SURTEK

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TECHNICAL PROGRESS 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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Report for the Period of
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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.

This report examines the effect of polymer addition to different combinations of alkaline agents and surfactants. Xanthan gum and polyacrylamide polymers were evaluated. In addition, the effect of alkali and polymer on the critical micelle concentration of different surfactant types was investigated.

II. Summary of Technical Progress

A 42 API gravity crude oil from the Adena Field¹ was selected for the study. Solutions were dissolved in 1,000 mg/l NaCl except where designated.

Interfacial Tension with Alkali and Surfactant - A series of interfacial tension measurements at 72°F were made with 0.1 and 0.2 wt% surfactant in the presence of alkali from 0.0 to 2.0 wt%. Surfactant structures and molecular weights were varied. Five alkaline agents tested were Na_2CO_3 , NaHCO_3 , Na_3PO_4 , Na_2HPO_4 , and NaOH . Alkali addition alone did not reduce the interfacial tension. Na_3PO_4 is the exception and did achieve interfacial tension reductions of up to 400 fold. The interfacial tension reduction with surfactant in the absence of alkali ranged from less than 2 fold to in excess of 3,200 fold. Addition of alkali to the surfactant solutions lowered the interfacial tension values for all surfactants tested. Ultra low interfacial tension values of 0.001 dyne/cm or less were measured for a number of the surfactants. Surfactant structure and alkali type resulted in different interfacial tension reduction characteristics. Differences were also observed with alkali concentration for each surfactant and alkali type.

Effect of Temperature on Interfacial Tension - Selected alkaline-surfactant solutions had the interfacial tension determined at 125°F and 180°F and the data compared with the 72°F data. Changes in interfacial tension were observed with the various alkaline-surfactant solutions. How the interfacial tension changed with temperature was generally consistent for the different alkaline agents for a single surfactant. No consistent trend was observed for the different surfactants.

Effect of Polymer on Interfacial Tension of Alkaline-Surfactant Solutions - A xanthan gum and polyacrylamide polymer were added to selected solutions of alkali and surfactant at 400, 800 and 1,200 mg/l. Each of the 5 alkaline types were tested with a linear alkyl aryl sulfonate, a branched alkyl aryl sulfonate, and a alpha olefin sulfonate. With the alkali concentrations tested the interfacial tension values

increased with the addition of polymer. Increasing the polymer concentration above 400 mg/l resulted in only minimal changes of interfacial tension values. Polymer type and alkali type did not affect the alteration of interfacial tension values.

Effect of Alkali and Surfactant on Polymer Solutions Viscosity - The effect of blending alkali, surfactant and alkali plus surfactant on polyacrylamide, xanthan gum, and hydroxyethyl cellulose was monitored. As expected the polymer solution viscosities decreased with just alkali addition for each of the three polymers at 72°F. At 180°F polyacrylamide and hydroxyethyl cellulose solution viscosities decreased as well but the xanthan gum solution viscosities increased. Addition of surfactant to the alkaline-polymer or polymer solutions resulted in increases and decreases of viscosity which were dependent of surfactant type for polyacrylamide and hydroxyethyl cellulose. The alkyl aryl sulfonate and alpha olefin sulfonate significantly reduced the viscosity of the polyacrylamide and hydroxyethyl cellulose at 180°F with a slight reduction of solution viscosity at 72°F. The linear alkyl aryl sulfonate addition to the polyacrylamide solution increased the solution viscosity significantly at 180°F and to a lesser extent at 72°F. Xanthan gum solution viscosities increased with branched alkyl aryl sulfonate and linear alkyl aryl sulfonate addition but not with alpha olefin sulfonate. With alkali addition to the polymer solution, the linear alkyl aryl sulfonate and alpha olefin sulfonate addition increased xanthan gum solution viscosity while branched alkyl aryl sulfonate did not. In both the polymer and alkaline-polymer solutions, surfactant addition effects were more pronounced at 72°F than at 180°F.

The intrinsic viscosity and hydrodynamic radius was calculated from the apparent viscosity data.² The data for sodium carbonate are listed in the following table.

<u>Polymer type</u>	<u>Alkaline Agent</u>	<u>Surfactant Type</u>	<u>$[\eta]$ ml/g</u>	<u>hydrodynamic radius micron</u>
Xanthan Gum	none	none	6,370	0.256
	none	0.1 wt% LXS 420	7,969	0.276
	none	0.2 wt% LXS 420	10,801	0.305
	none	0.5 wt% LXS 420	10,134	0.299
	2 wt% Na ₂ CO ₃	none	8,535	0.282
	2 wt% Na ₂ CO ₃	0.1 wt% LXS 420	3,117	0.202
	2 wt% Na ₂ CO ₃	0.2 wt% LXS 420	2,287	0.182
	2 wt% Na ₂ CO ₃	0.5 wt% LXS 420	3,547	0.211

