DETERMINATION OF MISCIBILITY PRESSURE
BY DIRECT OBSERVATION METHOD

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Background

The objective of the project is to conduct laboratory tests to:

1. develop a method for determining MMP through direct observation using a high pressure cell;
2. determine feasibility of in-situ foam generation by visual observation and microphotographic technique.

The project is presently organized and carried out in three major fronts, i.e., (1) MMP test; (2) high pressure sampling and chemical analysis; and (3) foam study and displacement test. The technical progress in each of these areas is discussed as follows:

(A) MMP test

SACROC Crude Oil

Investigation of miscibility development for SACROC crude was continued at 72°F and 140°F. Volumetric and phase behavior at 140°F were very similar to that at 120°F as described in the last quarterly report. The principal difference is the higher pressures at which the CO₂-rich liquid emerged and became miscible with the vapor phase. Again, we have observed that the emergence of a CO₂-rich liquid phase was the key to the development of a transition zone miscible with both fresh crude oil and the driving CO₂. At the forward contacts, the CO₂-rich liquid becomes enriched through multiple contact until it becomes miscible with fresh crude. At the rear of the transition zone, the CO₂-rich liquid phase becomes miscible with the driving CO₂ at a pressure equivalent to MMP. It is also clear that the regeneration of the CO₂-rich phase is necessary to maintain a miscible displacement and the absence of CO₂-rich phase would result in an immiscible type displacement.

For the 72°F experiment, there was no distinguished CO₂-rich phase as was observed at 120°F and 140°F runs. This is because that as soon as the CO₂-rich phase was formed, it immediately mixed with the liquid CO₂. This enriched liquid CO₂ was observed to be miscible with fresh CO₂ but immiscible with the stripped crude. In the later multiple contact experiment, the liquid CO₂ was continuously enriched through contact with drops of fresh crude and finally became completely miscible with crude oil.

This experiment tends to show that for low temperature reservoirs, miscibility could be developed between the liquid CO₂ and crude oil through multiple contact process. The CO₂-rich liquid phase may be obscured as opposed to those at higher temperatures.

Penn-Grade Oil

MMP experiments were conducted on Penn-Grade oil at 84°F, 120°F, and 140°F. The CO₂-rich liquid appeared at 1157 psig and became miscible with vapor phase at 1400 psig in the experiment at 120°F. At 140°F, the pressure at which CO₂-rich phase emerged and became miscible with the vapor phase were 1300 psig and 1481 psig, respectively.
Slaughter Estate Crude Oil

Experiments conducted on Slaughter Estate at 72°F, 120°F, and 140°F produced volumetric behavior similar to that exhibited by SACROC oil. The key difference was that the pressures at which the CO2-rich phase emerged and became miscible with CO2 vapor were higher. Also, the amount of asphaltic precipitation that fell out of this oil were so great that a large part of the sight glass was obscured.

Rock Creek Oil

Experiments conducted on Rock Creek oil at 70°F, 120°F, and 140°F produced results very similar to those of Penn-Grade crude oil. Both crudes exhibited large swelling factors from 1.7 to 1.8 at 120°F and 140°F. The amount of CO2-rich liquid generated was much greater in the experiments at 120°F and 140°F. Special attention was given to the experiment conducted on Rock Creek oil at 70°F, its true reservoir temperature. Swelling of the crude oil phase began at approximately 515 psig and continued up to 880 psig to reach its maximum swelling factor of 1.4. At this point, the CO2 began to enter the system in liquid phase and the crude oil phase was observed to shrink, indicating that the major extraction of hydrocarbons by liquid CO2 had begun. As described earlier in the SACROC experiment, it was almost impossible to identify a distinct CO2-rich liquid column due to the mixing nature of CO2-rich phase and liquid CO2. When fresh crude oil was charged, it liquid CO2 was further enriched and changed its color from misty-white to yellow and then became miscible with crude oil.

Gilbertown Crude Oil

Gilbertown crude oil is a 17° API from southwest Alabama. A swelling factor of 1.3 was observed at 120°F as compared to 1.13 and 1.1 at 140°F and 74°F.

