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Summary Annual Report

DOE Contract No DE-AC22-92 BC14886

Investigation of Oil Recovery Improvement by Coupling
an Interfacial Tension Agent and a Mobility Control Agent
in Light Oil Reservoirs

submitted by
Surtek, Inc.

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Anticipated Completion Date: September 30, 1995

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Report for the Period of
October 1994 to September 1995

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I. Objectives of Study

The study will investigate two major areas concerning co-injecting an interfacial tension reduction agent(s) and a mobility control agent into petroleum reservoirs. The first will consist of defining the mechanisms of interaction of an alkaline agent, a surfactant, and a polymer on a fluid-fluid and a fluid-rock basis. The second is the improvement of the economics of the combined technology.

II. Summary of Progress

The first year of "Investigation of Oil Recovery Improvement by Coupling an Interfacial Tension Agent and a Mobility Control Agent in Light Oil Reservoirs" investigation focus was on fluid-fluid studies. The second year of the investigation finalized the fluid-fluid portion of evaluation and began a series of relative permeability and oil recovery coreflood evaluations. Please refer to the prior two Annual Summaries for work performed in these time periods. The third year of the study finished the oil recovery coreflood studies and evaluated different techniques to improve alkaline-surfactant-polymer solution economics.

A partial objective the oil recovery coreflood studies performed in the third year was to determine the effect of rock on alkaline-surfactant-polymer solution oil recovery. Oil recovery efficiency of two alkaline-surfactant-polymer solutions were evaluated in Berea sandstone, J Sand sandstone, and Muddy sandstone core. Oil recoveries varied from 1 to 2% OOIP in Muddy sandstone up to 20-30% OOIP in Berea and J Sand sandstone. SEM and X-ray analysis of the rock indicated the Muddy sandstone had 8 to 10% clay composed mostly of kaolinite and chlorite with some illite and smectite. The Berea and J Sand analysis were essentially identical having 5 to 6% clay composed mostly of kaolinite and illite. Rock composition and the rocks ability to remove interfacial tension active components and mobility control agents from the aqueous solution is a key parameter effecting oil recovery efficiency.

The final major element in the study was to evaluate different methods to improve the economics of the alkaline-surfactant-polymer technology. Parameters which were evaluated were:

- Volume of alkaline-surfactant-polymer solution injected
- Alkali gradient
- Surfactant gradient
- Polymer gradient
- Alkali pre-flush
- Alkali post-flush

Varying the volume of the alkaline-surfactant-polymer solution resulted in the oil recovery decreasing significantly once the injected chemical solution volume dropped below 20% pore volume. Oil recovery costs varied from \$17.44 per barrel with polymer alone to a minimum of \$3.32 with 20% pore volume of alkaline-surfactant-polymer solution. Increasing the volume of alkaline-surfactant-polymer solution to 30% increased oil recovery from 0.101 PV to 0.106 PV with the corresponding increase in per incremental oil recovery costs from \$3.32 to \$4.01. The economic optimum for the J Sand oil and the particular alkaline-surfactant-polymer solution is around 20% pore volume of chemical solution injected.

A different method to reduced the cost of chemicals injected is to decrease one or more of the components concentration during injection. Different decline rates of surfactant concentration over a 30% pore volume injection were evaluated. Oil recoveries dropped as the concentration of surfactant was tapered with the greatest loss of oil recovery efficiency occurring when the rate of concentration decrease in the taper was the greatest. Cost per incremental barrel of oil increased from \$4.01 with no taper to \$7.60. Tapering the surfactant concentration did not improve the alkaline-surfactant-polymer economics due to the loss in oil recovery efficiency.

Since polymer is the either most costly or second most costly component in the alkaline-surfactant-polymer mixture, a polymer taper was evaluated. Tapering the polymer concentration in the polymer drive solution injected after the alkaline-surfactant-polymer solution resulted in a little change in oil recovery and cost per incremental barrel. Increasing the volume of the taper also had no effect on oil recovery. Beginning the polymer taper during injection of the alkaline-surfactant-polymer solution did not change oil recovery when the initial concentration was increased so the mass of polymer injected was equal to the non-tapered solution. In this case, the cost per incremental barrel was not altered.

