



## Annual Report: Unconventional Fossil Energy Resource Program – Next Generation EOR

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30 September 2013  
NETL Technical Report Series



**Office of Fossil Energy**

NETL-TRS-UFER-2013

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**Cover Illustration:** NETL flow-through-porous medium apparatus, can be used to collect the pressure drop data for CO<sub>2</sub> flowing through a dry core, and for neat CO<sub>2</sub> or CO<sub>2</sub>/surfactant solutions flowing into an initially brine-saturated or surfactant solution-saturated core up to the desired pressure of ~2700 psi.

**Suggested Citation:** Yee Soong, Technical Coordinator, George Guthrie, Focus Area Lead, UFER Annual Report, NETL-TRS-UFER-2013, NETL Technical Report Series, U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA, 2013, p 14.

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**Office of Research and Development, National Energy Technology Laboratory**

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30 September 2013

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## Acronyms, Abbreviations, and Symbols

Acronym	Descriptive Name
CMU	Carnegie Mellon University
CO <sub>2</sub>	carbon dioxide
CO <sub>2</sub> EOR	Carbon Dioxide Enhanced Oil Recovery
DOE	Department of Energy
EO	ethylene oxide
EOR	Enhanced Oil Recovery
FWP	Field Work Proposal
NETL	National Energy Technology Laboratory
NETL-RUA	NETL Regional University Alliance
NP	nonylphenol
ORD	Office of Research and Development
PEG	polyethylene glycol
Penn State	The Pennsylvania State University
Pitt	University of Pittsburgh
PSIA	pounds per square inch absolute
RES	Research and Engineering Services
SAG	surfactant alternating gas
SCNGO	Strategic Center for Natural Gas and Oil
TDA	tridecyl alcohol
TDS	total dissolved solids
UFER	Unconventional Fossil Energy Resource Program
URS	URS Corporation
UV	ultraviolet
UV-Vis	ultraviolet-visible
WVU	West Virginia University

## 1.0 Executive Summary

The United States Department of Energy (DOE) National Energy Technology Laboratory (NETL) was conducting research to develop “next generation” Carbon Dioxide Enhanced Oil Recovery (CO<sub>2</sub> EOR) technologies that can increase recovery from existing CO<sub>2</sub> EOR activities and accelerate the application of the process to other mature oil fields around the country. This annual report was in response to the NETL Field Work Proposal (FWP) for Unconventional Fossil Energy Research Program (UFER) research to be conducted by NETL Office of Research and Development (ORD). ORD research efforts were supported by the NETL Regional University Alliance (NETL-RUA), URS Corporation (URS), and URS subcontractors. NETL-RUA included the following research institution: University of Pittsburgh (Pitt). This project was supported by the NETL Strategic Center for Natural Gas and Oil (SCNGO) and addresses activities performed in FY13.

High pressure CO<sub>2</sub> (carbon dioxide) has been used for decades to enhance the recovery of oil (primarily in the Permian basin of Texas); however, the experience is restricted with respect to types of reservoirs and limitations (even for conventional reservoirs), including factors relating to sweep efficiency, miscibility, and flow through tight and/or fracture-dominated reservoirs. One area of enhanced oil recovery (EOR) research under the SCNGO research portfolio is CO<sub>2</sub> EOR.

The challenge for the CO<sub>2</sub> EOR process was the poor sweep efficiency that could result from the difference in mobility between oil/brine and CO<sub>2</sub> in the reservoir. This might result in early CO<sub>2</sub> breakthrough, high utilization of CO<sub>2</sub> per barrel of oil recovered, prolonged duration of the displacement, and poor sweep efficiency. One approach to address this issue was to increase the viscosity of CO<sub>2</sub> by adding surfactants to create CO<sub>2</sub> foam *in situ*.

The overall objective of this project was to conduct laboratory and field-based research to develop and demonstrate cost-effective CO<sub>2</sub>-soluble surfactants via *in-situ* foaming to enhance the sweep efficiency for EOR. The specific objectives involved:

- Reservoir modeling and evaluation of potential target sites
- Site selection
- Laboratory design of suitable surfactants
- Design and execution of the field-based mobility control experiment with industry

One of the objectives of this project was to identify promising commercial surfactants that could be added to CO<sub>2</sub> as it is being injected for EOR. The Huntsman ethoxylated alcohols types (T-9 to T-20) of surfactants were assessed extensively under reservoir conditions during this year. The low surfactant solubility in CO<sub>2</sub> at reservoir conditions made it unappealing to perform enhanced oil recovery by injecting a surfactant dissolved in CO<sub>2</sub>.

Due to the reservoir conditions of the potential field demonstration site being not suitable for dissolving surfactant in the CO<sub>2</sub>, the new approaches were adapted on an aqueous Surfactant solution Alternating CO<sub>2</sub> Gas (SAG) process, which has the surfactant dissolved only in the produced brine of the field. The SAG represents the injection surfactant-in-brine alternately with CO<sub>2</sub>. The foam will reduce the flow of CO<sub>2</sub> into thief zones and inhibit CO<sub>2</sub> gravity override and fingering, such that the increases in incremental oil and decreases in CO<sub>2</sub> purchases and recycling/re-compression costs will render the project profitable. Therefore, this project began testing the foam stability of ionic surfactants in brine for the remainder of FY13.

A potential surfactant was identified for this approach. An anionic surfactant, Huntsman alkyl alkoxy sulfates type, when dissolved in the produced brine, formed the stable foam under reservoir conditions of higher than 60°C and 2,300 pounds per square inch absolute (psia).

A protocol was developed to determine the amount of surfactant dissolved in brine *via* Ultraviolet-Visible (UV-Vis) measurements. In addition, an attempt was made to quantify the adsorption of surfactant by the consolidated Berea Sandstone cores in the Core Flow lab at NETL under reservoir conditions.

