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Quarterly Technical Progress Report

IMPROVED EFFICIENCY OF MISCIBLE CO<sub>2</sub> FLOODS AND ENHANCED PROSPECTS FOR CO<sub>2</sub> FLOODING HETEROGENEOUS RESERVOIRS

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New Mexico Petroleum Recovery Research Center  
New Mexico Institute of Mining and Technology  
Socorro, NM 87801  
(505)835-5142

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Program Manager: Reid B. Grigg

Principal Investigators: Reid B. Grigg  
David S. Schechter

Other Major Contributors: Shih-Hsien (Eric) Chang  
Boyun (Gordon) Guo  
Jyun-Syung Tsau

Contracting Officer's Representative: Jerry F. Casteel

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## Abstract

Progress has been made in each of the three project areas during this quarter. Each quarter we are highlighting one project area. This quarter, Task 1 is being highlighted with expanded details.

In Task 1, a foam-durability apparatus was used to evaluate surfactant and foam properties (interfacial tension (IFT) of surfactant solution with dense CO<sub>2</sub>, the critical micelle concentration, foaming ability of the mixture and foam stability) at high pressure condition. These data were correlated with the dynamic properties of foam measured in coreflooding experiments. For the five surfactants tested the results show that effectiveness of mobility reduction of foam in porous media is strongly correlated with the stability of foam in the bulk phase and the mobility reduction factor increases with the reduction of IFT. Factors that favor reducing the mobility of CO<sub>2</sub>/brine, lead to more favorable selective mobility reduction in heterogeneous core.

During this quarter in Task 2 a new series of core flood tests was completed, that measured the effects of CO<sub>2</sub> flow fraction and rock permeability on foam-flow behavior. Also, an apparatus was designed, built, and tested under reservoir conditions that measures volume and composition of CO<sub>2</sub> hydrocarbon extractable components. This aids in understanding the development of multi-contact miscibility and is a rapid method for determining the minimum miscibility pressure (MMP). In three systems the results compared well with slim tube tests MMP's. Additional effort was made to history match the production data from the East Vacuum field CO<sub>2</sub>-Foam pilot during the SAG injection; the immediate problem is developing a layered model accurately emulating the reservoir geology.

In Task 3 this quarter, a core was prepared to aid in the determination of the effect of water saturation on the efficiency of CO<sub>2</sub> gravity drainage. A whole core with porosity of 11% and permeability to water of 0.38 md was saturated with brine, reduced to an initial water saturation of 30% using oil, and then water was reinjected to simulate waterflooding until the water saturation reached 45%. The core was then placed vertically in a drainage cell where CO<sub>2</sub> is being injected. Initially both water and oil were produced from the core, but water production ceased at day 55. Water saturation was reduced 6% to 39%. The oil production rate has increased since water production has stopped, and at day 70, 11.5 volume % of the oil in place at the start of the drainage experiment has been produced. Free water in the core, initially hindered oil recovery due to two-phase flow relative permeabilities.

## **Executive Summary**

Progress has been made in each of the three project areas during this quarter. Each quarter we are highlighting one project area. This quarter, Task 1 is being highlighted with expanded details.

In Task 1, a foam-durability apparatus was used to evaluate surfactant and foam properties (interfacial tension (IFT) of surfactant solution with dense CO<sub>2</sub>, the critical micelle concentration, foaming ability of the mixture and foam stability) at high pressure condition. These data were correlated with the dynamic properties of foam measured in coreflooding experiments. For the five surfactants tested the results show that effectiveness of mobility reduction of foam in porous media is strongly correlated with the stability of foam in the bulk phase and the mobility reduction factor increases with the reduction of IFT. Factors that favor reducing the mobility of CO<sub>2</sub>/brine, lead to more favorable selective mobility reduction in heterogeneous core.

During this quarter in Task 2 a new series of core flood tests was completed, that measured the effects of CO<sub>2</sub> flow fraction and rock permeability on foam-flow behavior. Also, an apparatus was designed, built, and tested under reservoir conditions that measures volume and composition of CO<sub>2</sub> hydrocarbon extractable components. This aids in understanding the development of multi-contact miscibility and is a rapid method for determining the minimum miscibility pressure (MMP). In three systems the results compared well with slim tube tests MMP's. Additional effort was made to history match the production data from the East Vacuum field CO<sub>2</sub>-Foam pilot during the SAG injection; the immediate problem is developing a layered model accurately emulating the reservoir geology.

