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ABSTRACT/ EXECUTIVE SUMMARY

A three-year contract for the project, DOE Contract No. DE-FG26-01BC15364, “Improving CO₂ Efficiency for Recovering Oil in Heterogeneous Reservoirs,” was awarded and started on September 28, 2001. This project examines three major areas in which CO₂ flooding can be improved: fluid and matrix interactions, conformance control/sweep efficiency, and reservoir simulation for improved oil recovery.

This report discusses the activity during the six-month period covering October 1, 2002 through March 31, 2003 that covers the first and second fiscal quarters of the project’s second year. During these two quarters of the project we have been working in several areas: reservoir fluid/rock interactions and their relationships to changing injectivity, and surfactant adsorption on quarried core and pure component granules, foam stability, and high flow rate effects. We also had a very productive project review in Midland, Texas. A paper on CO₂–brine–reservoir rock interaction was presented and included in the proceedings of the SPE International Symposium on Oilfield Chemistry, Houston, 5–8 February, 2003.¹ Papers have been accepted for the Second Annual Conference on Carbon Sequestration in Alexandria, VA in May,² the Society of Core Analysis meeting in Pau, France in September,³ and two papers for the SPE Annual Meeting in Denver, CO in October.

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INTRODUCTION

Of the available advanced oil recovery methods, CO₂ injection has the greatest potential for improved oil recovery (IOR) from light oil reservoirs in the United States. Presently eleven states have CO₂ injection projects, with 75% found in west Texas and southeast New Mexico. Almost universally, CO₂ injection has been a technical success when applied, and has proven profitable in the majority of reported projects. New CO₂ projects commence yearly but many reservoirs are not considered for CO₂ flooding because of low fracture pressure, poor injectivity, and/or extreme heterogeneity. The proposed work centers on crucial research to optimize CO₂ injection to maximize domestic hydrocarbon reserves. This project will expand the range of reservoirs amenable to CO₂ flooding.

During the course of our investigations, we will determine parameters and methodologies that will result in more efficient CO₂ flooding in heterogeneous reservoirs. Major areas of interests are: identifying reservoirs amenable to CO₂ flooding, characterizing CO₂ foaming agents, CO₂ flooding predictions, and parameters that effect CO₂ sweep efficiency, production rate, reservoir retention, and injectivity change effecting CO₂ and water injection rates.

Benefits will include: increasing the range of reservoirs amenable to CO₂ flooding, improving efficiency and lowering cost of CO₂ foam systems, improving CO₂ flooding predictions, improving sweep efficiency, controlling production timing, and optimizing retention and injectivity changes.

This report discusses the activity covering October 1, 2002 through March 31, 2003 that coincides with the first and second fiscal quarter of the project's second year.

EXPERIMENTAL/RESULTS AND DISCUSSION

Injectivity Changes⁴

"Co-injected CO₂-Brine Interactions with Indiana Limestone," is a paper in preparation for the annual Society of Core Analysts meeting in September.³ The paper will report findings of coreflooding limestone with co-injected carbon dioxide (CO₂) and brine at reservoir pressure and temperature. Metal chlorides were added as tracer components to the injection brine and appeared in quantities well above natural levels in any deposited carbonates. Core segment porosity and permeability are reported to indicate dissolution and deposition. Finally the core

was sectioned and analyzed by chemical and back-scattered electron imaging (BSEI) and chemical titration for compositional changes.

Porosity and permeability increased and decreased corresponding to suspected dissolution and precipitation similar to what was expected from earlier work.⁵ Figure 1 shows the solution channel in the first segment of the core. Qualitative and quantitative analyses confirmed the deposition of trace metals within deposited carbonate material, providing direct evidence of deposition. Figure 2 shows the increase of manganese (Mn) and strontium (Sr), indicating deposition with the highest concentration near the termination of the solution channel shown in Fig. 1. These phenomena can occur during CO₂ injection into carbonate geological formations, whether it is for improved oil recovery (IOR) or greenhouse gas sequestration. In IOR concerns are for injectivity changes while sequestration issues are long-term storage capacity, seal integrity, and injectivity.

Fig. 1. Core segments cut in half longitudinally after the end of the flood.

Fig. 2. Composition of Mn. and Sr. along the core length at the end of the flood.