<u>Polymer type</u>	<u>Alkaline Agent</u>	<u>Surfactant Type</u>	<u>[η] ml/g</u>	<u>hydrodynamic radius micron</u>
Polyacrylamide	none	none	21,710	0.556
	none	0.1 wt% LXS 420	15,621	0.498
	none	0.2 wt% LXS 420	12,290	0.460
	none	0.5 wt% LXS 420	12,208	0.459
	2 wt% Na ₂ CO ₃	none	4,685	0.333
	2 wt% Na ₂ CO ₃	0.1 wt% LXS 420	3,137	0.292
	2 wt% Na ₂ CO ₃	0.2 wt% LXS 420	3,118	0.291
	2 wt% Na ₂ CO ₃	0.5 wt% LXS 420	3,726	0.309
hydroxyethyl cellulose	none	none	2,293	0.119
	none	0.1 wt% LXS 420	2,025	0.114
	none	0.2 wt% LXS 420	2,144	0.116
	none	0.5 wt% LXS 420	2,269	0.118
	2 wt% Na ₂ CO ₃	none	1,376	0.100
	2 wt% Na ₂ CO ₃	0.1 wt% LXS 420	1,067	0.092
	2 wt% Na ₂ CO ₃	0.2 wt% LXS 420	1,162	0.095
	2 wt% Na ₂ CO ₃	0.5 wt% LXS 420	1,259	0.097

Critical Micelle Concentration - Critical micelle concentrations of 0.02 to 0.06 wt% active were measured for alpha olefin, linear alkyl aryl, branch alkyl aryl, and internal olefin sulfonates. Addition of Na₂CO₃, NaOH, NaHCO₃, Na₃PO₄, and Na₂HPO₄ to the surfactant solution decreased the critical micelle concentration to 0.005 to 0.02 wt%. Addition of polyacrylamide and xanthan gum polymers to the surfactant solutions appeared to decrease the critical micelle concentration like alkali addition but did not alter the critical micelle concentration of the alkaline plus surfactant solution.

Effect of Addition of Sodium Chloride on Interfacial Tension, Critical Micelle Concentration, and Polymer Solution Viscosity - Addition of sodium chloride to the surfactant plus alkali solutions resulted in the critical micelle concentration decreasing until the surfactant precipitates from solution. Sodium chloride and alkali addition affecting the critical micelle concentration in a similar manner.

Sodium chloride addition to the alkaline plus surfactant solutions generally showed an increase of the interfacial tension. As the sodium chloride concentration increased, the alkyl aryl sulfonate surfactants precipitated from solution. Increasing the temperature resulted solution stability at higher sodium chloride concentrations. The data for addition of 0.5 to 2.0 wt% NaOH plus surfactant is listed in the following table.

Interfacial Tension (dyne/cm) of NaOH plus Surfactant Solutions							
Surfactant	Temperature °F	Sodium Chloride Concentration (mg/l)					
		1,000	5,000	10,000	15,000	20,000	30,000
alpha olefin	72	0.167	0.159	0.161	0.143	0.108	0.112
sulfonate	125	0.095	0.218	0.160	0.152	0.154	0.158
molecular wt = 314	170	0.103	0.190	0.326	0.166	0.192	0.179
internal olefin	72	0.148	0.116	0.105	0.081	0.079	0.067
sulfonate	125	0.072	0.128	0.161	0.175	0.166	0.100
molecular wt = 348	170	0.060	0.197	0.148	0.135	0.142	0.149
branched alkyl	72	0.008	0.075	0.154	ppt	ppt	ppt
toluene sulfonate	125	0.001	0.014	0.054	0.054	0.080	ppt
molecular wt = 430	170	0.001	0.009	0.009	0.022	0.036	0.103
linear alkyl	72	0.105	0.281	0.256	ppt	ppt	ppt
toluene sulfonate	125	0.019	0.284	0.243	0.169	ppt	ppt
molecular wt = 446	170	0.014	0.184	0.153	0.126	0.045	ppt
linear alkyl	72	0.008	0.040	0.104	0.008	0.002	ppt
aryl sulfonate	125	0.105	0.006	0.054	0.036	0.024	0.004
molecular wt = 370	170	0.046	0.003	0.002	0.048	0.025	0.005
linear alkyl	72	0.002	0.303	0.416	0.464	ppt	ppt
aryl sulfonate	125	0.014	0.188	0.350	0.409	0.376	0.576
molecular wt = 420	170	0.046	0.003	0.002	0.048	0.025	0.005
branched alkyl	72	0.007	0.003	0.001	ppt	ppt	ppt
aryl sulfonate	125	0.001	0.012	0.009	ppt	ppt	ppt
molecular wt = 410	170	0.001	0.033	0.018	ppt	ppt	ppt

* - ppt = precipitated

The effect of sodium chloride addition to either a polyacrylamide or surfactant plus polyacrylamide solution resulted in a decrease in polymer solution viscosity. When alkali was dissolved in the polymer or surfactant plus polymer solution, the solution viscosity did not change significantly until the sodium chloride concentration approached 30,000 mg/l. Then the apparent viscosity decreased. The difference between the alkaline plus surfactant plus polymer solutions is that with alkali added to the solution it becomes stable at a lower salinity. The data for polyacrylamide with Na_2CO_3 and a linear alkyl aryl sulfonate is listed in the following table.

