleaning

→

Extraction experiments
Monitor weight of hydrocarbons extracted

→

Grind core to powder
Extract oil with methylene chloride/acetone

Experimental conditions:

- Confined huff n' puff
- Bathing huff 'n puff
- HPHT Contact angle measurements

Shale samples:

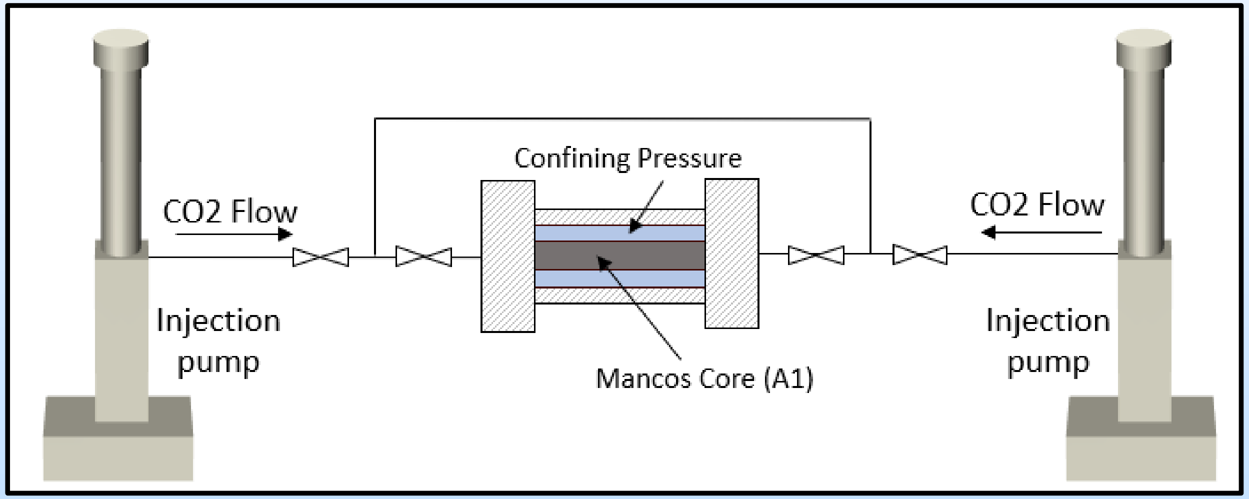
- Eagle Ford,, Mancos, Bakken, Wolfcamp

Oil:

- Eagle Ford, Bakken, Wolfcamp Live Oil

Partner for samples:

- HFTS Project (Wolfcamp)



Confined cores to better model field conditions using NETL's core flow apparatus

✓ Milestone 9D. 06/2019 Obtain shale samples for future CO_2 hydrocarbon extraction tests
✓ Milestone 9F. 12/2019 Quantify hydrocarbon oil from shale

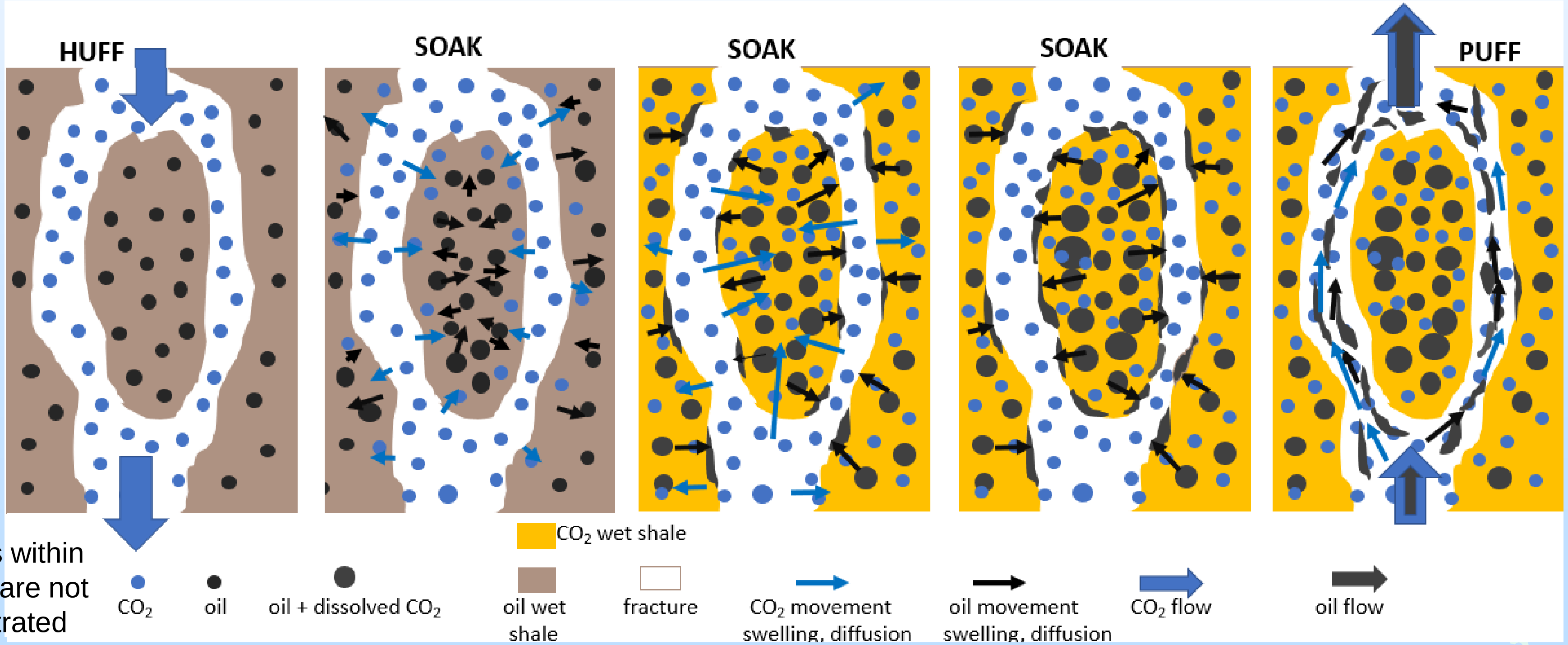
CO_2 huff 'n puff for EOR in unconventional formations

Oil Recovery Mechanisms

- CO_2 extraction of oil
- CO_2 diffusion into oil
- Oil diffusion into CO_2
- Oil swelling
- Oil viscosity reduction
- Solution gas drive

New mechanism

Wettability alteration during soaking due to the dissolution of nonionic surfactants in the CO_2



Pores within shale are not illustrated

Why nonionic surfactants in CO_2

CO_2 is a solvent for nonionic surfactants

Long-term application in conventional formations →

In-situ generation of CO_2-in-water mobility control foam as the surfactant partitions into the in situ brine