Lignosulfonate Adsorption on Berea Core and Bentonite Clay

The idea of preflushing a reservoir with cheaper chemicals in order to block the adsorption sites and reduce subsequent surfactant adsorption has been extensively studied and recognized. Lignosulfonate, a cheap paper waste product, was thought to be an effective sacrificial agent as its exciting laboratory experiment results and its successful field application have indicated.

This study examines adsorption tests carried out with calcium lignosulfonate on Berea core and bentonite clay. Circulation experiments were performed to determine the adsorption isotherm of lignosulfonate on Berea core and the effect of temperature and injection rate on adsorption mass. Flow-through experiments were carried out to assess its adsorption and desorption rate. Static adsorption experiments were used to analysis which factors influence lignosulfonate adsorption on Bentonite clay.

The results show that lignosulfonate adsorption isotherm depends on a number of factors such as concentration, mineral composition, temperature, brine strength and composition. In the Berea sandstone core an increase in temperature decreased adsorption mass, see Fig. 3, while an increasing in dissolved solids increased adsorption mass over the study range. Divalent ion and dissolved solids resulted in higher lignosulfonate adsorption on Bentonite clay by ion exchange, see Fig. 4. An increase in injection rate can slightly decrease adsorption mass, Fig. 5. Adsorption

and desorption are not completely reversible. Higher lignosulfonate concentration accompanies higher adsorption rate, and adsorption is a faster process than desorption. The results—that slower post flush rates follow higher effluent concentrations—indicate that the actual adsorption and desorption process occurring in a coreflood appears to be a non-equilibrium process. Stopping and restarting the flow in the experiment was helpful for recognizing lignosulfonate transportation and equilibrium mechanisms.

Fig. 3. Effect of temperature on lignosulfonate adsorption (Berea core).

Fig. 4. Effect of salinity on lignosulfonate adsorption (bentonite clay).

Fig. 5. Effect of injection rate on lignosulfonate adsorption (Berea core, con. =10000mg/l, T=25C).

Determination of CO₂ Foam Stability and Interfacial Tension

During this work period we have reviewed interfacial tension (IFT) measurement methods, reconstructed the apparatus for measuring IFT and stability of high-pressure CO₂ foams, and reexamined how we analyze the test results. A CO₂ foam stability test was conducted in the lab. The results show that the decreasing volume of the foam lower boundary is caused by gravity drainage and the moving of the upper boundary by foam destruction (coalescence). CO₂ foams have a dynamic IFT behavior that covers the period required to saturate the aqueous phase with CO₂ saturation. The bubbles in persistent foams are polyhedral and their drop-sizes are relatively smaller and more homogeneous than those of less stable foams.

For Chaser CD1045™, the foams did not collapse even when the concentrations became lower than its CMC of 0.06 weight % (Fig. 6). But the volume of the foam layer kept decreasing (Fig 7), because there will always be a tendency for liquid to drain due to the force of gravity after foam generation. This liquid will drain by flowing downward through the existing liquid-films, the interior of the lamellae. Eventually the gas bubbles will no longer be even approximately spherical (a wet foam), and relatively planar lamellae will separate polyhedral-shaped bubbles (a dry foam). At this point, capillary forces will become competitive with gravity forces.

Figure 8 shows that some time is required to establish the equilibrium IFT. This is the time required to saturate the brine with CO₂. Bubbles in persistent foams are polyhedral and not spherical. The drop-sizes are relatively smaller and more homogeneous than those of less stable foams.

Fig. 6. Decay of CO₂ foam in CD1045 solution.

Fig. 7. Drainage of CO₂ foam in CD1045 solution.

Fig. 8. Bubble IFT vs. time (CD1045 solution).

Review Meeting – Midland, TX, March 27, 2003

The meeting was attended by 34 individuals. This was not a widely publicized meeting because we wanted it to be a group that was small enough for good and open discussions. The invitations were done by word of mouth and email invitations. Besides the PRRC there were 17 other organizations represented: two governmental (PTTC and DOE/NPTO), three consultant firms, and 12 oil-producing companies, most of whom had CO₂ injection projects (Amerada Hess, Oxy Permian, Bass, Kinder Morgan CO₂, ChevronTexaco, JODCO, Denbury Resources, ExxonMobil, Pure Resources, Anadarko, Marathon Oil, and Energen Resources). Appendix A is the agenda that was used for the meeting. We had invited several engineers to review current field issues in several areas; conformance problems, injectivity changes, and other effects. These were followed by presentations of the PRRC's activities in these areas to understand or alleviate the problem. This was followed by open group discussions.