In Task 3 this quarter, a core was prepared to aid in the determination of the effect of water saturation on the efficiency of CO<sub>2</sub> gravity drainage. A whole core with porosity of 11% and permeability to water of 0.38 md was saturated with brine, reduced to an initial water saturation of 30% using oil, and then water was reinjected to simulate waterflooding until the water saturation reached 45%. The core was then placed vertically in a drainage cell where CO<sub>2</sub> is being injected. Initially both water and oil were produced from the core, but water production ceased at day 55. Water saturation was reduced 6% to 39%. The oil production rate has increased since water production has stopped, and at day 70, 11.5 volume % of the oil in place at the start of the drainage experiment has been produced. Free water in the core, initially hindered oil recovery due to two-phase flow relative permeabilities.

## **Introduction**

Because of the importance of CO<sub>2</sub> flooding to future oil recovery potential in New Mexico and West Texas, the Petroleum Recovery Research Center (PRRC) has maintained a vigorous experimental program in this area of research.

New concepts are being investigated to improve the effectiveness of CO<sub>2</sub> flooding in heterogeneous reservoirs. Research is being conducted in three closely related areas: 1) further exploring the application of selective mobility reduction (SMR) in foam flooding, 2) exploring the possibility of higher economic viability of floods at reduced CO<sub>2</sub> injection pressures, and 3) understanding low interfacial tension (IFT) mechanisms with application to CO<sub>2</sub> flooding in tight vertically fractured reservoirs. Each of these areas have potential of increasing oil production and/or reducing cost in fields presently under CO<sub>2</sub> flooding. Also, the results of this research should expand viable candidates for future CO<sub>2</sub> flooding. Also, the results of this research should expand viable candidate fields to include lower pressure and much more heterogeneous or fractured reservoirs.

## **Summary of Progress**

Progress was made in each of the three project areas during this quarter and is summarized in the next three paragraphs. Each quarter we highlight one project area. Thus, an expanded summary of Task 1 follows the summary paragraphs of the three tasks.

In Task 1, a foam-durability apparatus was used to evaluate surfactant and foam properties at high pressure condition. The properties obtainable from these tests include the interfacial tension of surfactant with dense CO<sub>2</sub>, critical micelle concentration of surfactant, foaming ability of surfactant and stability of foam. These data were then correlated with the dynamic properties of foam as measured from the core flooding experiment. For the five surfactants tested the results show that effectiveness of mobility reduction of foam in porous media is strongly correlated with the stability of foam in the bulk phase. The mobility reduction factor increases with the reduction of interfacial tension between CO<sub>2</sub> and aqueous phase. Furthermore, factors that favor reducing the mobility of CO<sub>2</sub>/brine also lead to a more favorable selective mobility reduction in a composite core consisting of differing permeabilities.

During this quarter in Task 2 a new series of core flood tests has been completed. This experimental study concentrated on the effects of CO<sub>2</sub> flow fraction and rock permeability on foam-flow behavior. We have designed, built, and tested under reservoir conditions an apparatus for determining the hydrocarbon extraction composition and weight per weight of injected CO<sub>2</sub>. This aids in mechanistic understanding of multi contact miscibility development and appears to be a rapid method for determining the minimum miscibility pressure. In three systems the MMP's compare well within experimental accuracy of slim tube tests. Additional effort was made to history match the production data from the East Vacuum field CO<sub>2</sub>-Foam pilot during the SAG injection in order to validate and calibrate the foam model using field data. The most difficult problem is developing a layered model accurately emulating the reservoir geology.