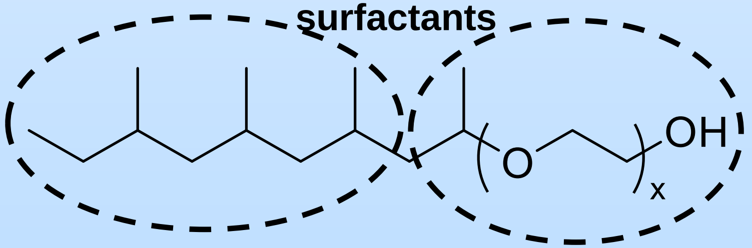
to improve sweep efficiency

Objective of this study →

Wettability alteration

toward more oil-phobic and CO_2-philic

Basic structure of nonionic surfactants

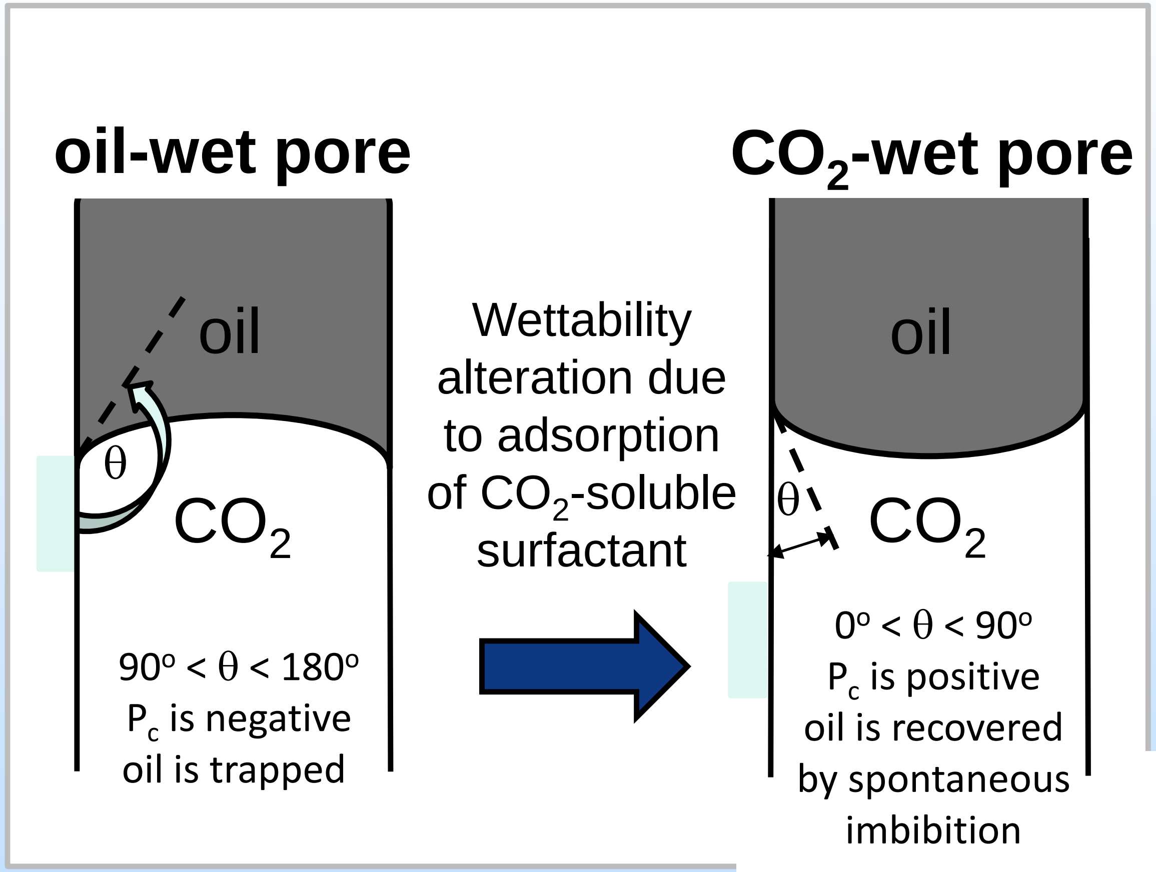


Oleophilic segment Oleophobic segment

- ✓ To combine the advantages of low viscosity CO_2 with the IFT and wettability-altering capabilities of surfactants in a single phase
- ✓ Inexpensive and commercially available
- ✓ Many options, can be oil-soluble or water-soluble
- ✓ Even low surfactant solubility (0.1-1.0 wt.%) in high pressure CO_2 may be more than enough for EOR

Surfactants added to CO_2

Potential wettability alteration during CO_2 fracturing and CO_2-EOR

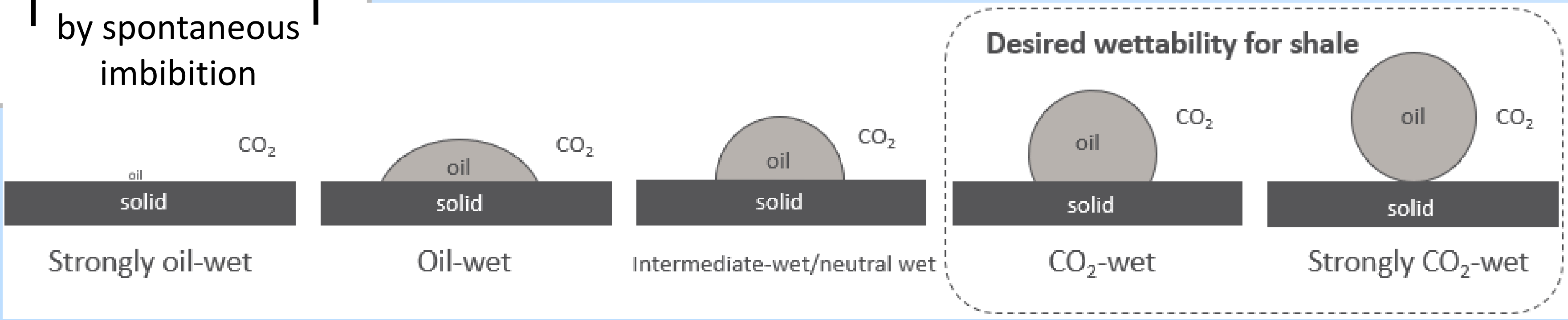


Large positive P_c

Surfactant needs to make the surface as CO_2-wet as possible while reducing the IFT by as little as possible

Risk

With ultralow IFT wettability alteration may not have a significant effect on improving the displacement of oil