800 mg/l Polyacrylamide Solution Apparent Viscosity at 72°F (cp)							
Sodium Chloride Concentration (mg/l)							
Alkali	Surfactant	1,000	5,000	10,000	15,000	20,000	30,000
none	none	26.2	11.4	8.2	6.9	6.4	5.6
2% Na ₂ CO ₃	none	5.4	6.1	6.0	5.6	5.5	5.4
2% Na ₂ CO ₃	0.1% LXS 420	6.1	6.1	6.1	5.9	5.6	ppt*
2% Na ₂ CO ₃	0.2% LXS 420	6.1	6.1	6.1	6.1	ppt*	ppt*
2% Na ₂ CO ₃	0.5% LXS 420	6.6	6.4	6.4	6.8	ppt*	ppt*
none	0.1% LXS 420	26.6	11.6	8.4	7.0	6.5	6.0
none	0.2% LXS 420	27.1	12.3	8.7	7.2	6.8	6.6
none	0.5% LXS 420	28.4	13.9	9.4	7.8	7.9	8.0

* - ppt = material precipitated from solution

Xanthan gum solutions demonstrated a different trend. As the salinity was increased, sodium chloride addition increased the xanthan gum solution viscosity with salinity at 180°F but have little effect on the solution viscosity at 72°F. Xanthan gum plus surfactant showed similar characteristics. Alkali addition to the xanthan gum or surfactant plus xanthan gum solutions did not alter the sodium chloride effect. Like polyacrylamide solutions, the solutions were unstable at lower sodium chloride concentrations when xanthan gum was added to the solution. The effect of sodium chloride addition to the hydroxyethyl cellulose solutions was similar to the xanthan gum solutions.

Solution Long Term Stability - NaOH, Na₂CO₃, and Na₃PO₄ were mixed with a linear alkyl aryl sulfonate, a branched alkyl aryl sulfonate, and an alpha olefin sulfonate in 500, 1,000, and 1,500 mg/l polyacrylamide solutions. The solutions were aged at 72, 92, 132, and 180°F for 50 days. The alkaline solutions and the alkaline plus surfactant solutions were stable. Addition of polyacrylamide polymer to the linear and branched alkyl aryl sulfonates plus alkali solutions resulted in solution instability at the higher polymer concentrations and at higher surfactant concentrations. The following table shows the data for Na₂CO₃ plus a brached alkyl aryl sulfonate solution.

Polyacrylamide Solution Stability*						
Temperature °F						
Alkali	Surfactant	Polyacrylamide	72	92	132	180
1% Na ₂ CO ₃	none	none	S	S	S	S
1% Na ₂ CO ₃	0.1% Petro B-100	none	S	S	S	S
1% Na ₂ CO ₃	0.2% Petro B-100	none	S	S	S	S
1% Na ₂ CO ₃	0.5% Petro B-100	none	S	S	S	S

Polyacrylamide Solution Stability*						
Alkali	Surfactant	Polyacrylamide	Temperature °F			
			72	92	132	180
1% Na ₂ CO ₃	none	500	S	S	S	S
1% Na ₂ CO ₃	0.1% Petro B-100	500	S	S	S	S
1% Na ₂ CO ₃	0.2% Petro B-100	500	S	S	S	I
1% Na ₂ CO ₃	0.5% Petro B-100	500	SI	SI	S	I
1% Na ₂ CO ₃	none	1,000	S	S	S	S
1% Na ₂ CO ₃	0.1% Petro B-100	1,000	S	S	S	S
1% Na ₂ CO ₃	0.2% Petro B-100	1,000	S	S	S	I
1% Na ₂ CO ₃	0.5% Petro B-100	1,000	S	S	S	I
1% Na ₂ CO ₃	none	1,500	S	S	S	S
1% Na ₂ CO ₃	0.1% Petro B-100	1,500	S	S	S	S
1% Na ₂ CO ₃	0.2% Petro B-100	1,500	SI	I	I	I
1% Na ₂ CO ₃	0.5% Petro B-100	1,500	I	I	I	I

* - S = stable solution, SI = slightly instable solution, and I = instable solution

A linear alkyl aryl sulfonate demonstrated the same relationship between surfactant and polyacrylamide for solutions stability. An alpha olefin sulfonate demonstrated no solution instability at any polymer or surfactant concentration.

III. Continued Evaluations

Future studies will be to investigate the effect of increasing cation as well as increasing salinity with cation on the interfacial tension, apparent viscosity, and critical micelle concentration. Rock-fluid interactions and the effect of chemical composition and rock type will be investigated.

IV. References/Publications

1. Holm, L.W.: "Propane-Gas-Water Miscible Floods in Watered-Out Areas of the Adena Field, Colorado," J. Pet. Tech., October 1972, pages 1264 to 1270.
2. Sorbie, K.S.: Polymer-Improved Oil Recovery, Blackie, Glasgow and London, CRC Press Inc., Boca Raton, Florida, 1991, pages 45-48.

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