This quarter has seen continued progress in the investigation of CO<sub>2</sub> gravity drainage in fractured reservoirs as part of Task 3. A whole core with porosity of 11% and permeability to water of 0.38 md is being used to examine the effects of water saturation on the efficiency of CO<sub>2</sub> gravity

drainage. The core was saturated with brine, reduced to an initial water saturation of 30% using oil, and then water was reinjected to simulate waterflooding until the water saturation reached 45%. The core was then placed vertically in a drainage cell where CO<sub>2</sub> is being injected. Produced hydrocarbons are collected through a condenser to minimize vaporization. Initially both water and oil were produced from the core. Water production ceased at 55 days. Water saturation was reduced 6% to 39%. The oil production rate has increased since water production has stopped, and at day 70, 11.5 volume % of the oil in place at the start of the drainage experiment has been produced. Free water in the core, initially hindered oil recovery due to two-phase flow relative permeabilities.

### **Summary of Technical Progress for Task 1**

The objective of Task 1 is to identify the phenomena of selective mobility reduction (SMR), understand when and why it occurs, and to facilitate the use of this phenomena in field application. In this study mobility reduction and the extent of SMR are tested under reservoir conditions for a number of surfactants. These results are compared with measured interfacial tension (IFT), foam formation, and foam durability at similar pressures and temperatures. The objective being to develop rapid screen criteria for identifying candidate surfactants for mobility control and especially those with good SMR tendencies.

### **Foam Durability and Foam Mobility Tests**

In the course of our CO<sub>2</sub>-foam study, a high pressure foam-durability test apparatus was constructed<sup>1</sup> and screening tests were successfully conducted to select surfactants for field foam application.<sup>2</sup> This test determines the foaming ability of each surfactant, exhibits the stability of foam, and provides other valuable information of surfactant properties such as the interfacial tension (IFT) between a surfactant and dense CO<sub>2</sub>, and the critical micelle concentration of a surfactant.

A visual cell is filled with the surfactant solution for the test. Dense CO<sub>2</sub> is introduced through a needle at the lower end of the cell, is bubbled upward inside the cell, and the bubbles are formed and then collected at the upper end of the cell. Depending on the effectiveness of the surfactant, these bubbles will then either form a layer of foam-like dispersion at the top of the sapphire tube or coalesce into a clear layer of dense CO<sub>2</sub>.

The tested Surfactants are described in Table 1. Different batches of surfactant solution (each at 1 wt% active component) were prepared by dissolving the surfactant as received from the suppliers into a brine system consisting of 5.6 wt% NaCl and 1.4 wt% CaCl<sub>2</sub>. Different concentrations of the surfactant solution were subsequently prepared by diluting the batch solution with the 7 wt% brine. All screening tests were conducted at 77 °F and 2000 psig. The bubble volumes are determined and used to calculate IFT's.<sup>1</sup> Foam creation and stability are determined by observing and timing the life span of the foam layer.

In order to assess flowing foam properties and verify the existence of SMR in a heterogeneous porous media, core systems containing well-defined high and low permeability regions were constructed and arranged in the flow system as different portions of a heterogeneous reservoir. These experiments involved two well-defined permeability regions in capillary contact and arranged in series, is discussed here.

All the mobility measurements were conducted at 77°F and 2000 psig. The two composite cores used in the experiments had permeabilities ranging from 525 md to 128 md (composite core

#1) and 819 md to 106 md (composite core #2). During the foam experiments, 0.1 wt% surfactant solutions were used in the core #1 experiments and 0.05 wt% surfactant solutions were used in the core #2 experiments.

## Results and Discussion.

The results of calculated IFT's are plotted as a function of surfactant concentration and presented in Fig. 1. The surfactant concentration where the IFT no longer decreases significantly as the surfactant concentration increases corresponds to the critical micelle concentration (CMC). The IFT curves and CMC values vary with surfactant formula and for surfactants Alipa™ CD128, Chaser™ CD1040, Chaser™ CD1045, Chaser™ CD1050, and Dowfax™ 8390 the CMC's are 0.04, 0.06, 0.07, 0.07, and 0.35 wt%, respectively.

The typical results of static decay of the CO<sub>2</sub>-foam using surfactant CD1050 are presented in Fig. 2 with the optimum concentration to generate the longest-lasting foams being near the CMC. The effectiveness of surfactant to stabilize the foam was determined and surfactant Chaser™ CD1045 generates the most stable foams, followed by surfactants Chaser™ CD1050, Alipa™ CD128, Chaser™ CD1040 and Dowfax™ 8390.