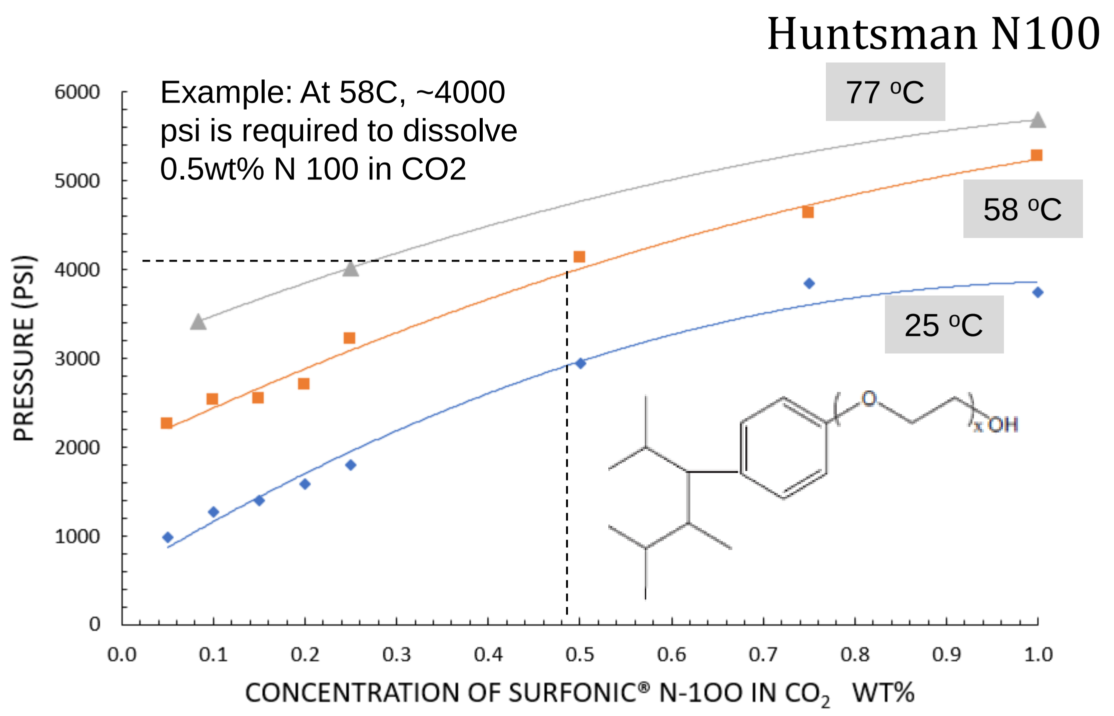


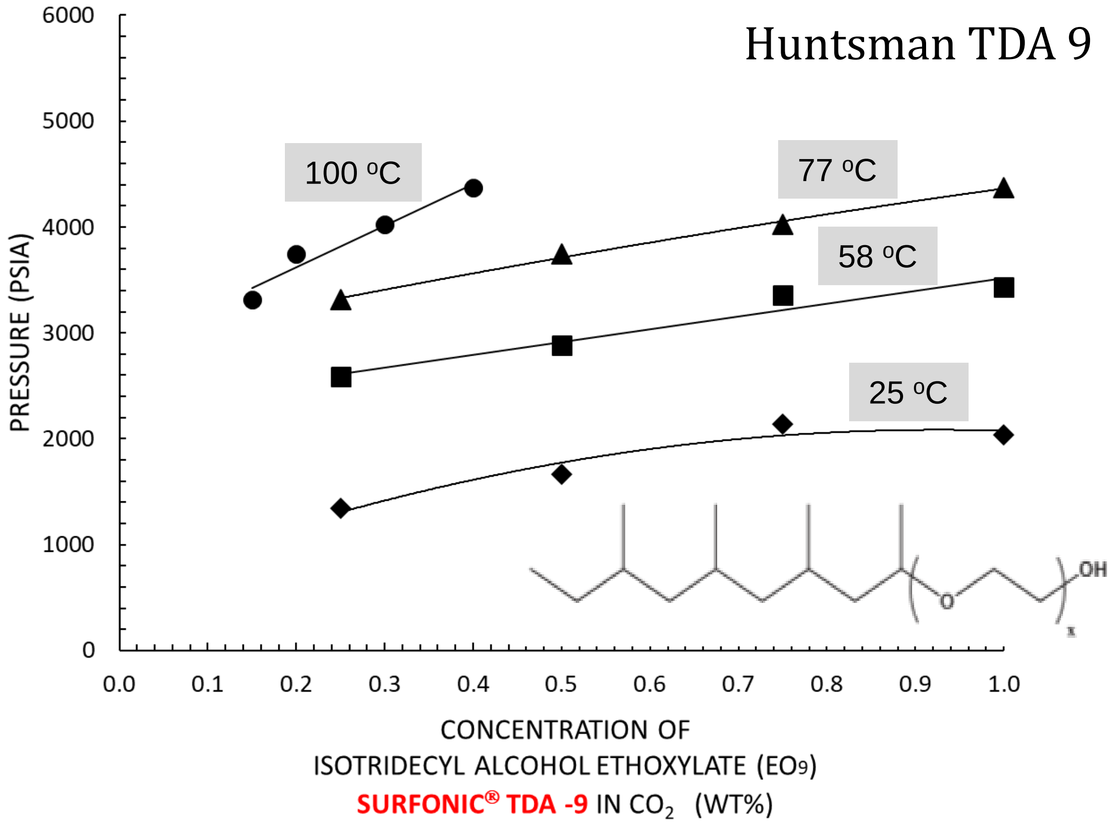
Identification of CO_2-Soluble Surfactants

Two water-soluble, nonionic ethoxylated alcohols were selected for this study.

Huntsman N100, a branched nonylphenol ethoxylate with an average of 10 EO groups (left, average x = 10) and

Huntsman TDA 9, a branched ethoxylated tridecylalcohol with an average of 9 EO groups (right, average x = 9).

