Coupling the Alkaline-Surfactant-Polymer Technology and
The Gelation Technology to Maximize Oil Production

Semi-Annual Technical Progress Report

October 1, 2003
To
March 31, 2004

Malcolm Pitts, Surtek
Jie Qi, Surtek
Dan Wilson, Surtek
Phil Dowling, Surtek

May 2004

Award Number DE-FC26-03NT15411

Surtek, Inc.
1511 Washington Avenue
Golden, Colorado 80401

Disclaimer

“This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, produce, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.”

Abstract

Gelation technologies have been developed to provide more efficient vertical sweep efficiencies for flooding naturally fractured oil reservoirs or more efficient areal sweep efficiency those with high permeability contrast “thief zones”. The field proven alkaline-surfactant-polymer technology economically recovers 15% to 25% OOIP more oil than waterflooding in the swept pore space of an oil reservoir. However, alkaline-surfactant-polymer technology is not amenable to the naturally fractured reservoirs or those with thief zones because much of the injected solution bypasses the target pore space containing oil. The objective of this work is to investigate whether combining these two technologies could broaden the applicability of alkaline-surfactant-polymer flooding into these reservoirs.

Fluid-fluid interaction with different gel chemical compositions and alkaline-surfactant-polymer solution with pH values ranging from 9.2 to 12.9 have been tested. Aluminum-polyacrylamide gels are not stable to alkaline-surfactant-polymer solutions at any pH. Chromium – polyacrylamide gels with polymer to chromium ion ratios of 25 or greater were stable to alkaline-surfactant-polymer solutions if solution pH was 10.6 or less. When the polymer to chromium ion was 15 or less, chromium-polyacrylamide gels were stable to alkaline-surfactant-polymer solutions with pH values up to 12.9. Chromium-xanthan gum gels were stable to alkaline-surfactant-polymer solutions with pH values of 12.9 at the polymer to chromium ion ratios tested. Silicate-polyacrylamide, resorcinol-formaldehyde, and sulfomethylated resorcinol-formaldehyde gels were also stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9. Iron-polyacrylamide gels were immediately destroyed when contacted with any of the alkaline-surfactant-polymer solutions with pH values of 9.2 to 12.9.

Table of Contents

Disclaimer	2
Abstract	3
Table of Contents	4
List of Figures	5
Introduction	6
Executive Summary	6
Experimental	6
Results and Discussion	8
Gel Formation	8
Stability of Gels to Alkaline-Surfactant-Polymer Solutions	11
Conclusions	14
References	15

List of Figures

Figure	Title
1	Aluminum-Polyacrylamide Gel in 0.1% Na ₂ SO ₄ Stability with ASP Solutions
2	Aluminum-Polyacrylamide Gel in 1.0% NaCl Stability with ASP Solutions
3	Chromium (III)-Polyacrylamide Gel in 0.1% Na ₂ SO ₄ Stability with ASP Solutions
4	Chromium (III)-Polyacrylamide Gel in 0.1% Na ₂ SO ₄ Stability with ASP Solutions
5	Chromium (III)-Xanthan Gum Gel in 0.1% Na ₂ SO ₄ Stability with ASP Solutions
6	Silicate-Polyacrylamide Gel in 0.1% Na ₂ SO ₄ Stability with ASP Solutions
7	Resorcinol-Formaldehyde Gel in 0.1% Na ₂ SO ₄ Stability with ASP Solutions
8	Sulfomethylated Resorcinol-Formaldehyde Gel in 0.1% NaCl Stability with ASP

Introduction

Gelation technologies provide more efficient vertical sweep efficiencies for flooding naturally fractured oil reservoirs or more efficient areal sweep efficiency for those with high permeability contrast “thief zones”. The field proven alkaline-surfactant-polymer technology economically recovers 15% to 25% OOIP more oil than waterflooding in the swept pore space of an oil reservoir. However, alkaline-surfactant-polymer technology is not amenable to the naturally fractured reservoirs or those with thief zones because much of the injected solution bypasses the target pore space containing oil. The objective of this work is to investigate whether combining these two technologies could broaden the applicability of alkaline-surfactant-polymer flooding.