The last chemical component to be altered was the alkali. A gradient with a higher concentration of alkali than the block alkaline-surfactant-polymer solution was injected. The higher initial concentration of alkali was evaluated because: (1) the solution maintained ultra low interfacial tension values, (2) the rock alkali consumption will be satiated earlier, and (3) an ionic gradient is developed which force the solution to move through optimum phase behavior conditions as the injected solution moves through the reservoir. Oil recoveries increased from 30 to 39% of the waterflood residual oil saturation for the Na_2CO_3 -Petrostep B-100-Flopaam 3330S system and from 20% to 44% of the waterflood residual for the Na_2CO_3 -LXS 420-Flopaam 3330S system. Economics of oil recovery improved from \$4.00 per incremental barrel of oil to \$2.90.

An alkali gradient can be injected as a pre-flush followed by the designed alkaline-surfactant-polymer solution and achieve the same improvement in oil recovery.

However, economics are adversely effected due to the increased mass of chemical injected and time for pre-flush injection.

Injection of an alkaline-polymer solution after the alkaline-surfactant-polymer solution and before the polymer drive solution to counter any chromatographic effects did not improve oil recovery. Economics were adversely effected due to the increased mass of alkali injected.

The final series of corefloods compared the oil recovery efficiency of the alkali gradient in Berea sandstone and J Sand sandstone. Oil recovery efficiency was essentially the same in both types of core, 13 to 15% PV of oil. Cost of chemical per incremental barrel of oil with 30% pore volume of alkaline-surfactant-polymer solution injected were \$3.20 for the Na_2CO_3 -Petrostep B-100-Flopaam 3330S solution and \$2.56 per incremental barrel for the Na_2CO_3 -LXS 420-Flopaam 3330S solution in both types of core.

III. Significant Accomplishments

To keep some continuity with the 1992-93 and 1993-94 work performed for this contract, the accomplishments from the beginning of the contract through 1995 are listed. The accomplishments of the research are:

1992-93 Accomplishments

- Ultra low interfacial tensions can be achieved between 42 degree API crude oil and a variety of low cost chemical solutions.
- Combining an alkaline agent and surfactant produces low interfacial tension values in a synergistic manner.
- Surfactant structure is not a critical factor in producing low interfacial tension. Molecular weight and water solubility are more important factors.
- Alkali type is not a critical factor in producing ultra low interfacial tension values.
- Addition of polymer of any type will alter the interfacial tension. The design of the alkaline-surfactant-polymer solution must account for polymer addition.
- Addition of alkali and surfactant to a polymer solution will reduce solution viscosity.
- Surfactant and polymer interact to affect the solution characteristics. Alkyl aryl sulfates interact with polymer to precipitate from solution, while linear chain surfactants interact with polymer but do not precipitate from solution.

- Surfactant critical micelle concentration is decreased with polymer and alkali addition.
- Surfactant, polymer and alkali all interact in solution. Each component will affect the characteristics expressed by the other components, i.e. apparent viscosity, critical micelle concentration, etc. The components will interact together to express joint characteristics, i.e. low interfacial tension, precipitation from solution.
- Well designed chemical combinations are stable at temperatures up to 170°F for an extended period of time.
- The characteristics expressed by the combined chemical solution, i.e. interfacial tension, apparent viscosity, solution stability, etc, change with increasing temperature.

1993-94 Accomplishments

- Cation type had little effect on the ability of an alkaline-surfactant solution to produce low interfacial tension values but did significantly alter solution stability. Sodium ions produced the most stable solutions.
- Increasing reservoir brine salinity and hardness of up to 60,000 mg/l total dissolved solids adversely affected alkyl aryl sulfonates but improved linear alkyl sulfonates interfacial tension reduction capabilities. Surfactant selection with solution design is reservoir specific.
- Alkali adsorption decreases surfactant retention by rock. When polymer is added to the solution, surfactant adsorption reduction is still observed with linear alkyl surfactants but alkyl aryl surfactants adsorption increases.
- Polymer adsorption decreases with Na_2CO_3 but increases with NaOH . Surfactant causes the polymer to adsorb at a lower rate. Alkali plus polymer results in decreased polymer adsorption.
- Alkali adsorption is not changed when surfactant is added to the solution. When polymer is added either with or without surfactant, Na_2CO_3 adsorption increases while NaOH adsorption decreases.
- Mobility ratio is increased when an interfacial tension agent is injected.
- Addition of polymer to an interfacial tension solution decreases the mobility ratio over the same saturation shift caused by the alkaline-surfactant solution. However, the mobility ratio ultimately increased with polymer addition due to the production of additional oil.