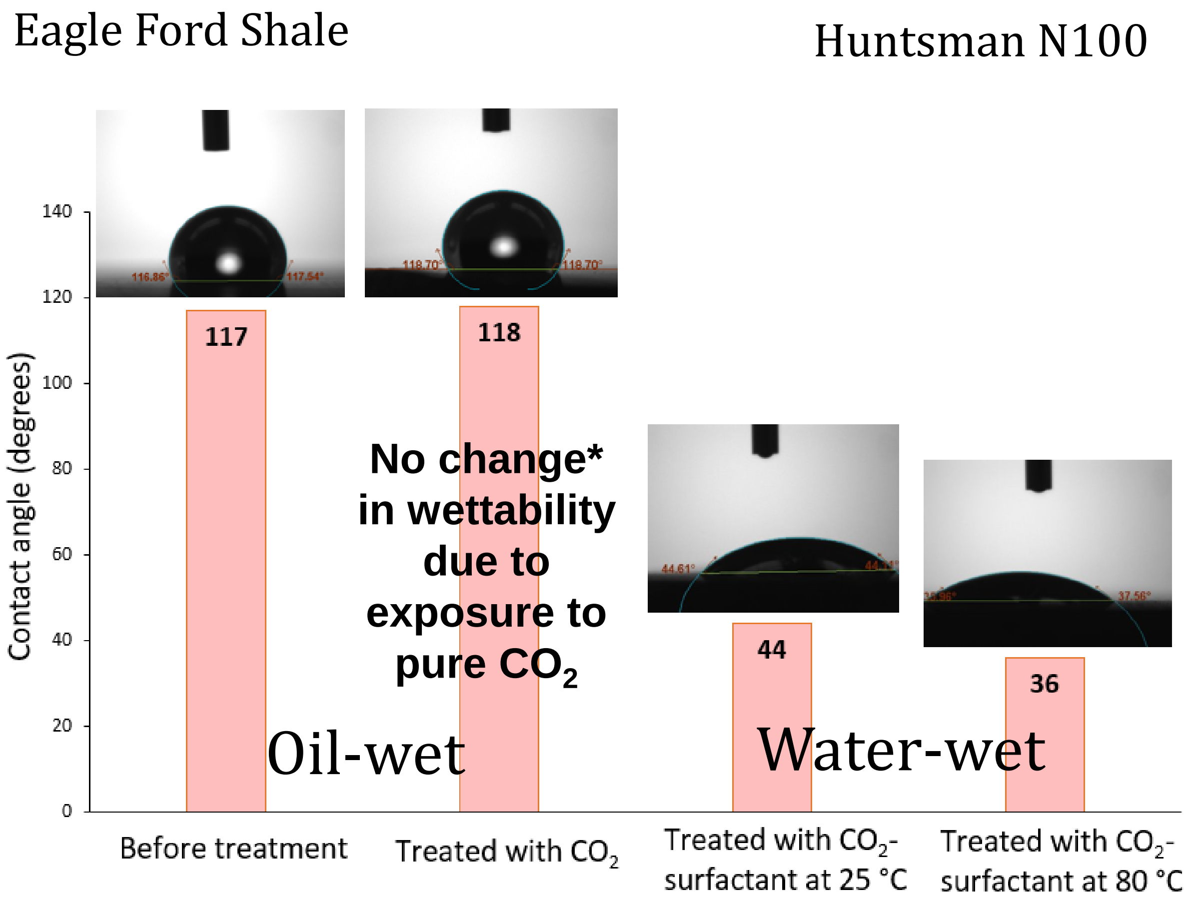


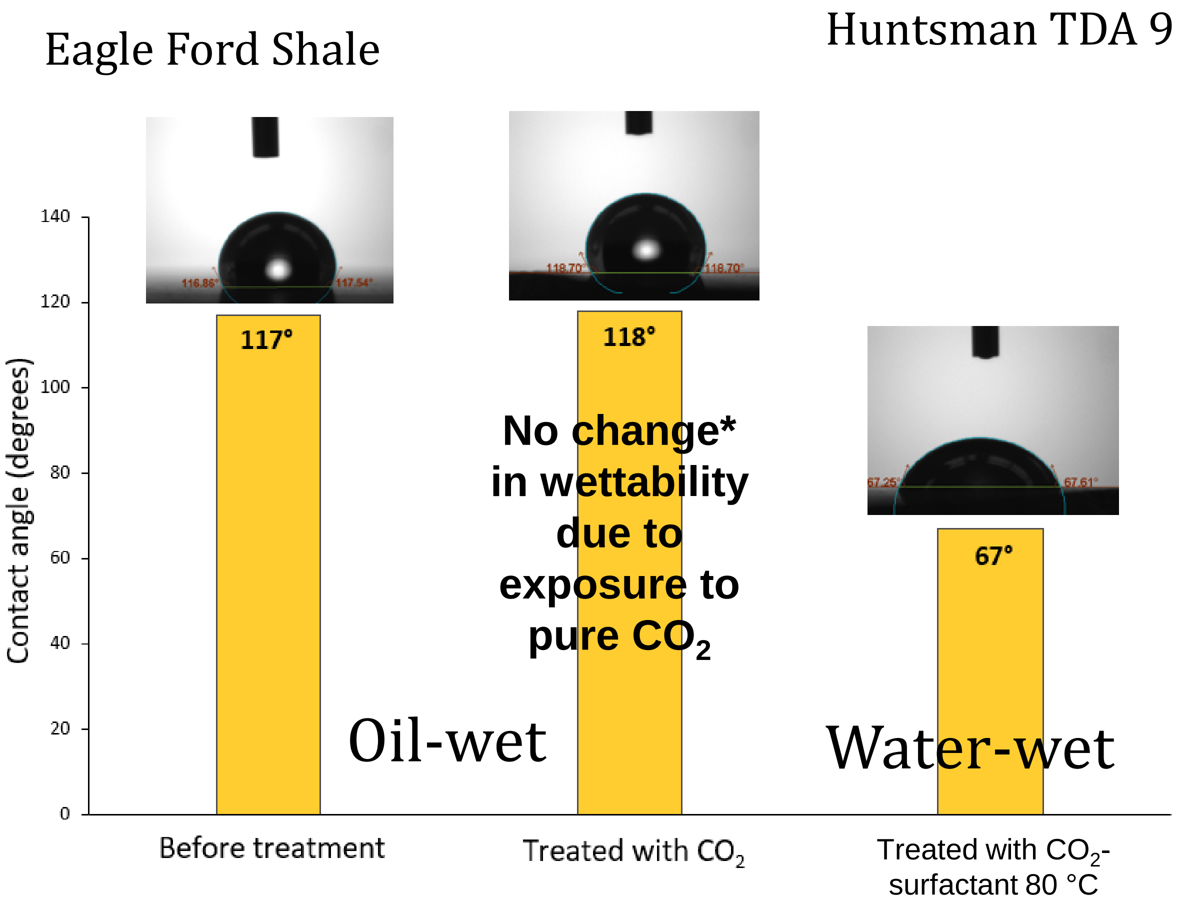


- ✓ Milestone 9I. 03/2020 Generate surfactant solubility in CO_2 data for one surfactant at a low temperature and compare with literature data.

Contact angle measurements (Wettability)

✓ Milestone 9.H 03/2020 Complete shakedown of contact angle apparatus, in preparation for measurement of the wetting properties of shale exposed to CO_2

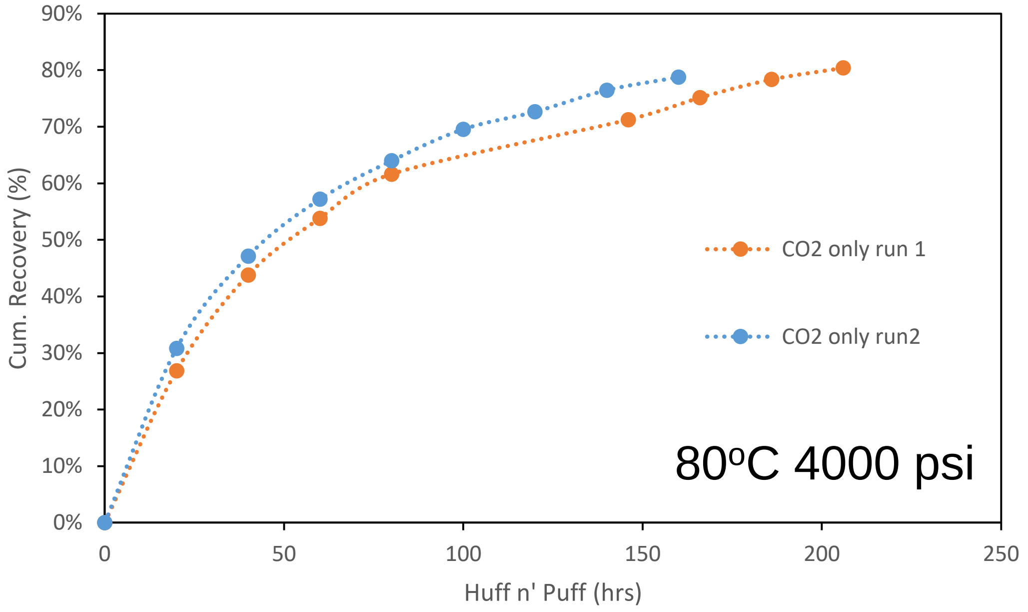


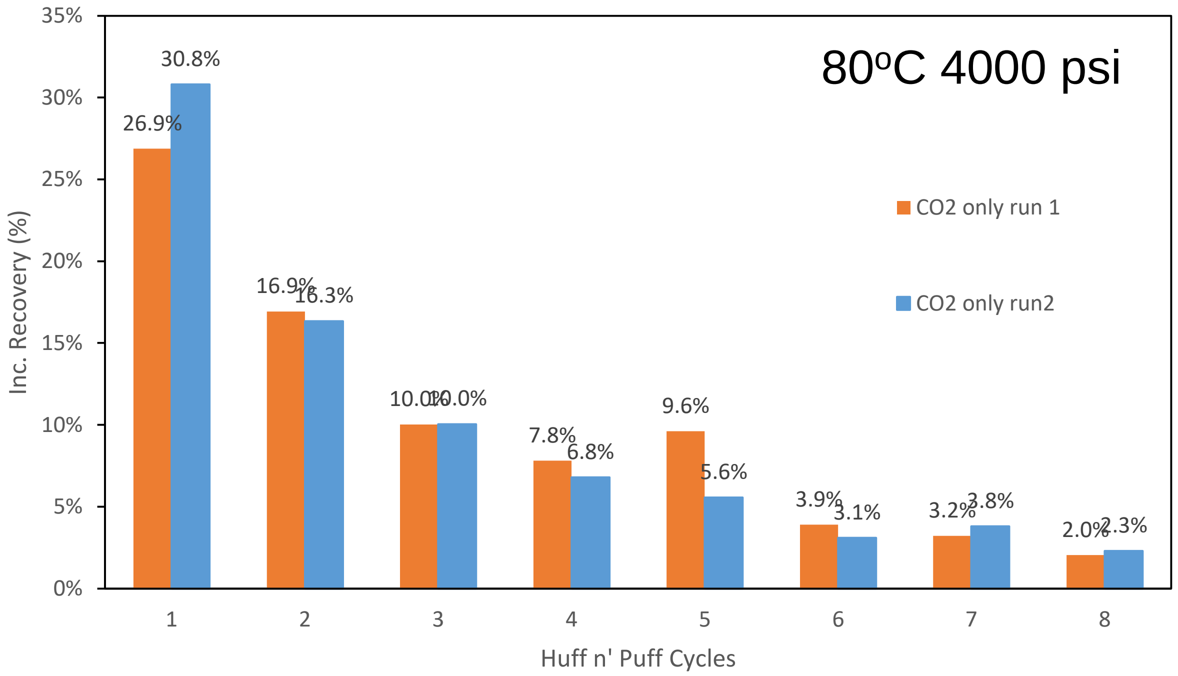


* Note: a prior study did observe a shift toward water-wet for samples exposed to pure CO2. Alharthy, N., Teklu, T., Kazemi, H. et al. 2015. Enhanced Oil Recovery in Liquid-Rich Shale Reservoirs: Laboratory to Field. Presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, 28 – 30 September. SPE-175034-MS.