Executive Summary

Aluminum-polyacrylamide and iron-polyacrylamide gels were not stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.6. Chromium-polyacrylamide, chromium-xanthan gum, silicate-polyacrylamide, resorcinol-formaldehyde, and sulfomethylated resorcinol-formaldehyde gels were stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.6. Chromium-polyacrylamide gels with high polymer to chromium ion ratio of 25 or greater were not stable with alkaline-surfactant-polymer solutions greater than 10.6. Stability evaluations consisted of layering alkaline-surfactant-polymer solutions over formed gels. Stability of gel to flowing alkaline-surfactant-polymer solutions in corefloods will be performed as the next phase of the study.

Experimental

Chemicals were dissolved either in 0.1wt% sodium sulfate or 1.0 wt% sodium chloride.

Aluminum citrate-Polyacrylamide solutions were mixed in the above brine solutions at varying concentration ratios. Polyacrylamide stock solution was made prior to blending with aluminum citrate. Aluminum citrate was WaterCut 677 (4.3% aluminum ion) supplied by Tiorco, Inc. Polyacrylamide polymers evaluated varied in degree of hydrolysis as shown in the following Table 1.

Table 1
Polyacrylamide Polymers Used in Gelation Studies

<u>Polymer Type</u>	<u>Degree of Hydrolysis</u>	<u>Supplier</u>
AN 905	5%	SNF Floerger
AN 923	23%	SNF Floerger
Watercut 204	7%	Tiorco, Inc.
HiVis 350	30%	Tiorco, Inc.

Chromium acetate-Polyacrylamide solutions were mixed identically to the aluminum citrate-polyacrylamide solutions. Chromium acetate was Watercut 684 (10.3% Chromium ion) supplied by Tiorco, Inc. Watercut 204 was the polymer.

Chromium (III)-xanthan gum solutions were mixed identically to the aluminum citrate-polyacrylamide solutions. Xanthan gum was Flopaam 4800 supplied by SNF Floerger. Chromium (III) was chromium trichloride hexahydrate.

Silicate based gels were developed according to Lakatos et.al.¹ Polyacrylamide was AN 923. Colloidal silicate was Ludox SM from Grace Davison. Calcium (II) was calcium dichloride dihydrate. Calcium chloride, polyacrylamide, and Ludox SM were mixed as separate stock solutions and then mixed as appropriate.

Mixing ferric trichloride, polyacrylamide, hydrochloric acid and sodium hydroxide developed iron hydroxide based gels as described by Lakatos.² Ferric chloride and hydrochloric acid were mixed in a separate stock solution from sodium hydroxide and polyacrylamide. Four polymers tested are listed in Table 1.

Resorcinol-formaldehyde and sulfomethylated resorcinol-formaldehyde gels were developed as described by Zhuang et.al.³ Stock solutions were mixed as appropriate. pH was adjusted to 9 with NaOH immediately upon mixing.

Alkaline-surfactant-polymer solutions were developed by mixing sodium bicarbonate, sodium carbonate, and sodium hydroxide at appropriate concentrations with 0.06 wt% active ORS-46HF and 1300 mg/L Alcoflood 1275. Alcoflood 1275, a 30% hydrolyzed polyacrylamide, was supplied by Ciba Specialty Chemicals. pH of alkaline-surfactant-polymer solutions varied from 9.0 to 12.9 as shown in Table 2. Ionic strength of all solutions is 0.25.

Table 2
Alkaline-Surfactant-Polymer Solution Composition and pH

Solution Number	NaHCO ₃ wt%	Na ₂ CO ₃ wt%	NaOH wt%	ASP Dissolved in	ASP Dissolved in
				1.0 wt% NaCl pH	0.1 wt% Na ₂ SO ₄ pH
1	2.10	0.00	0.00	9.21	9.00
2	1.68	0.18	0.00	9.38	9.09
3	1.26	0.35	0.00	9.49	9.39
4	0.84	0.53	0.00	9.68	9.70
5	0.42	0.71	0.00	9.97	10.10
6	0.00	0.89	0.00	10.56	11.21
7	0.00	0.71	0.20	12.27	12.48
8	0.00	0.53	0.40	12.62	12.68
9	0.00	0.35	0.60	12.78	12.77
10	0.00	0.18	0.80	12.86	12.81
11	0.00	0.0	1.00	12.94	12.84

All inorganic salts were analytical grade. All solutions were aged at ambient temperature. Solution 11 is the alkaline-surfactant-polymer formulation injected into the Mellott Ranch Field in Wyoming.