## 2.0 Technology Highlights and Key Results

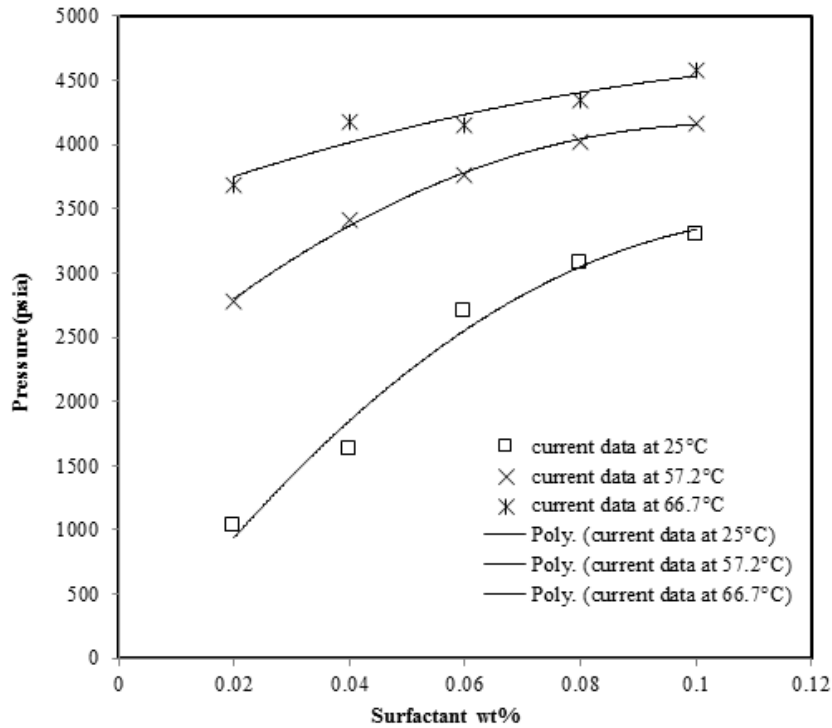
### Experimental Developments of CO<sub>2</sub>-Soluble Surfactants for *In-Situ* Foaming

One of the objectives of this project was to identify promising commercial surfactants that could be added to CO<sub>2</sub> as it was being injected for EOR. The efficacy of these surfactants would be assessed by determining their solubility in CO<sub>2</sub>, their ability to reduce the mobility of CO<sub>2</sub> flowing through a brine-saturated core, and by CT imaging and oil recovery results associated with high pressure tertiary oil recovery core floods.

The most promising nonionic surfactant identified in prior work (Huntsman ethoxylates alcohols types-T types) was assessed. The preliminary results for surfactant screening are summarized below. The objective was to identify a field in which a liquid nonionic surfactant is soluble both in CO<sub>2</sub> and reservoir brine at reservoir conditions. Ideally the “best” field for a CO<sub>2</sub>-soluble surfactant field test would be the field that requires a surfactant that is liquid at surface conditions, even in the winter, and exhibits a greater solubility in CO<sub>2</sub> at reservoir conditions than any of the other type of surfactants. The best potential field was a CO<sub>2</sub> EOR site in Mississippi; T-9 (the lowest melting point T type surfactant) was 1 wt% soluble only in a high salinity brine at reservoir temperature. Higher melting point samples with longer polyethylene glycol (PEG) hydrophilic segments were required to dissolve the T type surfactant in the other brine samples.

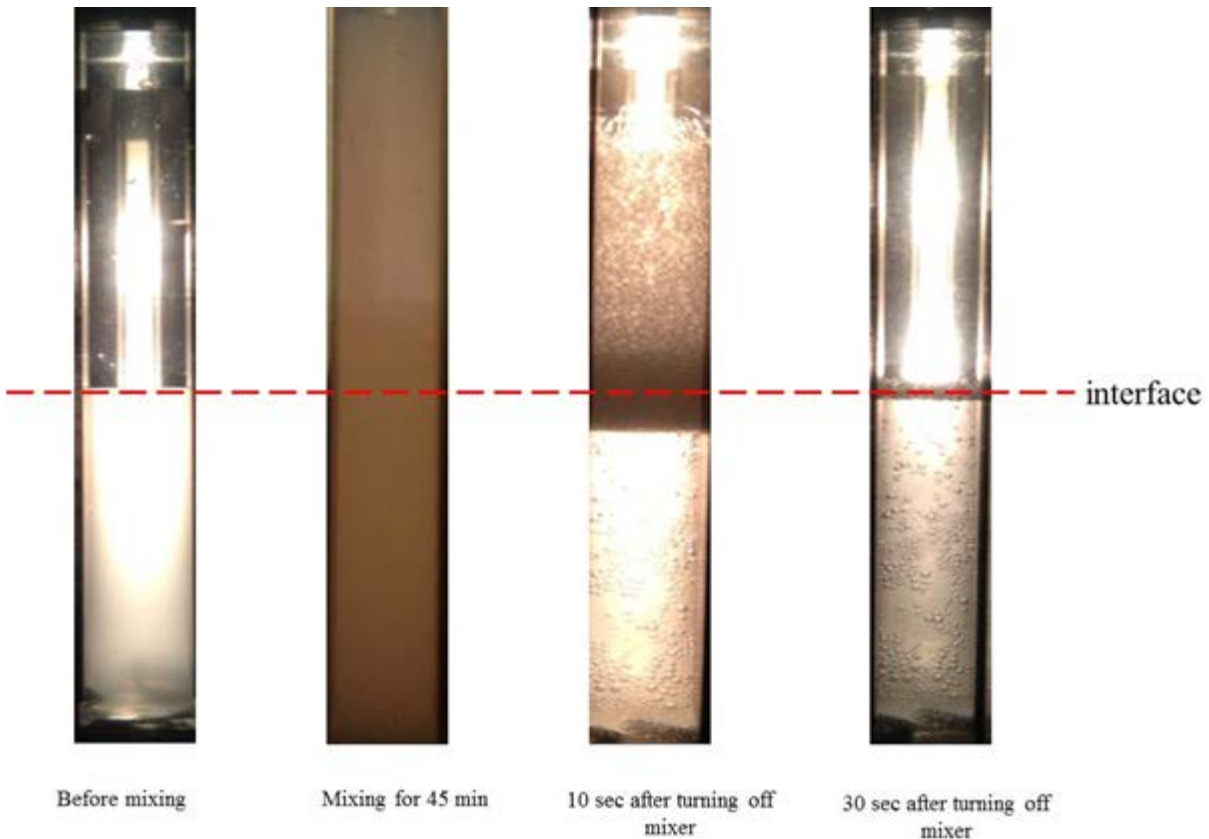
Experiments verified that the addition of 10% water to the surfactants could lower their melting point better than any alcohol (methanol – pentanol), ethylene glycol, or propylene glycol. The addition of 5, 10, and 15 wt% water to T-9 lowered its melting point to -2°C, -12°C, and -15°C, respectively. Cloud point pressure versus T-9 wt% in carbon dioxide curves (Figure 1) were shown for three temperatures: (1) 25°C, (2) 57.2°C, and (3) 66.7°C. The experiments were difficult to perform because cloud point detection is a visual technique that is challenging at low (<0.1 wt%) concentration, the T-9 surfactant is a polydisperse product (there is a range of ethylene oxide [EO] groups that averages 9 and there are many C<sub>13</sub> isomers in the C<sub>13</sub> hydrophobe). For the CO<sub>2</sub> EOR site formation, temperature of higher than 60°C and the upper limit of flowing bottom hole pressure of higher than 2,300 psi, one could dissolve roughly 0.04 wt% T-9 in CO<sub>2</sub>. This is a conservative clouds point measurement considering the sample is measured before it becomes opaque (at these low concentrations a substantial portion of the surfactant would need to come out of solution, leading to an overestimation of the surfactant solubility in CO<sub>2</sub>); rather the cloud point is designated as at pressure during expansion from a high pressure transparent solution at which a fine cloud, or mist, first appears making it impossible to detect the outline of objects in or behind the windowed sample volume. There is an uncertainty of +/- 200 psi with each datum.