Huff n’ Puff Experiments with CO_2

8 Huff n’ Puff Cycles: 79% recovery with pure CO_2





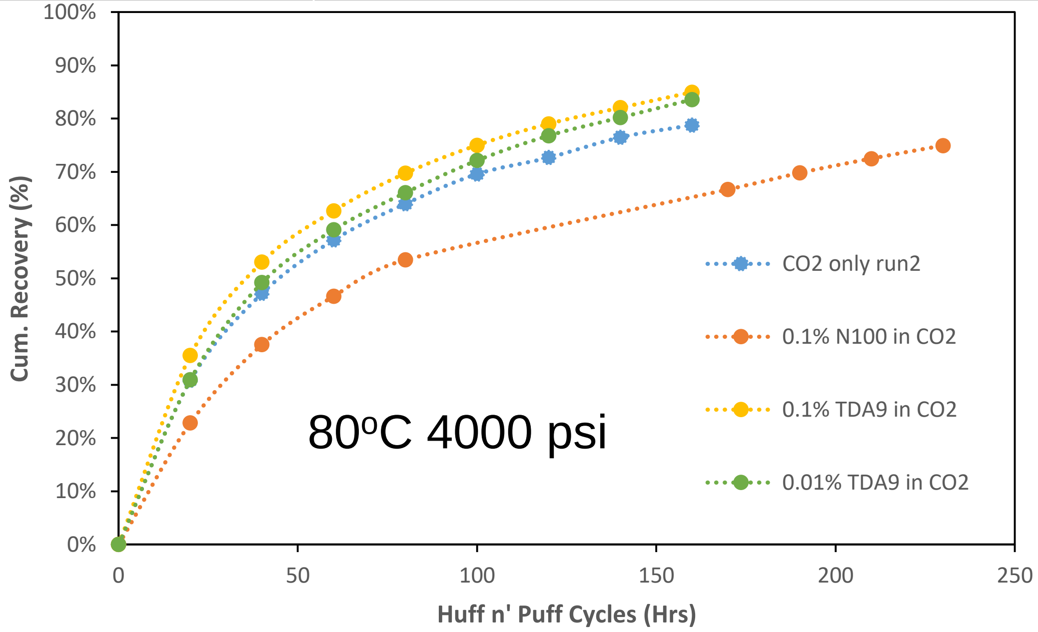
	Core	Length	Diameter	Bulk Volume	Pore Volume	Porosity	Permeability	Dry Weight	Soaked Weight	oil in place
		cm	cm	cc	cc	%	µD	g	g	g
CO2 run 1	Eagleford	5.076	2.552	25.95	1.96	7.55	5-15	56.45	58.78	2.33
CO2 run 2	Eagleford	5.022	2.555	25.74	1.69	6.56	5-15	56.12	58.26	2.15

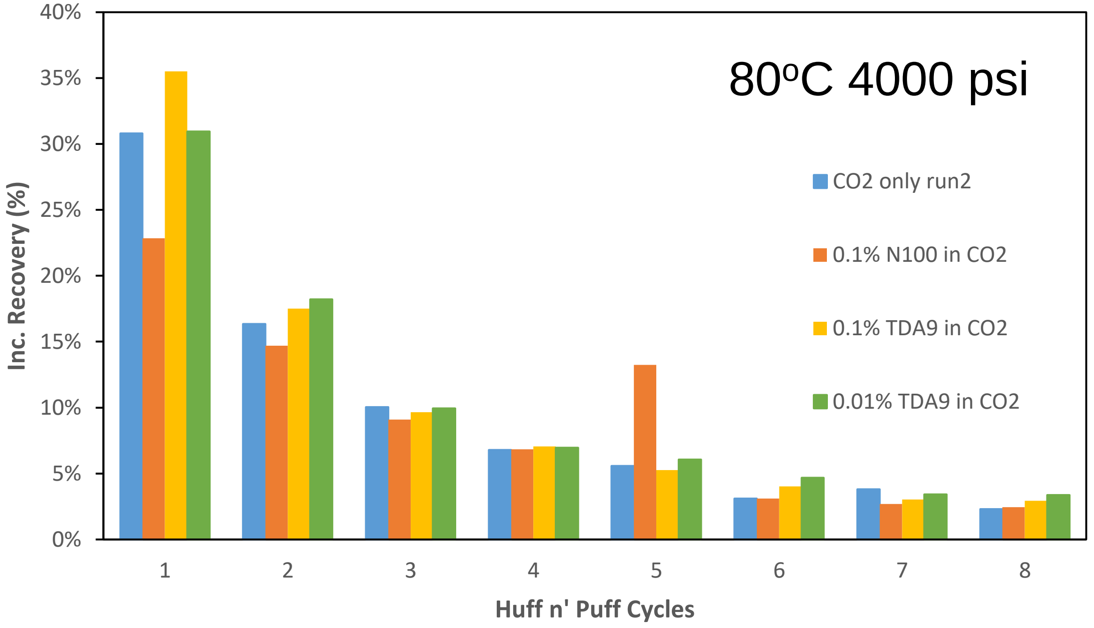
✓ Milestone 9.C 06/2020 Complete shakedown of continuous core flooding apparatus, in preparation for hydrocarbon extraction from tight and shale cores using supercritical CO_2

Huff n' Puff Experiments with CO_2 and Surfactant

8 Huff n' Puff Cycles:

- 79% recovery with pure CO_2
- 85% recovery with surfactant (TDA9) dissolved in CO_2
- 75% recovery with surfactant (N100) dissolved in CO_2



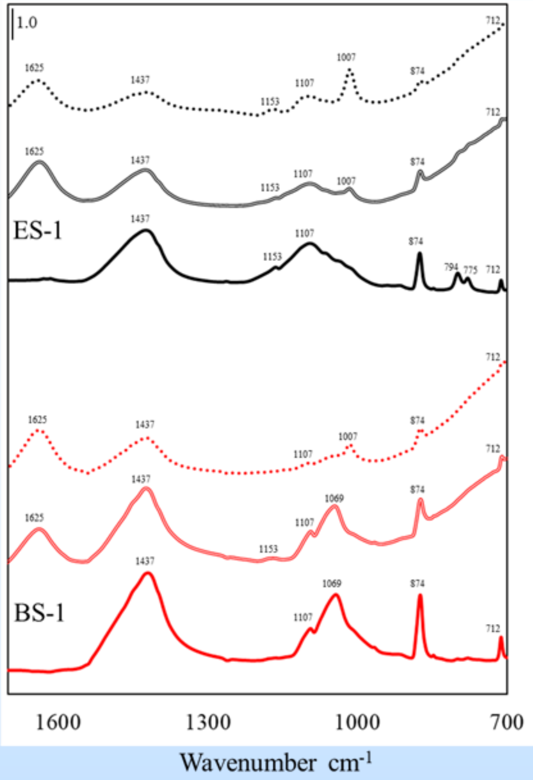


	Core	Length	Diameter	Bulk Volume	Pore Volume	Porosity	Permeability	Dry Weight	Soaked Weight	oil in place
		cm	cm	cc	cc	%	µD	g	g	g
CO2 run 2	Eagleford	5.022	2.555	25.74	1.69	6.56	5-15	56.12	58.26	2.15
0.1% TDA9 in CO_2	Eagleford	4.523	2.556	23.20	1.80	7.78	5-15	50.33	52.30	1.97
0.01% TDA9 in CO_2	Eagleford	4.719	2.556	24.20	1.81	7.48	5-15	52.49	54.56	2.07
0.1% N100 in CO_2	Eagleford	5.032	2.553	25.75	1.86	7.22	5-15	55.99	58.24	2.24