In the experiment at 120°F and 140°F, only a thin layer of CO2-rich liquid was generated at approximately 1250 psi and became miscible with vapor at 1400 psi and 1550 psi in the 120°F and 140°F experiments, respectively. Because of the scanty amount of CO2-rich liquid, miscible condition with the crude oil was never observed.

The effects of temperature on MMP and appearance of CO2-rich phase for each of the four crude oils tested are plotted on Figures 1-5. The MMP is the pressure at which the CO2-rich phase becomes miscible with CO2 vapor.

Comparison with Other MMP Techniques

In order to verify the results from the study, comparisons have been made with published Yellig and Metcalf correlations. In Figure 6, the observed MMP are superimposed on the correlation curve. While the majority of MMPs determined by direct observation fall within the limits of the
correlation, our data appear to show slightly low MMP at higher temperatures. This would be expected since they used recombined reservoir oil rather than stock tank oil in their displacement tests. The MMP would be higher to obtain a comparable recovery for a recombined reservoir oil than for a stock tank oil because of methane content.

Comparison of MMP was also made with Maljamar crude oil. The MMP of stock tank Maljamar crude determined by slim tube displacement tests at the New Mexico Petroleum Recovery Research Center (NMPRRC) was 1200 psi at 90°F. The direct observation study at our laboratory indicates that an upper CO₂-rich liquid phase emerged at 1025 psi and became miscible with CO₂ vapor at 1181 psi. This compares favorably with NMPRRC's results.

(B) Sampling and Chemical Analysis

The Hewlet-Packard 5880-A gas chromatograph has been tested and a BASIC program has been incorporated with the unit to determine C₅ to C₃₆. The results of analysis for the four crude oils tested are shown in Figure 7. It is obvious that the SACROC crude oil is the richest in C₅ to C₂₀ components, followed by Penn-Grade, Slaughter Estate and Gilbertown crude oils. The deficiency of C₅ to C₂₀ in the Gilbertown oil may explain why no miscibility between the CO₂-rich liquid and crude oil was observed. As previously stated that the richness of C₅ to C₂₀ components is the key factor for determining the quality and stability of the miscible transition zone.

(C) Foam Displacement Test

Apparatus and Procedure

The high pressure foam testing unit has been revised as shown in Figure 8. The system has a working pressure of 3000 psi at 140°F. The foam generator was constructed using a 3-inch piece of 1/8-inch stainless tubing for the body, and glass wool as the packing material; two small metal screens were placed at the two ends to prevent glass wool being flushed out. Preliminary testing of the packing materials indicated that the glass wool is more effective in generating foam than glass beads for a practical CO₂ injection rate of approximately 8 cc/hr; this can be explained as glass wool's greater surface area promotes more mixing between CO₂ and surfactant solution. The generator has porosity and permeability of approximately 70% and 8 darcies respectively.

The observation cell is a Jerguson liquid level indicator with a linear scale attached to the outside of the glass window. A conversion factor of 3.79 cc/cm was calculated for this cell to convert from height into volume.

Surfactant solution is supplied by an adjustable rate pump made by Milton Roy Co.. Carbon dioxide is supplied by a custom made rod-cell; the CO₂ rate is controlled by a Ruska positive displacement pump pumping water into the lower part of the cell to move a rod connected piston separating the two fluid chambers, the upward moving piston displaces CO₂ into the foam generator, and the rod indicates the relative position of the piston.
The surfactant solution used in the test was prepared by adding Alipal·CD-128 into distilled water to a concentration of 0.5% by volume.

The system is first charged with liquid CO₂, and the heater is then turned on to bring it to the desired temperature. After the temperature is stabilized, the outlet pressure is set by adjusting the CO₂ pressure and the back pressure regulator. The CO₂ pump and the surfactant pump are then turned on to begin the injection of these two fluids into the foam generator. It will take approximately one hour before the foam first appears in the observation cell. The foam level in the observation cell, CO₂ and surfactant injection pressure, system pressure and the surfactant level in the reservoir are recorded at this instant. The system is left to continue without altering the running condition and readings are taking again after one hour interval. The increase in foam level and the surfactant level are determined which are then used to calculate foam quality.

