

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

Topical Report
Gel Stability to Alkaline-Surfactant-Polymer Solutions

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Abstract

Gelation technologies have been developed to provide more efficient vertical sweep efficiencies for flooding naturally fractured oil reservoirs or reservoirs with different sand lenses with high permeability contrast. The field proven alkaline-surfactant-polymer technology economically recovers 15% to 25% OOIP more crude oil than waterflooding from swept pore space of an oil reservoir. However, alkaline-surfactant-polymer technology is not amenable to naturally fractured reservoirs or reservoirs with high permeability contrast zones because much of injected solution bypasses target pore space containing oil. This work investigates whether combining these two technologies could broaden 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 ranging from 9.2 to 12.9.

Gel solutions under dynamic conditions of linear corefloods showed similar stability to alkaline-surfactant-polymer solutions as in the fluid-fluid analyses with the exception of the xanthan gum-chromium acetate gels. Aluminum-polyacrylamide flowing gels are not stable to alkaline-surfactant-polymer solutions of either pH 10.5 or 12.9, either in linear corefloods or in dual separate radial core, common manifold corefloods. Chromium acetate-polyacrylamide flowing and rigid tonguing gels are stable to subsequent alkaline-surfactant-polymer solution injection. Rigid tonguing chromium acetate-polyacrylamide gels maintained permeability reduction better than flowing chromium acetate-polyacrylamide gels. Chromium acetate gels were stable to injection of alkaline-surfactant-polymer solutions at 72°F, 125°F and 175°F in linear corefloods. Chromium acetate-polyacrylamide gels maintained diversion capability after injection of an alkaline-surfactant-polymer solution in stacked; radial coreflood with a common well bore. Chromium acetate-polyacrylamide gel used to seal fractured core maintain fracture closure if followed by an alkaline-surfactant-polymer solution.

Chromium acetate-xanthan gum rigid gels are not stable to subsequent alkaline-surfactant-polymer solution injection at 72, 125, and 175°F. Silicate-polyacrylamide gels are not stable with subsequent injection of either a pH 10.5 or a 12.9 alkaline-surfactant-polymer solution. Resorcinol-formaldehyde gels were stable to subsequent alkaline-surfactant-polymer solution injection.

When evaluated in a dual core configuration, injected fluid flows into the core with the greatest effective permeability to the injected fluid. The same gel stability trends to subsequent alkaline-surfactant-polymer injected solution were observed.

Aluminum citrate-polyacrylamide, resorcinol-formaldehyde, and the silicate-polyacrylamide gel systems did not produce significant incremental oil in linear corefloods. Both flowing and rigid tonguing chromium acetate-polyacrylamide gels and the xanthan gum-chromium acetate gel system produced incremental oil with the rigid tonguing gel producing the greatest amount. Higher oil recovery could have been due to higher differential pressures across cores.

Aluminum citrate-polyacrylamide gels, chromium acetate-polyacrylamide gels, silicate-polymer, and chromium-xanthan gum gels did not alter an alkaline-surfactant-polymer solution's ability to produce incremental oil. Incremental oil was reduced with the resorcinol-formaldehyde gel system. Total waterflood plus chemical flood oil recovery sequence recoveries were generally similar.

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Introduction

Gelation technologies provide more efficient vertical sweep efficiencies for flooding naturally fractured oil reservoirs and divert injected fluid into lower permeability zones in reservoirs with high permeability contrast layers. Field proven alkaline-surfactant-polymer technology economically recovers 15% to 25% OOIP more oil than waterflooding from swept pore space of an oil reservoir. However, alkaline-surfactant-polymer technology is not amenable to naturally fractured reservoirs or those with high permeability contrast zones because much of the injected solution bypasses target pore space containing oil. This work investigates whether combining these two technologies could broaden 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 12.9. 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 12.9. Chromium-polyacrylamide gels with high polymer to chromium ion ratio of 25 or greater were not stable with alkaline-surfactant-polymer solutions greater than pH 10.6. Stability evaluations consisted of layering alkaline-surfactant-polymer solutions over formed gels and monitoring gel stability over a number of days.