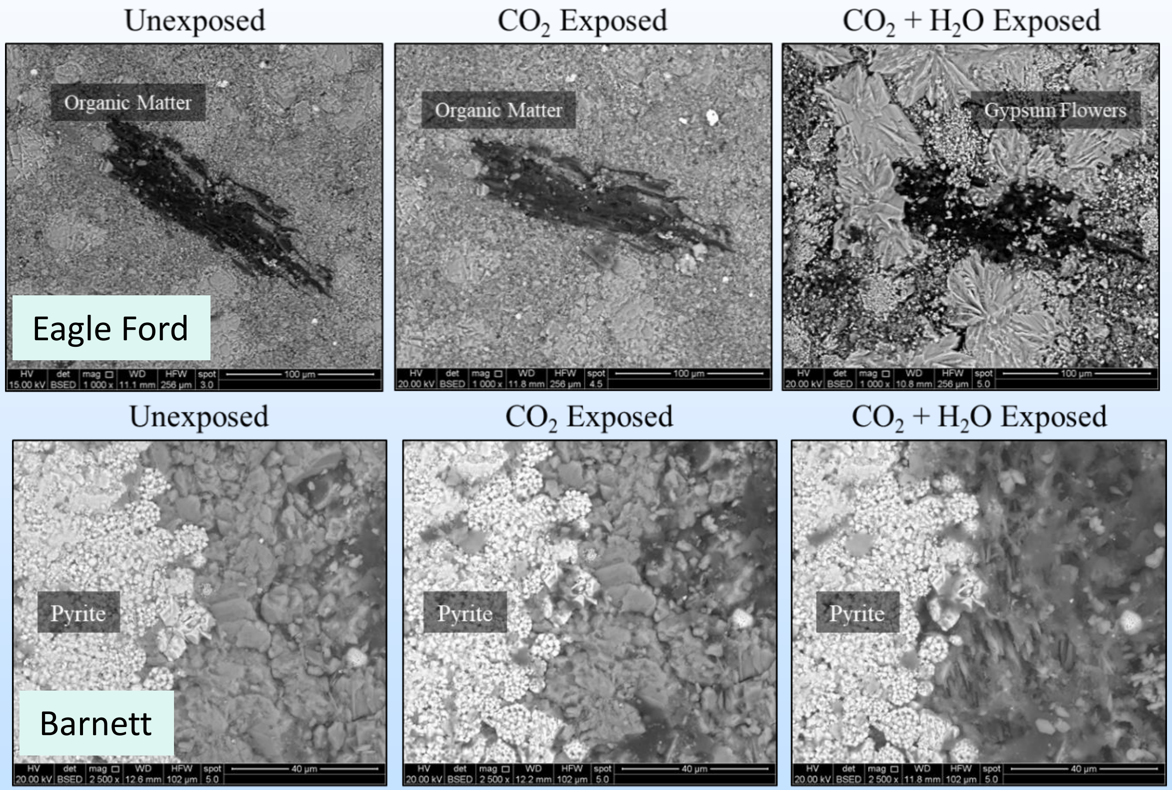
✓ Milestone 9.J 06/2020 Perform core flooding experiments for one type of shale using CO_2 and using CO_2-surfactant solutions

Physical and chemical alterations of Eagle Ford and Barnett Shale after hydrocarbon extraction with CO_2

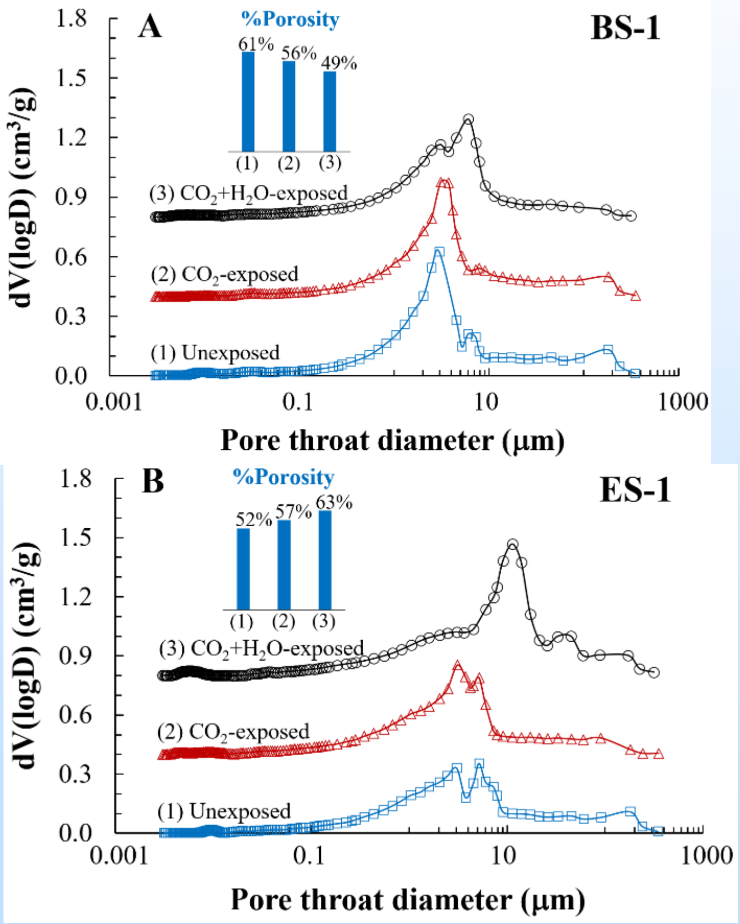
✓ Milestone 9G. 03/2020 Identify key physical and chemical alterations for Eagle Ford and Barnett Shales after hydrocarbon extraction with CO_2.



FTIR:
In situ characterization



SEM: Visualization of shale matrix alterations

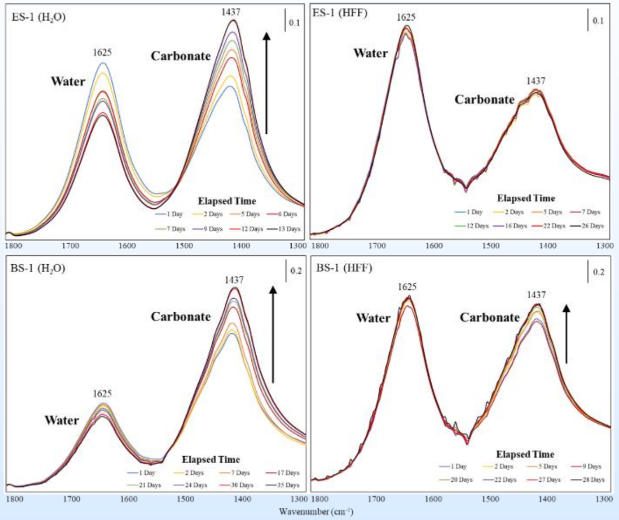


BET: Pore size distribution changes

Physical and chemical alterations of Eagle Ford and Barnett Shale after hydrocarbon extraction with CO_2

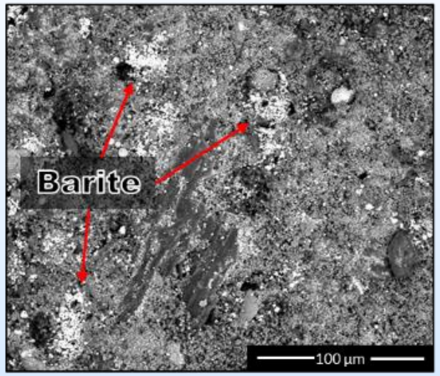
- ✓ Milestone 9G. 03/2020 Identify key physical and chemical alterations for Eagle Ford and Barnett Shales after hydrocarbon extraction with CO_2.