- Incremental oil production was not altered when a waterflood was performed before alkaline-surfactant-polymer injection.
- Simply lowering the interfacial tension to ultra low levels is not sufficient to produce incremental oil.

1994-95 Accomplishments

- Demonstrated that the rock and its composition are critical to the success of an alkaline-surfactant-polymer flood. If chemical adsorption by the rock is high, oil recovery will decrease.
- Integrity of the design chemical solution composition based on the interfacial tension and phase behavior is critical to achieve maximum oil recovery. Either decrease of surfactant or alkali to values outside the ultra low interfacial or decrease of polymer concentration to insufficient values to give adequate mobility control results in loss of oil recovery efficiency.
- Injection of a higher than design concentration of alkali and reducing the concentration in a graded manner to the design concentration improves alkaline-surfactant-polymer oil recovery significantly (over 100% with one of the chemical systems). The graded alkaline slug can be injected either as a pre-flush or as a part of the alkaline-surfactant-polymer solution. A pre-flush has adverse economic considerations due to time and money for injectants which will not produce incremental oil.
- The polymer concentration of the injected fluids can be graded as well. Beginning the polymer concentration gradient in the polymer drive solution does not alter oil recovery but has a minimal effect on economics. If the polymer gradient is started during the alkaline-surfactant-polymer solution, the initial concentration must be increased to maintain oil recovery at maximum levels so economics do not change.
- Decreasing surfactant concentration in a graded manner reduces oil recovery and increases the cost per incremental barrel of oil for the alkaline-surfactant-polymer technology.
- Optimum volume of alkaline-surfactant-polymer solution to inject is between 20 and 30% PV. Oil recoveries begin to asymptote at approximately 20% PV of alkaline-surfactant-polymer injection with 20% PV injected being the most economic.

- Alkaline-surfactant-polymer technology can recover up to 15% PV incremental oil from J Sand oil reservoirs at a chemical cost as low as \$2.56 per barrel.
- Initially oil industry convention was that the alkaline-surfactant-polymer technology was applicable to mid 20 or lower API gravity crude oils. This investigation demonstrated that incremental oil can be produced with mid 40 API gravity oil, disproving the API gravity limitation myth.

IV. **Significance of EOR Research Plan**

The combined injection of an interfacial tension agent and a mobility control agent has the potential of recovering significant amounts of oil beyond a waterflood economically. Combining an alkaline agent and a surfactant allows a wide range of crude oils to be recovered using the combined injected technology.

"Investigation of Oil Recovery Improvement by Coupling an Interfacial Tension Agent and a Mobility Control Agent in Light Oil Reservoirs" is a research program to define the mechanisms of the combined injection technology so that independents and major oil companies will obtain a better understanding of the technology and to gain confidence in the technology. Hopefully with greater understanding and confidence, the technology will be utilized to improve oil recovery from the nation's oil reservoirs.

Significant goals of the research program are:

1992-95 Research Efforts

- To define how the surfactant and alkali interact in a synergistic manner to produce ultra low interfacial tension values. Understanding this interaction will allow laboratory studies to more efficiently design chemical systems which can recover incremental oil and allow numerical simulation programs to more effectively model the technology.
- To define how polymer addition affects the alkali-surfactant interaction and how alkali and surfactant affect solution characteristics expressed by a polymer solution. Understanding this interaction will allow laboratory studies to more efficiently design chemical systems which can recover incremental oil and allow numerical simulation programs to more effectively model the technology.
- To define how the three components interact with the rock when co-injected. Again, better laboratory design and numerical simulation can be developed.

- To define how changes in salinity and cation type and content will affect the fluid-fluid as well as fluid-rock characteristics. Like the prior specified goals, better laboratory design and numerical simulation is the objective.

1994-95 Research Efforts

- Rock-fluid interfaces comprise two thirds of the interfaces which exist in an oil reservoir: oil-rock and water-rock. This makes the rock characteristics and how chemicals interact with the rock a critical factor. How different rock types affect oil recovery will be a key objective.
- After the mechanisms of the fluid-fluid and fluid-rock interactions of the combined injection technology are defined, refinement of alkaline-surfactant-polymer oil recovery economics will be a major objective. The ultimate goal of defining how the process can produce the maximum amount of incremental oil for the lowest cost indicated an alkaline gradient works the best and can produce oil for as low as \$2.56 per incremental barrel.

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