Linear coreflood evaluations indicate that aluminum citrate-polyacrylamide and silicate-polyacrylamide gels were not stable to either subsequent injection of NaOH or Na₂CO₃ alkaline-surfactant-polymer solutions. Dual cores radial corefloods with isolated cores connected to a common manifold showed that the aluminum citrate-polyacrylamide gel was not stable to subsequent alkaline-surfactant-polymer injection even though a second rock containing less gel was available for chemical injection. Prior injection of different gel mixtures did not affect total oil recovery. Alkaline-surfactant-polymer solutions ability to produce incremental oil was not effected by prior gel injection.

Both flowing and rigid tonguing chromium acetate-polyacrylamide were stable to both types of alkaline-surfactant-polymer solutions. Rigid tonguing gel maintained permeability reduction better than a flowing gel system. Chromium acetate-polyacrylamide gel was stable to subsequent injection of an alkaline-surfactant-polymer solution in dual isolated cores with a common manifold, and dual stacked cores with the same well bore configuration. Linear and radial corefloods indicate that the chromium acetate-polyacrylamide gel integrity is maintained after injecting alkaline-surfactant-polymer solution at 72, 125, and 175°F. Chromium acetate-polyacrylamide gel used to close fractures and divert fluid into the matrix maintains diversion capability after injection of an alkaline-surfactant-polymer solution. Prior injection of gel systems did not reduced alkaline-surfactant-polymer solutions ability to produce incremental oil.

Linear corefloods evaluations indicate that rigid tonguing chromium acetate-xanthan gum gel was not stable to subsequent injection of NaOH and Na₂CO₃ alkaline-surfactant-polymer solutions. Xanthan gum-chromium acetate gels were not stable at 72, 125, and 175°F.

Resorcinol-formaldehyde gel system was stable to subsequent injection of NaOH and Na₂CO₃ alkaline-surfactant-polymer solutions in linear corefloods.

Experimental

Crude oil from the Big Sinking field was used in the 72°F evaluations was supplied by Bretagne in Lexington, Kentucky. Big Sinking crude oil is a 42° API gravity, 3 cp crude oil. Evaluations at 125°F and 175°F used a 19.4° API gravity crude oil with a viscosity of 30 and 13 cp at the elevated temperatures, respectively.

A series of polyacrylamide-aluminum, polyacrylamide-chromium acetate, xanthan gum-chromium acetate, and resorcinol plus formaldehyde gel matrices were mixed and incubated either at 72, 125, or 175°F. Approximately 10 ml of gel solution was mixed in 1-inch diameter, 25 ml scintillation vials. Gels were allowed to sit for one to seven days to allow gels to form. Once gels were formed, alkaline-surfactant-polymer solutions were layered over the top of appropriate gels and incubated at the original temperature for 19 to 40 days. Alkaline-surfactant-polymer solutions pH varied from pH 9.2 to 12.9. Gel stability was monitored visually. Gel systems tested are listed below.

Polymer Type	Concentration (mg/L)	Crosslinker	Polymer:Crosslink ratio
Polyacrylamide:Aluminum			
HiVis 350	300 and 500	Watercut 677	10:1 20:1 30:1 40:1
Polyacrylamide:Chromium			
Watercut 204	5,000 and 7,500	Watercut 684	30:1 35:1 40:1 45:1 50:1
Xanthan Gum:Chromium Gels			
Flocon 4800CC	4,000 and 6,000	Watercut 684	8:1 10:1 12:1 15:1 18:1 20:1