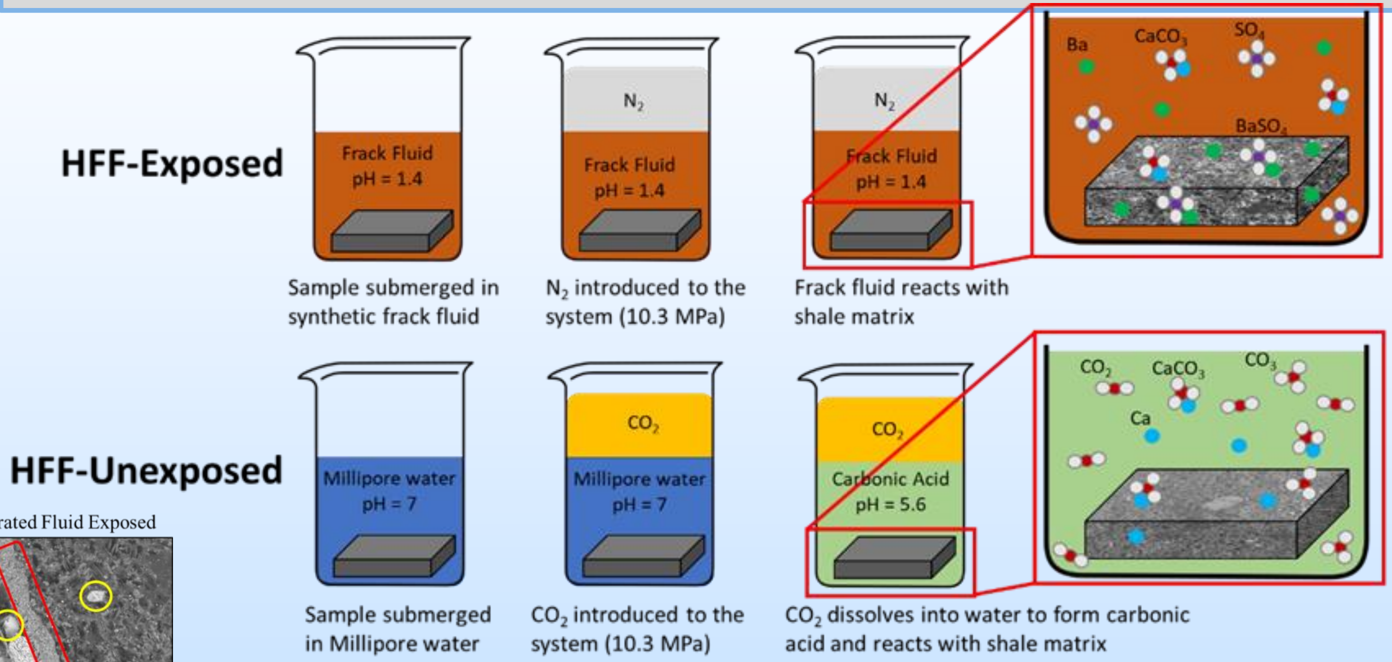
FTIR: In situ characterization



Barite Formation

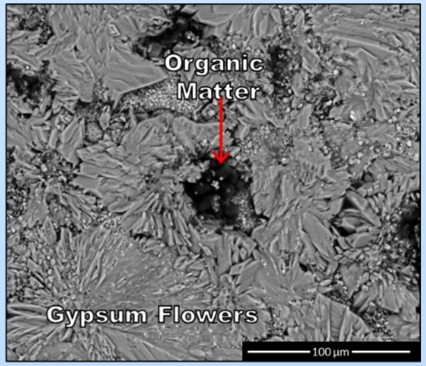
HFF Exposed

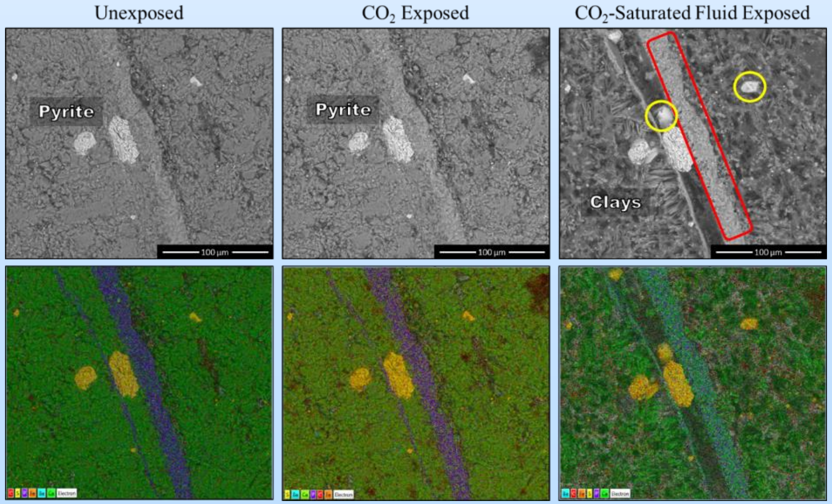




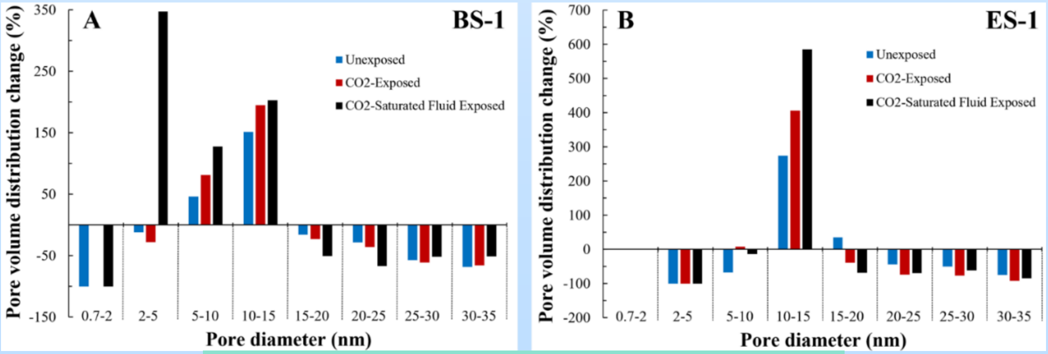
Gypsum Formation

CO₂-Saturated Fluid Exposed





SEM: Visualization of shale matrix alterations



BET: Pore size distribution changes

Technology Transfer

Published Papers

energy&fuels

A Literature Review of CO_2, Natural Gas, and Water-Based Fluids for Enhanced Oil Recovery in Unconventional Reservoirs
Lauren C. Burrows, Foad Haeri, Patricia Cvetic, Sean Sanguinito, Fan Shi, Deepak Tapriyal, Angela Goodman, and Robert M. Enick
Energy & Fuels **2020** *34* (5), 5331-5380
DOI: 10.1021/acs.energyfuels.9b03658

2019: Filed **patent application** 62/931,653 "Method of Oil Recovery Using Compositions of Carbon Dioxide and Compounds to Increase Water Wettability of Formations." Developed and submitted critical literature review to Energy and Fuels.