**Figure 1: Cloud point vs. surfactant wt% curves for mixtures of T-9 in carbon dioxide.**

It might be possible to inject a stable dispersion of T-9 in CO<sub>2</sub> rather than a transparent solution of T-9 in CO<sub>2</sub>. Consider a 0.10 wt% solution of T-9 in CO<sub>2</sub> at 60°C or higher and 2,300 or higher psi. About 0.04 wt% (40% of the surfactant) would be dissolved in the CO<sub>2</sub>, while the remaining 0.06 wt% (60% of the surfactant) would be in the form of extremely fine droplets (a “cloud”) suspended in the CO<sub>2</sub>. This foam stability experiment was repeated, altering only the concentration to 0.1 wt% T-9 (based on the mass of the CO<sub>2</sub> alone) in the same 1:1 mixture of CO<sub>2</sub> and high salinity brine. The foam collapsed after five minutes, which was a much better result than that obtained for the 0.04 wt% concentration, but might still not be sufficient for generating mobility control foam in porous media (Figure 2).



**Figure 2: Photographs of the mixture in the high-pressure cell at various points in the sample mixing process, for a T-9 wt% of 0.04 in a 1:1 mixture of high salinity brine and carbon dioxide, by volume.**

The potential surfactants must form a foam at reservoir conditions. The Louisiana brine sample formed the most stable foams upon mixing with surfactant and CO<sub>2</sub> as a result of both its relatively low total dissolved solids (TDS) content (78,000 ppm) and associated reservoir temperature (57°C). Therefore, the foam stability for various tridecyl alcohol (TDA) and nonylphenol (NP) surfactants at concentrations of 0.025 wt% and/or 0.050 wt% were conducted.

Figure 3 and Figure 4 plotted the stability of the foams, resulting from mixing equal amounts of CO<sub>2</sub> and Louisiana brine with a T type surfactant, with respect to time. The foam stability profiles given in Figure 3 were collected for a concentration of 0.05 wt% surfactant on a CO<sub>2</sub>-only basis. Interestingly, Figure 3 indicated that for this surfactant concentration, ethylene oxide (EO) monomer number did not have an appreciable effect on the foam stability profile, with similar results observed for the stability of T-11, T-15, T-18, and T-20. In Figure 4, however, there was marked improvement in the foam stability profile with respect to an increasing EO number at the lower surfactant concentration of 0.025 wt% on a CO<sub>2</sub>-only basis.

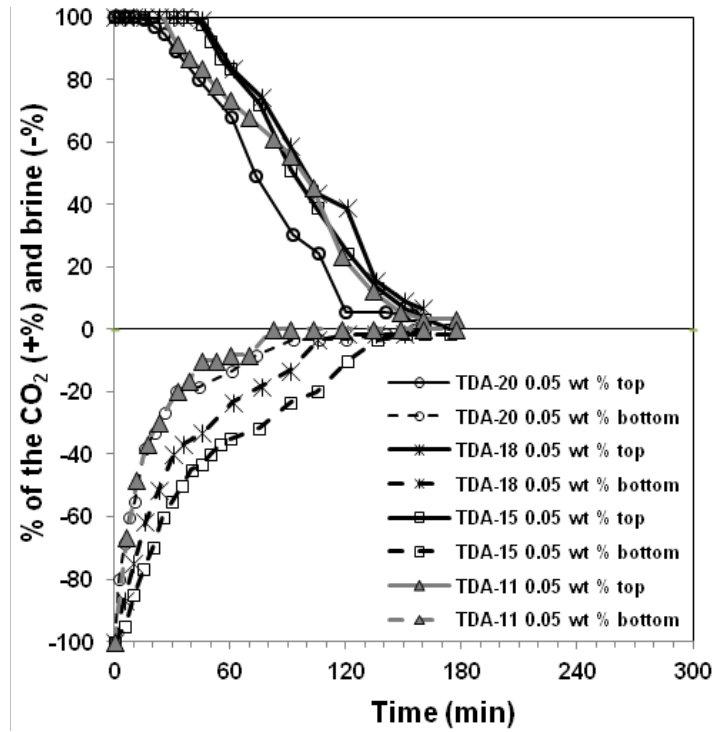


Figure 3: Foam stability of 0.05 wt% Huntsman T-11, T-15, T-18, and T-20 at 57°C, with Louisiana brine/CO<sub>2</sub> mass ratio of 1:1.