SMR is found to depend on the rock permeability, surfactant type, concentration and flow rate. Typical results of mobility dependence on rock permeability of a series composite core are presented in Fig. 3. On this log-log scale plot, the mobility of CO<sub>2</sub>/brine or CO<sub>2</sub>-foam is plotted against permeability. The slope values determined by regression based on each set of data points indicate how favorable the mobility dependence of fluid is to the permeability of porous media. A slope of one indicates that the mobility of the fluid is proportional to the rock permeability as described in Darcy's law. A value of less than one shows a favorable dependence of selective mobility reduction which will lead to a more uniform displacement front when the fluid is flowing through heterogeneous porous media. A slope of more than one as observed for the CO<sub>2</sub>/brine data indicates that an unfavorable mobility dependence on permeability occurs with CO<sub>2</sub> and brine. The results also show that foam can correct the problem by not only reducing the mobility of CO<sub>2</sub> but also changing the mobility dependence in a favorable direction (*i.e.*, when surfactant is added to the brine and generates the foam, the slope of foam mobility versus rock permeability data becomes less than that of CO<sub>2</sub>/brine, and preferably less than one).

The slopes of five surfactants at a 0.1 wt% concentration vary considerably, 0.98 for Dowfax™ 8390, 0.89 for Chaser™ CD1040, 0.56 for Alipa™ CD128 and 0.51 for Chaser™ CD1045 and CD1050. Similar results were also found for the five surfactants at a lower concentration (0.05 wt%) where the slopes vary from 1.09 to 0.55. Each showing a lower slope than CO<sub>2</sub> and brine. All the relevant data for both concentrations are summarized in Table 4 in which the slope values are found to depend on the surfactant, concentration and flow rate condition. In general, the value of the slope decreases when surfactant is added into brine as a foaming agent. This suggests that foam is useful in correcting the nonuniform flow of CO<sub>2</sub> and brine in a porous system consisting of differing permeabilities. At lower velocities, the value of the slope becomes smaller, indicating a more favorable SMR occurs at a lower displacement rate. This characteristic would be beneficial for foam application in the field, especially assuming radial flow applies in the reservoir. In that case, the desired SMR will become more evident as foam travels away from the injection wellbore, where the flow velocity of foam becomes slower.

When results from the foam durability tests are compared with the mobility tests, it is

observed that the stability of foam in the bulk phase can be correlated with the effectiveness of mobility reduction of flowing foam in the porous media. The mobility reduction is enhanced as foam stability increases. As shown in Fig. 4, the mobility reduction factor (MRF), defined as the ratio of total mobility of CO<sub>2</sub>/brine to the foam mobility, increases with the foam life. At 0.05 wt% surfactant concentration, a noticeable mobility reduction factor of three is found in cases where the foam life lasts less than a minute. This suggests that mobility reduction with a less stable foam can be achieved by breaking and reforming mechanisms during the foam flow.<sup>3,4</sup> When foams become more stable, more resistance to flow results in a higher mobility reduction. Based on these observations, it is believed that the effectiveness of foam in reducing the mobility of CO<sub>2</sub> is likely attributed to the capability of surfactant in stabilizing the bubble-film or lamella in the porous media. Furthermore, the MRF also increases as the reduction factor of the interfacial tension (designated as IFT RF in Fig. 4) between CO<sub>2</sub>/brine and CO<sub>2</sub>/surfactant increases. Since the reduction of interfacial tension is favorable for foam generation, more lamella can be generated in the flow path of porous media which will increase the resistance of flow during the foam displacement.

The stability of foam can also be correlated with the extent of SMR in the flowing foam. As indicated by the slope values summarized in Table 2, factors in favor of generating a more stable foam (such as higher surfactant concentration and lower displacement rate) also give more favorable SMR. This observation is not in agreement with the finding reported in the literature,<sup>3</sup> that a more stable foam will lead to a less favorable or unfavorable SMR. Since other factors such as surface viscosity of foam film, dynamic interfacial tension, capillary force, *etc.*, which effect the flow behavior of foam are not investigated in this study, more work needs to be pursued to understand the mechanism of SMR and clarify the discrepancy in these findings.