Accepted abstracts

UNCONVENTIONAL RESOURCES TECHNOLOGY CONFERENCE
FUELED BY SPE • AAPG • SEG
The integrated event for unconventional resource teams
SAVE THE DATE
20–22 JULY 2020
AUSTIN, TEXAS

SPE International
SPE ATCE SINCE 1924
SPE ANNUAL TECHNICAL CONFERENCE & EXHIBITION
5–7 October 2020
Denver, Colorado, USA |

2020 AIChE Annual Meeting
November 15-20, 2020
Hilton San Francisco Union Square, San Francisco, CA

URTeC: 2774
Improving CO_2-EOR In Shale Reservoirs using Dilute Concentrations of Wettability-Altering CO_2-Soluble Nonionic Surfactants
Foad Haeri[1,2], Lauren C. Burrows[1,3], Peter Lemaire[4], Parth G. Shah[4], Deepak Tapriyal[1,2], Robert M. Enick*[4], Dustin M. Crandall[1], Angela Goodman[1], 1. National Energy Technology Laboratory, 2. Leidos Research Support Team, 3. Oak Ridge Institute of Science and Education, 4. Dept. of Chemical and Petroleum Eng. University of Pittsburgh.

- ✓ Milestone 9.E 09/2019 Submit the article, "A Critical Review of Enhanced Oil Recovery in Unconventional Liquid Reservoirs" in a peer-reviewed journal.

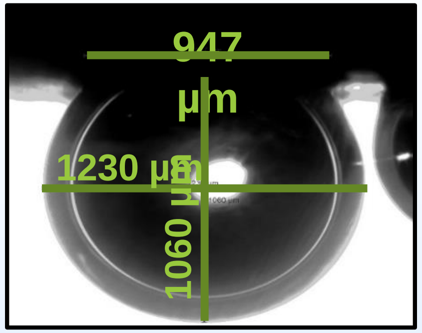
Summary

- We are determining how CO_2 and CO_2/surfactant can be used to increase EOR by simulating subsurface EOR conditions in the laboratory by changing wetting
- Successful EOR in shales would lead to tremendous increases in domestic oil production
- Examples of simulated laboratory EOR techniques we are performing include:
  - Confined huff n' puff and Bathing huff n' puff

In progress:

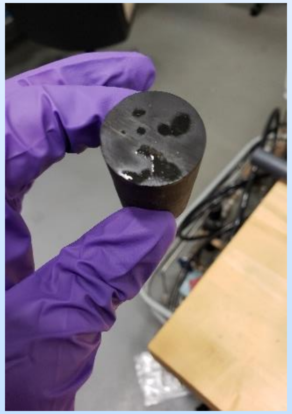
- Currently soaking Wolfcamp in live oil
- Preparing for Huff n' Puff (confined and bathing)
- Comparing oil recovery with CO_2 and CO_2 and surfactants (URTEC)
- Soaking cores in fracture fluid or brine prior to oil recovery
- Trying a new surfactant - Surfonic L12-6
- High pressure contact angle experiments with CO2 and oil in contact with oil-wet shale.
- High pressure IFT experiments to determine the degree of IFT reduction

High pressure cell for **Bathing Huff n' Puff**



Contact angle

Coreflood setup for confined **Huff n' Puff**



Extracted oil

Appendix

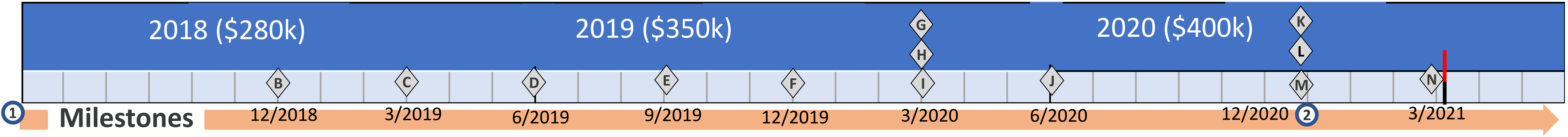
Organization Chart

- NETL: Angela Goodman, Foad Haeri, Lauren C. Burrows, Deepak Tapriyal, Sean Sanguinito, Dustin Crandall

- University of Pittsburgh: Robert Enick, Parth Shah

Gantt Chart Task 9 Project Timeline Overview

Characterizing Application of CO_2 as a Recovery Agent to Mobilize Hydrocarbons from Shale



A. Analysis of prior work that includes interactions of CO2, water, surfactants, and/or hydrocarbons with shales to refocus the research question(s) based on the analysis of prior work that will lead to increased ultimate recovery [includes CO2 Sand Frac project, Fundamental Shale projects by other National Laboratories, LBNL study under CERC regarding CO2 as a frac fluid, etc.]. Go/No-Go (12/2018).
B. Identify key physical, chemical, and mechanical alterations for at least two shale types upon supercritical shale extraction (This milestone was changed until the review the was completed and is documented in the Q3 report). (12/2018).
C. Revised from "Quantify hydrocarbon extract for at least two shale types upon supercritical CO2 shale extraction" to "Complete shakedown of continuous core flooding apparatus, in preparation for hydrocarbon extraction from tight and shale cores using supercritical CO2." (03/2019) and added milestone to (12/2019).
D. Obtain shale samples for future CO2 hydrocarbon extraction tests. (06/2019)
E. Submit the article, "A Critical Review of Enhanced Oil Recovery in Unconventional Liquid Reservoirs" in a peer-reviewed journal (09/2019)
F. Quantify hydrocarbon oil from shale (12/2019)
G. Identify key physical and chemical alterations for Eagle Ford and Barnett Shales after hydrocarbon extraction with CO2. (03/2020)
H. Complete shakedown of contact angle apparatus, in preparation for measurement of the wetting properties of shale exposed to CO2. (03/2020)
I. Generate surfactant solubility in CO2 data for one surfactant at a low temperature and compare with literature data. (03/2020)
J. Perform core flooding experiments for one type of shale using CO2 and using CO2-surfactant solutions (06/2020)
K. Generate pressure-surfactant concentration cloud point curves for three CO2-soluble surfactants (to achieve surfactant dissolution in CO2, one must operate above the cloud point pressure). (12/2020)
L. Perform contact angle experiments for one type of shale after exposure to CO2, and after exposure to CO2-surfactant solutions. (12/2020)
M. Go/No-Go: Draft report of current data analyzed that summarizes effectiveness of CO2 and CO2-surfactant solutions as oil recovery agents in unconventional oil-rich shale systems based on current laboratory measurements (Revised milestone date to "12/2020" from "3/2020")
N. Determine molecular weight distribution of oil from one type of shale after extraction with CO2, and after extraction using CO2-surfactant solutions (03/2021)

Impact

Key Accomplishments/Deliverables	Value Delivered
2016: Quantified effects of short and long term geochemical reactions of fracturing fluid with Marcellus Shale and Huntersville Chert (oil/gas program) **2017:** Quantified interactions of CO_2 with Utica Shale (coal program) **2018:** Quantified interactions of CO_2 with Marcellus Shale (coal program)	• A Critical Review of Enhanced Oil Recovery in Unconventional Liquid Reservoirs • Report summarizing use and effectiveness of CO_2 and surfactants as a recovery agent to mobilize hydrocarbons in tight shale systems

Chart Key

TRL Score | Go / No-Go Timeframe | Project Completion | Milestone