Gels were described as shown listed Table 3.

Table 3
Gel Identification

<u>Gel Type</u>	<u>Gel Description</u>
no gel	gel solution exhibits same viscosity as polymer solution
flowing gel	gel solution easily flows and solution viscosity is visually greater than original polymer solution
tonguing gel	solution flows and forms a thin, long tongue when bottle is tilted
rigid tonguing gel	solution flows with resistance and forms a wide, short tongue when bottle is titled.
rigid gel	gel does not flow when bottle is tipped but does deform
hard gel	gel does not flow and is not deformed when bottle is tipped

Results and Discussion

Gel Formation

Gels were formed with all gel systems. Colloid dispersion aluminum citrate-polyacrylamide gels were the first series of gels evaluated. HiVis 350 was mixed with aluminum citrate in ratios of 1:1, 1:2, 1:3, and 1:4 (as aluminum). Polymer concentrations were 300, 600, and 900 mg/l. Flowing gels were observed with all mixtures when dissolved in 1.0 wt% NaCl. When dissolved in 0.1 wt% Na₂SO₄, no gels formed.

A tonguing gel was developed with aluminum citrate when the polymer was switched to AN 905 and both polymer and aluminum citrate concentrations were increased. Tonguing gels were formed when AN 905 polymer concentrations were 3,000 mg/l or greater and the aluminum concentration was 0.25 to 1.67% that of the polymer. Syneresis was observed with all gelled solutions.

Chromium-polyacrylamide gels formed tonguing to rigid gels. Table 4 lists how gel type varied with chemical concentration and dissolution water.

Table 4
Chromium (III) – Polyacrylamide Gel Formation

Watercut 204			
Concentration	Ratio	Gel Description	
<u>mg/L</u>	<u>WC204:Cr (III)</u>	<u>1.0 wt% NaCl</u>	<u>0.1 wt% Na₂SO₄</u>
3,000	30:1 to 50:1	flowing gel	flowing gel
5,000	30:1 and 35:1	rigid tonguing gel	tonguing gel
5,000	40:1 to 50:1	tonguing gel	flowing gel
7,500	5:1 to 15:1	rigid gel	rigid tonguing gel
7,500	20:1 to 35:1	rigid tonguing gel	tonguing gel
7,500	40:1 to 50:1	tonguing gel	tonguing gel

Chromium (III) – polyacrylamide gels showed little syneresis over a two to four weeks.
Chromium-xanthan gum gels showed similar trends as listed in Table 5.

Table 5
Chromium (III) – Xanthan Gum Gel Formation

Flopaam 4800			
Concentration	Ratio	Gel Description	
<u>mg/L</u>	<u>WC204:Cr (III)</u>	<u>1.0 wt% NaCl</u>	<u>0.1 wt% Na₂SO₄</u>
1,000	8:1 to 10:1	no gel formed	flowing gel
1,000	12:1 to 20:1	no gel formed	no gel formed
2,000	8:1 and 10:1	tonguing gel	rigid tonguing gel
2,000	12:1 and 15:1	flowing gel	flowing gel
2,000	18:1 and 20:1	no gel formed	no gel formed
3,000	8:1 to 10:1	rigid tonguing gel	rigid gel
3,000	12:1 to 15:1	tonguing gel	rigid tonguing gel
3,000	18:1 to 20:1	flowing gel	flowing gel
4,000	8:1	rigid gel	rigid gel
4,000	10:1 to 12:1	rigid tonguing gel	rigid gel
4,000	15:1 to 18:1	tonguing gel	rigid tonguing gel
4,000	20:1	flowing gel	tonguing gel
5,000	8:1 to 10:1	rigid gel	rigid gel
5,000	12:1 to 15:1	rigid tonguing gel	rigid gel
5,000	18:1 to 20:1	tonguing gel	rigid tonguing gel
6,000	8:1 to 12:1	rigid gel	hard gel
6,000	15:1 to 20:1	rigid tonguing gel	hard gel
7,000	8:1 to 20:1	rigid gel	hard gel
8,000	8:1 to 20:1	rigid gel	hard gel

Some degree of syneresis was observed after four weeks with most chromium (III) – xanthan gum gels. When dissolved in 1.0 wt% NaCl, lower polymer and chromium concentration gels showed little syneresis while higher concentration gels demonstrated significant syneresis. When dissolved in 0.1 wt% Na₂SO₄, high concentration polymer and chromium ion gels showed little syneresis and low concentration gels did not shrink.