The CO₂ rate was kept constant at 8.1 cc/hr for every run. Different surfactant rates were tested to study the effect on foam quality and foam quantity at a particular temperature-pressure condition. The process was repeated to study the effect of pressure on foam properties by generating foam at different system pressures: 1000, 1500 and 2000 psi. Tests at different temperatures of 75, 120 and 140°F were also performed.

Results and Discussion

Because the densities of carbon dioxide are changed with temperatures and pressures, CO₂ mass flow rates were calculated to provide the basis for analysis. The surfactant/CO₂ ratio relative to foam quality and foam quantity are presented in Table 1 and plotted in Figures 9 to 14.

Figures 9, 10 and 11 show the foam qualities increased as the surfactant rates are decreased. At 75°F, the foam quality increases as the pressure is decreased whereas the reverse is true for temperature at 120°F. The reversal in behavior could be true since CO₂ is existed at 75°F in liquid phase and in gas phase at 120°F. For CO₂ injection rate of 8.1 cc/hr, foam did not appear at 1000 psi-120°F, 1000 psi-140°F and 1500 psi-140°F.

Figures 12, 13 and 14 show foam generating rate increase with increasing surfactant/CO₂ ratio. High temperatures tend to lower the rate and high pressures tend to increase the rate at 120°F but to decrease at 75°F. Foam quality was found to be affected more by surfactant/CO₂ ratio, and to a lesser degree by pressures and temperatures. For a specific foam quality and gaseous CO₂, more foam would be generated at higher pressures, however, the reverse is true whereas the CO₂ is liquid.

More testings are being planned to study the effects of foam properties in relation to brine and crude oil before conclusions can be drawn to which surfactant/CO₂ ratio is the best for later uses in foam flooding tests.
Figure 1. SACROC Crude Oil-CO₂
MMP vs. Temperature
Figure 2. Penn-Grade Crude Oil MMP vs. Temperature
Figure 3. Slaughter Estate Crude Oil MMP vs. Temperature
Figure 4. Rock Creek Crude Oil MMP vs. Temperature
Figure 5. Gilbertown Crude Oil MMP vs. Temperature
Figure 6. CO₂-Crude Oil MMP Correlation
Developed by Yellig and Metcalf
Figure 7. Component Area Percentage vs. Carbon Number for Crude Oils Studied
Figure 8 - Laboratory Set-Up for CO₂-Surfactant Foam Generating.

A - Observation Cell
B - Foam Generator
C - Crude Oil Loop
D - CO₂ Rod Cell
E - Water Feed Pump (CO₂ Pump)
F - Surfactant Pump
G - Surfactant Reservoir
H - Injection Pressure Gauges
I - System Pressure Gauge (Foam Pressure)

J - Back Pressure Regulator
K - Wet Test Meter
L - Constant Temperature Cage
Figure 9 - Effect of Surfactant/CO₂ ratio on Foam Quality at 75°F.
Figure 10 - Effect of Surfactant/CO₂ ratio on Foam Quality at 120°F.
Figure 11 - Effect of Surfactant/CO₂ ratio on Foam Quality at 140°F.
Figure 12 - Effect of Surfactant/CO$_2$ ratio on Foam Quantity at 75°F.
Figure 13 - Effect of Surfactant/CO₂ ratio on Foam Quantity at 120°F.
Figure 14 - Effect of Surfactant/CO\textsubscript{2} ratio on Foam Quantity at 140°F.
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<th>Foam Temperature (°F)</th>
<th>Injection Pressure (psi)</th>
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<th>Surfactant Inj. Rate (cc/hr)</th>
<th>Foam Gen. Rate (cc/hr)</th>
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Table 1 - Summary of Test Results for CO₂-Surfactant Foam Generating.