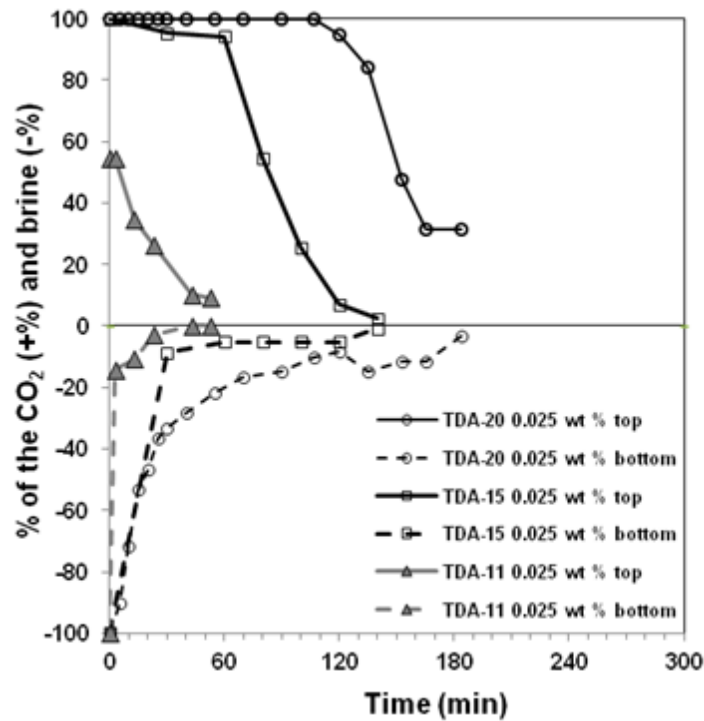


Figure 4: Foam stability of 0.025 wt% Huntsman T-11, T-15, and T-20 at 57°C, with Louisiana brine/CO<sub>2</sub> mass ratio of 1:1.

*Experimental Developments of Brine-Soluble Surfactants for In-Situ Foaming*

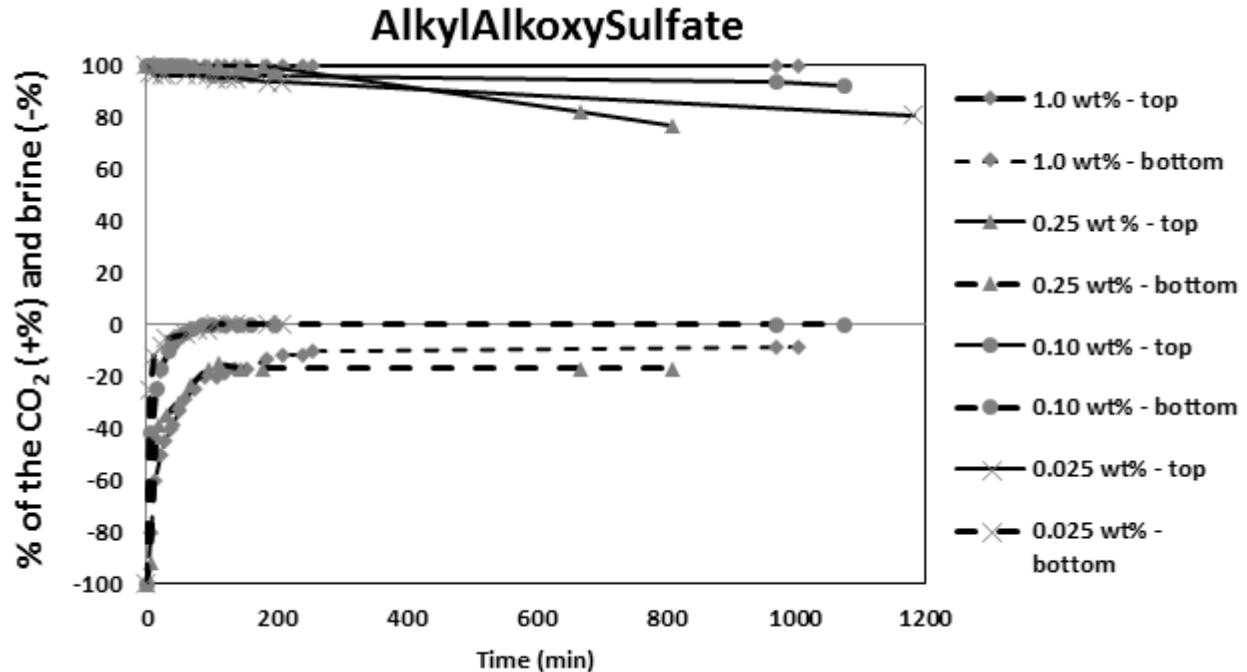
The low surfactant solubility in CO<sub>2</sub> at reservoir conditions made it unappealing to perform enhanced oil recovery by injecting a surfactant dissolved in CO<sub>2</sub>. Due to the reservoir conditions of the potential field demonstration site being not suitable for dissolving surfactant in the CO<sub>2</sub>, the new approaches were adapted on an aqueous SAG process, which has the surfactant dissolved only in the produced brine of the field. The SAG represents the injection surfactant-in-brine alternately with CO<sub>2</sub>. The foam will reduce the flow of CO<sub>2</sub> into thief zones and inhibit CO<sub>2</sub> gravity override and fingering, such that the increases in incremental oil and decreases in CO<sub>2</sub> purchases and recycling/re-compression costs will render the project profitable. Therefore, this project began testing the foam stability of ionic surfactants in brine for the remainder of FY13.