Silicate based solutions formed rigid gels if the Ludox SM concentration was 20,000 mg/L or greater, irrespective of polymer concentration. Polymer concentrations (AN 923) varied from 250 to 2,000 mg/l. Calcium chloride concentration was constant at 1000 mg/l. Gels were hard gels and no syneresis was observed.

Iron hydroxide solutions formed gels at limited iron, hydroxide, and polymer concentrations (AN 905 and Watercut 204) when dissolved in 1.0 wt% NaCl. Flowing and tonguing gels were formed at polymer concentrations of 5,000 mg/l at Fe (III) concentrations of 10 to 20 mg/l. No gels formed at lower polymer concentrations. Syneresis was not observed but gel solutions viscosity reduced as gels aged.

Resorcinol-formaldehyde gels formed hard gels when dissolved in 1.0 wt% NaCl but failed to form in 0.1 wt% Na₂SO₄. Gels formed at pH 9 but not at higher pHs at resorcinol concentrations of 1.0% or greater at formaldehyde concentrations of 0.85 wt% or greater. Syneresis was observed with all gels. Sulfomethylated resorcinol-formaldehyde formed rigid gels in both 1.0 wt% NaCl and in 0.1 wt% Na₂SO₄. Sulfomethylated resorcinol-formaldehyde gels formed at pH 9, 10 and 11 and at concentrations of sulfomethylated resorcinol of 1.00 % or greater with at sulfomethylated resorcinol: formaldehyde ratio of 1:1.7. No syneresis was observed with any of

Figure 1 Aluminum-Polyacrylamide Gel in 0.1% Na₂SO₄ Stability with ASP Solutions

Figure 2 Aluminum-Polyacrylamide Gel in 1.0% NaCl Stability with ASP Solutions

the sulfomethylated resorcinol-formaldehyde gels.

Stability of Gels to Alkaline-Surfactant-Polymer Solutions

Alkaline-surfactant-polymer solutions listed in Table 2 were layered over an equal volume of stable gel and allowed to age for 19 to 40 days. Gel stability was periodically monitored visually and mechanically. Mechanical stability was measured by determining if a gel would or would not be penetrated by a cylinder weighing up to 10 g.

Aluminum-polyacrylamide gels were not stable to alkaline-surfactant-polymer solutions when in contact for 24 days. This was true whether the gels were the flowing colloidal dispersion, low polymer concentration gel or the higher concentration polymer and aluminum tonguing gels. Figure 1 shows a flowing aluminum-polyacrylamide gel dissolved in 0.1% Na_2SO_4 stability when contacting alkaline-surfactant-polymer solutions with pH values from 9.2 to 12.9 for 24 days. All gels were unstable to the alkaline-surfactant-polymer solutions. Stability of the same gel mixture but dissolved in 1.0% NaCl is shown in Figure 2. Note the aluminum-polyacrylamide gels are less stable with the lower pH solutions. Similar trends were observed at 3,000 mg/l AN 905 and higher aluminum concentrations.

Chromium-polyacrylamide gels showed instability to alkaline-surfactant-polymer solutions of pH 10.6 and above when the polymer:chromium ion concentration ratio was 25 or greater. A

Figure 3 Chromium (III)-Polyacrylamide Gel in 0.1% Na_2SO_4 Stability with ASP Solutions

Figure 4 Chromium (III)-Polyacrylamide Gel in 0.1% Na_2SO_4 Stability with ASP Solutions

polymer:chromium concentration ratio of 15 or less was stable to alkaline-surfactant-polymer pH up to 12.9. Figures 3 and 4 depict unstable and stable chromium:polyacrylamide gel systems. Figure 3 is a tonguing gel and Figure 4 is a rigid tonguing gel.