Despite our reservations on the cause of SMR, it is expected that on the average the use of a proper CO<sub>2</sub>-foam could minimize the mobility contrast between high and low permeability zones in reservoir flow, thus increasing markedly the efficiency of oil displacement. The above and earlier experimental research makes it clear that the SMR property of CO<sub>2</sub>-foam is real, is observed in parallel-core and series-core tests with capillary contact, and can be presumed to function similarly in actual field situations. It should therefore be very useful in oil recovery from reservoirs containing crude oil of suitable composition.

## Conclusions

1. The stability of foam in the bulk phase can be correlated with the performance of foam flowing in porous media. When comparing different surfactants, a greater stability of foam gives more mobility reduction in foam displacement.
2. The mobility reduction factor increases as the reduction factor of the interfacial tension between CO<sub>2</sub> and the aqueous phase increases.
3. There exists an optimum concentration at which the stablest foam in the bulk phase is formed. This optimum concentration was found to be close to the CMC of each surfactant solution.
4. Factors that favor reducing the mobility of CO<sub>2</sub>/brine also lead to a more favorable SMR when foam flows in a composite core consisting of differing permeabilities.

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2. Tsau, J.S. and Heller, J.P.: "Evaluation of Surfactants for CO<sub>2</sub>-Foam Mobility Control," paper SPE 24013 presented at the 1992 Permian Basin Oil and Gas Recovery Conference, Midland, March 18-20, 1992.
  3. Yang, S.H. and Reed, R.L.: "Mobility Control Using CO<sub>2</sub> Foams," paper SPE 19689 presented at the 64th Annual Technical Conference, San Antonio, Oct. 8-11, 1989.
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Table 1. Foaming agents tested

Surfactant	Type	Active wt%	Formula	Manufacture
Chaser™ CD1040	Anionic	40.0	Alpha Olefin Sulfonate	Chaser International
Chaser™ CD1045	N/A	46.7	Proprietary	Chaser International
Chaser™ CD1050	Nonionic	70.0	Alkyl Phenol Ethoxylate	Chaser International
Alipa™ CD128	Anionic	58.0	Ethoxylated alcohol sulfate	GAF
Dowfax™ 8390	Anionic	35.0	C16-diphenylether disulfonate	Dow Chemical

Table 2. Slopes determined by the regression from the mobility measurements.

Fluid type	Core #	Injection rate @ cc/hr (Darcy velocity @ ft/day)		
		15 (9.4)	10 (6.3)	5 (3.1)
CO2/brine	2	1.311	1.330	1.342
CO2/0.05 wt% Dowfax 8390	2	1.089	1.115	1.079
CO2/0.05 wt% CD1040	2	1.083	1.011	0.939
CO2/0.05 wt% CD128	2	0.750	0.697	0.687
CO2/0.05 wt% CD1045	2	0.632	0.627	0.564
CO2/0.05 wt% CD1050	2	0.554	0.480	0.420
CO2/brine	1	1.465	1.525	1.523
CO2/0.10 wt% Dowfax 8390	1	0.976	0.936	0.921
CO2/0.10 wt% CD1040	1	0.894	0.880	0.831
CO2/0.10 wt% CD128	1	0.555	0.472	0.459
CO2/0.10 wt% CD1050	1	0.510	0.448	0.414
CO2/0.10 wt% CD1045	1	0.510	0.426	0.332

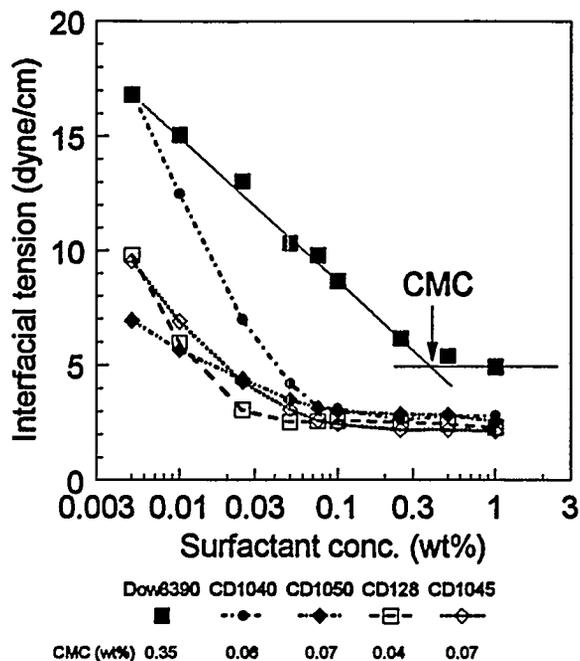


Fig. 1. IFT (dense CO<sub>2</sub> and surfactants) vs. surfactant concentration.