The experiments showed very encouraging results were obtained with the anionic surfactant, Huntsman alkyl alkoxy sulfates, when dissolved in the produced high salinity brine. The foams were made by mixing equal amounts of the aqueous surfactant solution (composed of the produced high salinity brine and the Huntsman alkyl alkoxy sulfates surfactant) and dense CO<sub>2</sub> for five minutes in the Robinson cell. Alkyl alkoxy sulfates surfactant is the sodium salt of an ethoxylated (2 EO units), sulfated, linear C<sub>12</sub> alcohol. The alkyl alkoxy sulfates surfactant established very stable foams in the high salinity brine at bottom hole injector conditions of higher than 60°C and 2,300 psia.

In Figure 5, the stabilities of the foams resulting from mixing of equal amounts of CO<sub>2</sub> and high salinity brine with Huntsman alkyl alkoxy sulfates surfactant were presented. The concentration of the surfactant in the brine was varied from 1.0 wt% to 0.025 wt%. A clear zone of brine collected under the foam due to drainage of water from the liquid films. In some cases, a clear zone of excess CO<sub>2</sub> appeared above the foam due to coalescence of the bubbles. After ~1,000 minutes (~16 hours) none of the foams had fully collapsed.

As expected, the 1.0 wt% foam was particularly stable. It did not exhibit a clear zone of CO<sub>2</sub>. After the clear brine zone was established (~250 minutes), the foam retained 100% of the CO<sub>2</sub> and ~10% of the brine. The foam bubbles were small and uniform along the entire column of the foam and large bubbles were not evident in the foam even after 1,000 minutes had elapsed.

A solubility test was conducted to demonstrate that the surfactant was soluble in the produced high salinity brine at room temperature. Huntsman alkyl alkoxy sulfates was added to the brine to create a solution that was 1.0 wt% active surfactant (maximum concentration used in experiments) and mixed for several minutes with a magnetic stirrer. A transparent solution resulted. This “proof of concept” test was conducted to demonstrate that preparing a surfactant solution using Huntsman alkyl alkoxy sulfates and produced high salinity brine at ~21°C should not be difficult.

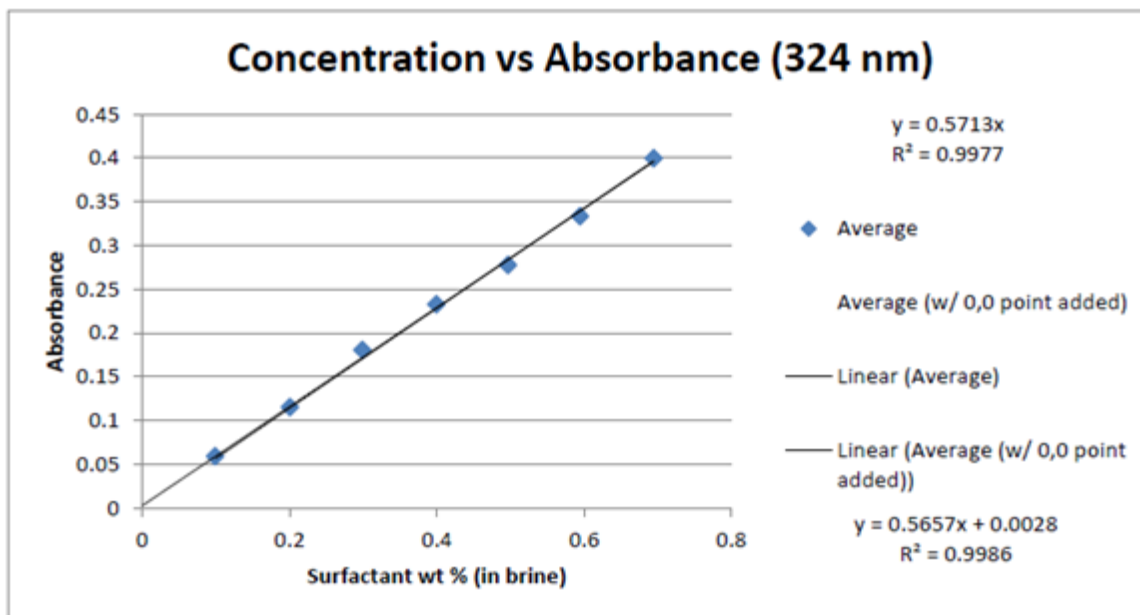


**Figure 5: Foam stability of Huntsman alkyl alkoxy sulfates at concentration of 1.0 wt%, 0.25 wt%, 0.1 wt%, and 0.025 wt% at 67°C, with high salinity brine/CO<sub>2</sub> mass ratio of 1:1.**

The Huntsman alkyl alkoxy sulfates surfactant established very stable foams in the high salinity brine at bottom hole injector conditions of higher than 60°C and 2,300 psia. Therefore, a field company is considering a SAG process for conformance/mobility control in the CO<sub>2</sub> EOR field.

*Development of Technique to Determine the Amount of Surfactant Dissolved in Brine via UV-Vis Measurements.*

Tests were conducted on the equilibrium adsorption of the Huntsman alkyl alkoxy sulfates surfactant on crushed CO<sub>2</sub> EOR site rock. A calibration curve (at 324 nm) was established for determining the concentration of the surfactant in a solution of the produced brine from the CO<sub>2</sub> EOR site over the 0.1 – 0.7 wt% range, as shown in Figure 6.