Chromium:xanthan gum gel were stable to up to pH 12.9 alkaline-surfactant-polymer solutions dissolved in either 0.1% Na_2SO_4 or 1.0% NaCl for 19 days. Gels were either tonguing or rigid tonguing gels (3,000 and 5,000 mg/L xanthan gum, respectively). Figure 5 shows the data for a rigid tonguing chromium:xanthan gum gel. Other stable gel types tested for stability to alkaline-surfactant-polymer solutions ranged from flowing to hard gels.

Silicate-polyacrylamide gels were stable to alkaline-surfactant-polymer solutions over a pH range of 9.2 to 12.9. Ludox SM (silicate) concentrations of 30,000 and 40,000 mg/l were tested with 250 mg/l AN 923 polymer. The lower concentration of Ludox SM showed some gel degradation while the higher concentration was unchanged. Gels were hard gels. Figure 6 shows the 40,000 mg/l Ludox SM data.

Figure 5 Chromium (III)-Xanthan Gum Gel in 0.1% Na_2SO_4 Stability with ASP Solutions

Figure 6 Silicate-Polyacrylamide Gel in 0.1% Na_2SO_4 Stability with ASP Solutions

Iron (III): polyacrylamide gels were not stable to any of the alkaline-surfactant-polymer solutions. Gels immediately broke up upon contact with the alkaline-surfactant-polymer solutions. A 5,000 mg/l Watercut 205 plus 15 mg/l ferric chloride tonguing gel was tested.

All resorcinol-formaldehyde and sulfomethylated resorcinol-formaldehyde gels were stable to alkaline-surfactant-polymer solutions from pH 9.2 to 12.9 for forty days. Gels were dissolved in 0.1% Na₂SO₄ and 1.0% NaCl. Gels were classified as hard. Figures 7 and 8 depict typical stability performance. Resorcinol-formaldehyde and sulfomethylated resorcinol-formaldehyde gels show slight softening of the gel at pH 12.8 and above at low formaldehyde concentration (1.7%). Resorcinol-formaldehyde gels did not show syneresis when mixed with alkaline-surfactant-polymer solutions having a pH greater than 12.5 but syneresis was observed with solutions having a pH less than 12.5. Sulfomethylated resorcinol formaldehyde gels did not synerese with any of the alkaline-surfactant-polymer solutions.

Figure 7 Resorcinol-Formaldehyde Gel in 0.1% Na₂SO₄ Stability with ASP Solutions

Figure 8 Sulfomethylated Resorcinol-Formaldehyde Gel in 0.1% NaCl Stability with ASP

Conclusions

1. Aluminum-polyacrylamide gels, either at low polymer and aluminum concentration or at high polymer and aluminum concentration, were not stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9.
2. Chromium-polyacrylamide gels were stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9 when the polymer to chromium ion ratio was 15 or less. At polymer to chromium ion ratio of 25 or greater, chromium-polyacrylamide gels were not stable to alkaline-surfactant-polymer solutions with pH values of 12 or greater.
3. Chromium-xanthan gum gels were stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9 at the polymer to chromium ion concentration ratios tested.
4. Iron-polyacrylamide gels were not stable to alkaline-surfactant-polymer solutions regardless of pH.
5. Silicate-polyacrylamide gels were stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9.
6. Resorcinol-formaldehyde and sulfomethylated resorcinol-formaldehyde gels were stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9.

References

1. Lakatos, I., Lakatos-Szabo, J., Tiszai, G., Palasthy, G., Kosztin, B., Tromboczky, S., Bodola, M., Pattman-Farkas, G.: "Application of Silicate-Based Well Treatment Techniques at the Hungarian Oil Fields," SPE 56739 presented at the 1999 SPE Annual Technical Conference and Exhibition held in Houston, TX 3-6 October 1999.
2. Lakatos, I., Lakatos-Szabo, J., Koszin, B., Palasthy, G., and Kristof, P.: "Application of Iron-Hydroxide-Based Well Treatment Techniques at the Hungarian Oil Fields," SPE 59321 presented at the 2000 SPE/DOE Improved Oil Recovery Symposium held in TulsaOK, 3-5 April 2000.
3. Zhuang, Y., Pandey, S.N., McCool, C.S., and Whllhite, G..P.: "Permeabilty Modification Using Sulfomethylated Resorcinol-Formaldehyde Gel System," SPE 37245 presented at the 1997 SPE International Symposium on Oilfield Chemistry held in Houston, TX 18-21 February 1997.