CONCLUSIONS

Current Work: There are several areas of concentration at this time:

1. Understanding problems related to injectivity changes in WAG processes. This includes both dialogs with field and supervision engineers and laboratory testing. In the

laboratory, we have been examining dissolution and precipitation of solids in reservoir core.

2. Testing and evaluating mixed surfactant systems and lower value components to be used as sacrificial agents to satisfy adsorption requirements in the reservoir.
3. Determining foam stability at reservoir pressure and temperature conditions.
4. Effects of high flow rate at near wellbore conditions.

Accomplishments

1. Completed literature survey and site visits with project personnel to summarize what is perceived as injectivity problems related to the WAG process. This was summarized in the First Annual Report.
2. Laboratory tests completed showing that we could add tracer metals to the brine that would aid in distinguishing between original and new carbonate deposition in a carbonate core. This is a follow-up on earlier findings that indicated precipitation of minerals that are dissolved upstream.
3. Laboratory test to evaluate rock composition, salinity, and temperature on adsorption trends for lignosulfonate.
4. Several presentations and papers accepted for presentations.
5. Project review meeting in Midland, TX attended by 34 individuals representing 18 organizations.

Technology Transfer: Technology/Information Transfer:

1. SPE 80228 "Evaluation of CO₂–Brine–Reservoir Rock Interaction with Laboratory Flow Tests and Reactive Transport Modeling," was presented and included in the proceedings of the SPE International Symposium on Oilfield Chemistry, Houston, 5-8 February, 2003.
2. Project review meeting in Midland, TX attended by 34 individuals representing 14 companies.

REFERENCES

1. Wellman, T.P, Grigg, R.B., McPherson, B.J., Svec, R.K., and Lichtner, P.C.: "Evaluation of CO₂-Brine-Reservoir Rock Interaction with Laboratory Flow Tests and Reactive Transport Modeling," paper SPE 80228 presented at the 2003 SPE Oilfield Chemistry Symposium, Houston, February 5-8.
2. Grigg, R.B., McPherson, B.J., and Svec, R.K.: "Laboratory and Model Tests at Reservoir Conditions for CO₂-Brine-Carbonate Rock Systems Interactions, " prepared for presentation at the DOE/NETL SECOND ANNUAL DOE CARBON SEQUESTRATION CONFERENCE, Washington, D.C., 5-8 May 2003.
3. Grigg, R.B. and Svec, R.K.: "Co-injected CO₂-Brine Interactions with Indiana Limestone," prepared for presentation at the 2003 Symposium of The Society of Core Analysts, 21-24 September, Pau, France.
4. Rogers, J. D. and Grigg, R.B.: "A Literature Analysis of the WAG Injectivity Abnormalities in the CO₂ Process," paper 59329 presented at the 2000 SPE/DOE Improved Oil Recovery Symposium, Tulsa, April 2-5.
5. Svec, R.K. and Grigg, R.B.: "Physical Effects of WAG Fluids on Carbonate Core Plugs," paper SPE 71496 presented at the 2001 SPE Annual Technical Conference and Exhibition, New Orleans, Sept. 30–October 3.

APPENDIX A

PRRC CO₂ Project Meeting – March 27, 2003 – CEED Building Midland/Odessa, Texas

Meeting Agenda

8:30 am – Continental Breakfast

CO₂ Breakthrough Session

9:00 am – Introduction

9:10 am – CO₂ Breakthrough – Field #1

9:30 am – CO₂ Breakthrough – Field #2

9:50 am – PRRC: Low cost mobility control research

10:30 am – Break

11:00 am – Group: General mobility problems, is foam a viable solution option, and what is required to start using or at least testing in the field?

Noon – Lunch at CEED

Injectivity Changes Session

1:00 Introduction

1:10 pm – Injectivity changes – Field #3

1:30 pm – Injectivity changes – Field #4

1:50 pm – PRRC: Dissolution – precipitation studies on dolomite and limestone

2:20 pm – Saturation, relative permeability, & wettability – Field #5

2:45 pm – Break

3:00 pm – PRRC: CO₂ flow behavior

3:15 pm – Group: How to determine causes of injectivity change in the field?

4:15 pm – Wrap up and adjourn