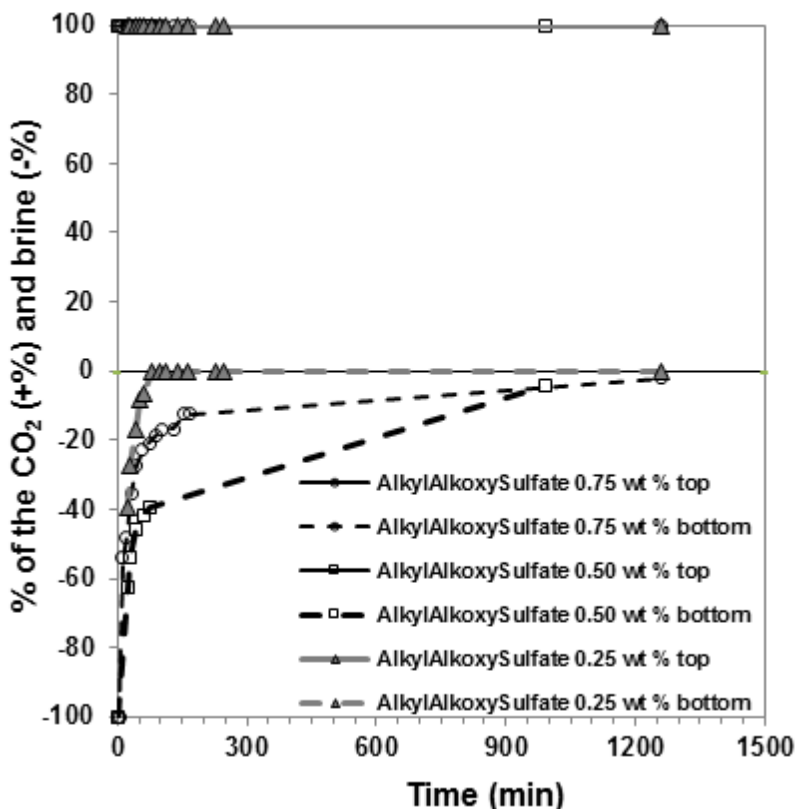


**Figure 6: UV-Vis calibration curve; Huntsman alkyl alkoxy sulfates surfactant in high salinity brine at room temperature.**

An attempt to determine the amount of adsorption of the surfactant on crushed CO<sub>2</sub> EOR site rock was initiated via material balance. The initial concentration of the surfactant in the brine was known. A specified amount of crushed rock would then be added to the solution and allowed to adsorb for several days. The decrease in surfactant concentration of the solution would then be determined. The loss of surfactant mass in solution would be attributed to adsorption. This would be repeated over a range of concentration.

UV-Vis spectrophotometry was used to measure the drop in surfactant concentration over time as the surfactant adsorbs on the sand particles. Before performing this test, it was necessary to clean the sand. This cleaning was performed by washing the sand with toluene under a fume hood. Approximately 100g of sand were mixed with ~150 mL toluene (because of low supply of toluene, sometimes a mixture of xylene isomers was used). The washing procedure was repeated six to seven times. The sand was dried by washing it twice with ~100 mL acetone. Next, four mixtures were prepared. The mixtures were approximately 5g sand underneath 7-8g of the following solutions of Huntsman alkyl alkoxy sulfates surfactant in brine: (1) 0.1 wt%, (2) 0.4 wt%, (3) 0.7 wt%, and (4) 1 wt%. All of the mixtures were placed in a temperature bath held at 67°C for 48 hours. After 48 hours, the samples were removed from the temperature bath and allowed to cool to room temperature. Visible range absorption spectra were then obtained. Unfortunately, the absorbance at 324 nm (the wavelength for which the calibration curve was prepared) actually increased! The absorption increase possibly occurred because a residue of hydrocarbons had not been removed from the sand. The sand needs to be cleaned more carefully and then dried at a temperature above the boiling points of the solvents. This observation was confirmed by the fact that, while in the temperature bath, the surfactant-brine solution turned light brown rather than remaining clear.

In Figure 7, the foam stability profiles resulting from mixing a small amount of crude oil from CO<sub>2</sub> EOR site and equal amounts of CO<sub>2</sub> and high salinity brine with Huntsman alkyl alkoxy sulfates surfactant were plotted with respect to time. The foam stability profiles at the reservoir temperature of higher than 60°C and bottom hole pressure of higher 2,300 psia were calculated for surfactant concentrations of 0.75 wt%, 0.50 wt%, and 0.25 wt% on a brine-only basis. Foams were produced by mixing for five minutes at the stated conditions in the Robinson cell. Excellent foam stability was observed even with the addition of oil. The foams generated with 0.50-0.75 wt% surfactant were able to stabilize the foams more efficiently than the 0.25 wt% solutions. The 0.25 – 0.75 wt% range is commensurate with the range of surfactant concentrations used in the ~dozen CO<sub>2</sub> SAG foams tests conducted in the 1980s and 1990s.



**Figure 7: Foam stability profiles for 20:20:1 mixtures of CO<sub>2</sub>: high salinity brine solution: crude oil at Huntsman alkyl alkoxy sulfates concentrations in the brine of 0.75, 0.50, and 0.25 wt%.**

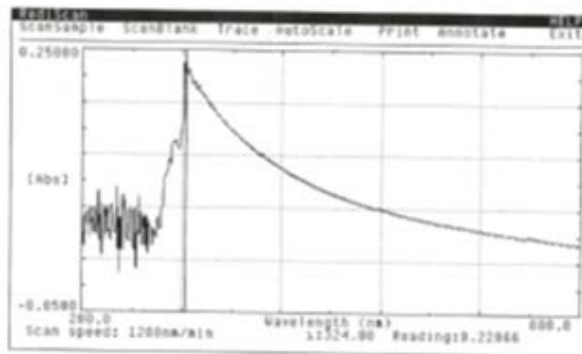
A series of tests were conducted to determine how much surfactant was absorbed by the sandstone from a CO<sub>2</sub> EOR site in Mississippi.