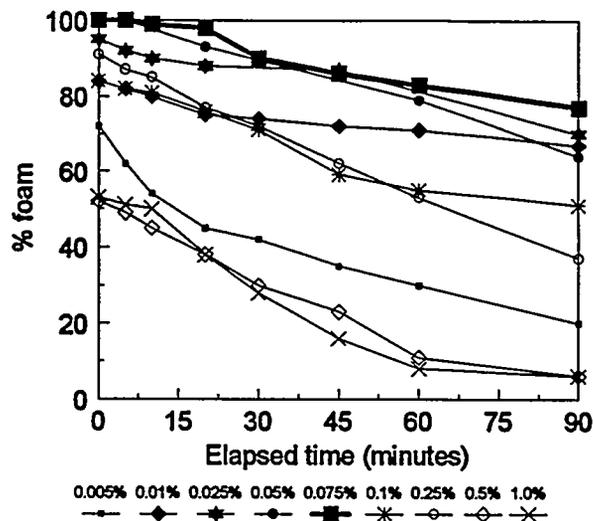


Fig. 2. Decay of CO<sub>2</sub> foam with surfactant CD1050.

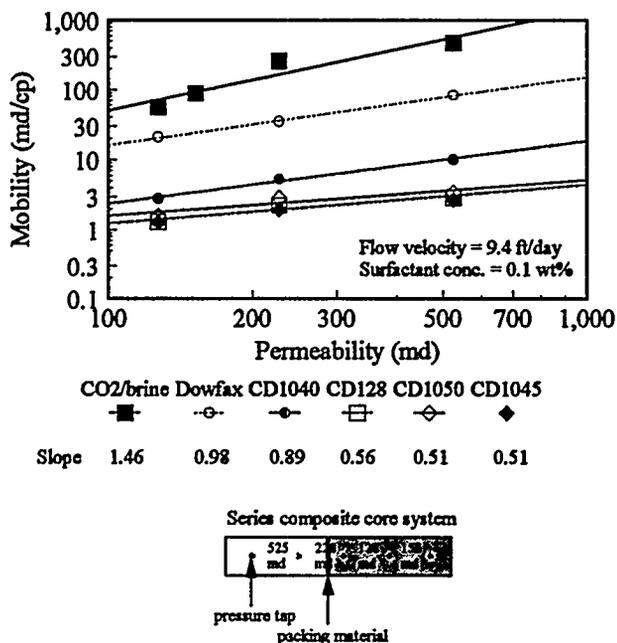


Fig. 3. Mobility dependence on permeability in a series composite core #1.

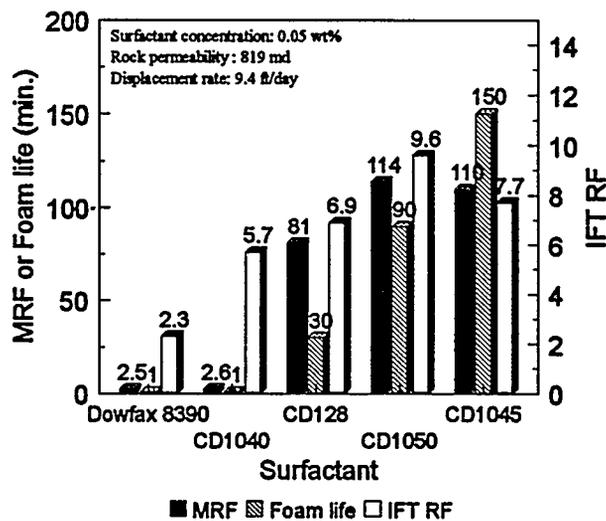


Fig. 4. Correlation between the property of foams and surfactants.