Crushed CO<sub>2</sub> EOR site rock core samples were mixed with Huntsman alkyl alkoxy sulfates surfactant/high salinity brine solution containing 0.3 wt% surfactant. Laboratory efforts concentrated on the use of UV-Vis spectrophotometry to measure surfactant adsorption by the rock core. The analytical method developed is based on Beer's law ( $Absorbance = \epsilon \cdot l \cdot c$ , where  $\epsilon$  is a constant specific to the material in question,  $l$  is the path length over which radiation is absorbed, and  $c$  is concentration). The initial results are discussed below.

In order for the method to work, no sand particles should be suspended in the liquid phase, as such behavior would cause clouding, distorting the UV-Vis spectrum. Therefore, an attempt was made at 25°C to attain a transparent aqueous phase after mixing with sand that was suitable for ultraviolet (UV)

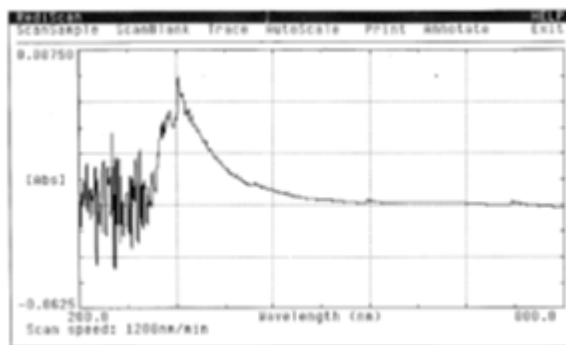
measurement of surfactant. The sand mixture was filtered to +80 mesh (particles larger than 177 microns) and shaken vigorously with brine for up to five minutes. The sand particles were allowed to settle, which took place in a matter of seconds. The resulting brine phase remained a dirty, milky color that was unsuitable for UV testing.

The centrifuge was then investigated as a possible alternative to producing an impurity-free brine/surfactant liquid phase. Approximately 12g of a 0.3 wt% surfactant in brine solution was mixed with 4g of sand. The centrifuge was run for five minutes at 3,600 rpm. Upon removal of the tube from the centrifuge, the brine phase was clear and the sand settled on the bottom of the tube. The UV-Vis spectrum of the brine prior to centrifugation, containing 0.3 wt% surfactant, is shown in Figure 8.



**Figure 8: UV-Vis spectrum for 0.3 wt% Huntsman alkyl alkoxy sulfates in high salinity brine solution, just before sand addition and subsequent centrifugation of the brine-sand mixture for five minutes at 3,600 rpm.**

After the centrifuge operation, the absorption of light at 324 nm fell from 0.22 down to 0.065 (Figure 9). Because the absorbance is proportional to concentration, this would imply that about two-thirds of the surfactant present was adsorbed onto the sand.



**Figure 9: UV-Vis spectrum for 0.3 wt% Huntsman alkyl alkoxy sulfates in high salinity brine solution, after sand addition and subsequent centrifugation of the brine-sand mixture for five minutes at 3,600 rpm.**

The equilibrium condition for this experiment at 25°C would be  $(0.3 \text{ wt\%} * (0.065/0.22)) = 0.089 \text{ wt\%}$  Surfactant in Brine; and  $[12\text{g} * (0.003 - 0.00065) \text{ g surfactant/g brine}] / 4 \text{ g sand} = 0.007 \text{ gr surfactant/gr brine}$ .

This experiment was repeated at 67°C with the sand obtained from the CO<sub>2</sub> EOR site for 10 minutes of mixing followed by 48 hours of quiescent contact. A protocol was developed for getting a perfectly transparent brine phase for UV-Vis measurements.



*To Quantify the Amount of the Adsorption Surfactant in Sandstone*

There have been some technical difficulties working with the Berea Sandstone. An attempt was made to quantify the adsorption of surfactant by the consolidated 600 md Berea Sandstone cores in the Core Flow lab at NETL. The day before running the experiment, the cores were saturated with a synthetic brine solution. The next morning, a solution of Huntsman alkyl alkoxy sulfates surfactant in brine was pumped through the core at a rate which would allow the total volume of eluting sample collected to be equivalent to >10 core pore volumes (the experiment is to be stopped once the core is saturated with surfactant). The plan was to determine the concentrations of both the injected solution and the eluting solution by UV-Vis spectrophotometry, and to determine total surfactant adsorbed from the plot of eluting surfactant concentration versus total volume eluted from the core.

Initially, an attempt was made to perform the test injecting Huntsman alkyl alkoxy sulfates surfactant at 0.5 wt% in synthetic brine. This surfactant structure is  $C_{12}\text{-2EO-SO}_4^- \text{Na}^+$ ; 70% active. No detectable amount of surfactant eluted from the column even after injecting ~300 mL (~20 pore volumes). The surfactant not being fully dissolved in the synthetic, laboratory-reformulated brine but only dispersed was the speculated reason for this result. The surfactant solution was somewhat translucent and cloudy, not completely transparent.

The experiment was repeated using a different type alkyl alkoxy sulfates surfactant (at 0.25 wt%) provided by Huntsman. This is a more hydrophilic surfactant. This surfactant structure is  $C_{12}\text{-3EO-SO}_4^- \text{NH}_4^+$ ; 70% active. Actual produced brine was used as the solvent for the surfactant, instead of the synthetic brine. This action resulted in reducing the cloudiness so that the new surfactant solution was mostly transparent. Still, some cloudiness remained. Next, 360 mL of this solution was injected and pumped through the core. Again, nothing eluted (as indicated by the UV-Vis spectrum).

The conclusion after this failed run is likely due to one of two causes:

1. The anionic surfactant is still not completely dissolved due to the very high TDS (>100,000 ppm) of the brine (>100,000 ppm is a value far in excess of brines used in prior CO<sub>2</sub> field tests of foams). Thus the core is actually trapping the dispersed surfactant phase on its surfaces as an immobile phase. To remediate this, the plan is to employ mixtures of distilled water and produced brine to enhance surfactant solubility and decrease adsorption.
2. Or, there is a surprisingly large degree of adsorption of this negatively charged anionic surfactant occurring on the (positively charged) Berea sandstone due to surface charges. Therefore, Huntsman was asked to provide a (positively charged) cationic surfactant and zwitterionic surfactants. After these tests are finished with the Berea Sandstone and the West Heidelberg cores arrive, anionic, cationic, and zwitterionic surfactants will be used for further tests.

The test to quantify the amount of adsorption surfactant in sandstone continues.

### 3.0 Conclusion

High pressure CO<sub>2</sub> has been used for decades to enhance the recovery of oil (primarily in the Permian basin of Texas); however, the experience is restricted with respect to types of reservoirs and limitations (even for conventional reservoirs), including factors relating to sweep efficiency, miscibility, and flow through tight and/or fracture-dominated reservoirs. This research sought to develop “next generation” CO<sub>2</sub> EOR technologies that could increase recovery from existing CO<sub>2</sub> EOR activities and accelerate the application of the process to other mature oil fields around the country. The challenge for the CO<sub>2</sub> EOR process was the poor sweep efficiency that could result from the difference in mobility between oil/brine and CO<sub>2</sub> in the reservoir. This might result in early CO<sub>2</sub> breakthrough, high utilization of CO<sub>2</sub> per barrel of oil recovered, prolonged duration of the displacement, and poor sweep efficiency.

One approach to address this issue was to increase the viscosity of CO<sub>2</sub> by adding surfactants to create CO<sub>2</sub> foam *in situ*. One of the objectives of this project was to identify promising commercial surfactants that could be added to CO<sub>2</sub> as it is being injected for EOR. The Huntsman ethoxylated alcohols types (T-9 to T-20) of surfactants were assessed extensively under reservoir conditions during this year. Due to the low surfactant solubility in CO<sub>2</sub> at reservoir conditions made it unappealing to perform enhanced oil recovery by injecting a surfactant dissolved in CO<sub>2</sub>.

Due to the reservoir conditions of the potential field demonstration site being not suitable for dissolving surfactant in the CO<sub>2</sub>, the new approaches were adapted on an aqueous SAG process, which has the surfactant dissolved only in the produced brine of the field. The SAG represents the injection surfactant-in-brine alternately with CO<sub>2</sub>. The foam will reduce the flow of CO<sub>2</sub> into thief zones and inhibit CO<sub>2</sub> gravity override and fingering, such that the increases in incremental oil and decreases in CO<sub>2</sub> purchases and recycling/re-compression costs will render the project profitable. Therefore, this project began testing the foam stability of ionic surfactants in brine for the remainder of FY13. Toward this end, a potential surfactant was identified for this new approach. An anionic surfactant, Huntsman alkyl alkoxy sulfates, when dissolved in the produced brine and formed the stable foam under reservoir conditions of higher than 60°C and 2,300 psia.

A protocol was developed to determine the amount of surfactant dissolved in brine *via* UV-Vis measurements. In addition, an attempt was made to quantify the adsorption of surfactant by the consolidated 600 md Berea Sandstone cores in the Core Flow lab at NETL under reservoir conditions.

From the study conducted this year, the results supported that due to the conditions of the first potential field demonstration site being not suitable for dissolving surfactant in the CO<sub>2</sub>, this project will focus on an aqueous SAG process in FY14, which has the surfactant dissolved only in the produced brine of the field.

The FY14 research under CO<sub>2</sub> EOR involves both applied laboratory- and pilot-scale research focused on developing new technologies for CO<sub>2</sub> EOR. The FY14 research encompasses four focus areas for CO<sub>2</sub> EOR technology and protocol development: (1) site selection, (2) experimental development of brine-soluble surfactants for *in situ* foaming, (3) reservoir modeling, and (4) economic analysis and field demonstration.

## 4.0 Technology Transfer

### Presentation

Burgess, W.A., Soong, Y., Crandall, D., McLendon, R., Goodman, A., Enick, R.M., and Buckwalter, S.A., "Study of CO<sub>2</sub>-Soluble and Brine-Soluble Surfactants for CO<sub>2</sub> Mobility Control," abstract submitted to the AIChE meeting, San Francisco, California, November 3-8, 2013.

### Publications

Xing, D., Wei, B., McNulty, S., Azmi, M., Trickett, K., McLendon, W., Eastoe, J., Crandall, D., Romanov, S., Soong, Y., and Enick, R., "CO<sub>2</sub>-Soluble Non-Ionic, Water –Soluble Surfactants that Stabilize CO<sub>2</sub>-in-Brine Foams," SPE 129907, *SPE Journal*, 17, 4, December 2012, p. 1172-1185.

McLendon, W.J., Koronaios, P., McNulty, S., Enick, R.M., Biemans, G., Miller, A., Salazar, L., Soong, Y., Romanov, V., and Crandal, D., "Assessment of CO<sub>2</sub>-Soluble Surfactants for Mobility Reduction Using Mobility Measurements and CT Imaging," submitted *SPE Journal*, 2013.

## 5.0 References

Unconventional Fossil Energy Resource Program, Program Facts Sheet, Program 100, October 2012, [www.netl.doe.gov](http://www.netl.doe.gov)



The National Energy Technology Laboratory (NETL) conducts cutting-edge energy research and technology development and analyzes energy systems and international energy issues for the U.S. Department of Energy. The NETL Regional University Alliance (NETL-RUA) is an applied research collaboration that combines NETL's energy research expertise with the broad capabilities of five nationally recognized, regional universities: Carnegie Mellon University (CMU), The Pennsylvania State University (Penn State), University of Pittsburgh (Pitt), Virginia Tech, and West Virginia University (WVU), and the engineering and construction expertise of an industry partner (URS). NETL-RUA leverages its expertise with current fossil energy sources to discover and develop sustainable energy systems of the future, introduce new technology, and boost economic development and national security.



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