<u>Polymer Type</u>	<u>Concentration (mg/L)</u>	<u>Crosslinker</u>	<u>Polymer:Crosslink ratio</u>
Polyacrylamide:Silicate Gels			
AN 923	250 to 2000	Ludox SM	1:200 1:160 1:120 1:80 1:60 1:50 1:40 1:30 1:25 1:20 1:15 1:10 1:5
Polyacrylamde:Iron Gels			
AN 923	500 to 2000	ferric chloride	133:1 33:1
AN 905	1000 to 3000	ferric chloride	200:1 67:1 33:1
Watercut 204	3000 to 7000	ferric chloride	700:1 500:1 333:1 250:1 200:1
Resorcinol/formaldehyde gels			
	Resorcinol wt%	Formaldehyde wt%	
	1.0	0.85	
	1.0	1.71	
	2.0	1.71	
	2.0	3.42	
	3.0	2.56	
	3.0	5.12	

pH of resorcinol/formaldehyde gel solutions were adjusted to pH 9 with NaOH.

Table 1
Polyacrylamide Polymers Used in Gelation Linear Corefloods

<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.
Alcoflood 1275A	30%	Ciba Specialty Chemicals

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

Aluminum citrate-Polyacrylamide solutions were mixed in brine 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 Table 1.

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 Flocon 4800C supplied by SNF Floerger. Chromium (III) was chromium trichloride hexahydrate or Watercut 684.

Silicate-Polyacrylamide 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 blended as appropriate.

Iron-Polyacrylamide based gels were developed by mixing ferric chloride, polyacrylamide, hydrochloric acid and sodium hydroxide 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 1275A. pH of alkaline-surfactant-polymer solutions varied from 9.0 to 12.9 as shown in Table 2. Ionic strength of all solutions was 0.25.

Table 2
Alkaline-Surfactant-Polymer Solution Composition and pH

Solution Number	NaHCO ₃	Na ₂ CO ₃	NaOH	ASP Dissolved in 1.0 wt% NaCl	ASP Dissolved in 0.1 wt% Na ₂ SO ₄
	wt%	wt%	wt%	pH	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	0.00	1.00	12.94	12.84

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 defined in 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

Corefloods performed are listed below.

Single Core Linear Corefloods

- Injection of a Na₂CO₃ alkaline-surfactant-polymer solutions and a NaOH alkaline-surfactant-polymer solution in separate corefloods with no prior gel injection. Sodium carbonate solution was 0.885 wt% Na₂CO₃ plus 0.06 wt% ORS-46HF plus 1300 mg/L Alcoflood 1275A. Sodium hydroxide solution was

1.0 wt% NaOH plus 0.06 wt% ORS-46HF plus 1300 mg/L Alcoflood 1275A. These floods provide a base for comparison with subsequent corefloods.

- Colloidal dispersion (aluminum citrate-polyacrylamide) gel solutions (400 mg/L HiVis 350 and 415 mg/L Watercut 677 or 20 mg/L Al^{+3}) were mixed in an injection tank as a single solution just prior to injection. Aluminum citrate was Watercut 677N (4.8% aluminum ion). Injection of gel solution from each tank was 2.5 hours maximum as defined by Smith et.al.⁴ As result, maximum gel solution age was 2.5 hours. Multiple tanks of gel solution were used during gel injection. Injected gel composition is listed in Table 4. Gel injection was followed by a Na_2CO_3 alkaline-surfactant-polymer solution and a NaOH alkaline-surfactant-polymer solution in separate corefloods.
- Flowing chromium acetate-polyacrylamide gel system was tested. Flowing gel system - polyacrylamide:chromium ion 30:9.7 (3000 mg/L WaterCut 204: 970 mg/L WaterCut 684 or 100 mg/L Cr^{+3}) was dissolved in 1% NaCl. Chromium acetate was Watercut 684 (10.3% chromium ion). Gel solution was mixed in an injection tank as a single solution just prior to injection. Injected gel composition is listed in Table 4. Gel injection was followed by a Na_2CO_3 alkaline-surfactant-polymer solution and a NaOH alkaline-surfactant-polymer solution in separate corefloods.
- Rigid-tonguing chromium acetate-polyacrylamide system was flooded. The rigid tonguing gel solution - polyacrylamide:chromium ion 30:9.7 WaterCut 204:Watercut 684 (7500 mg/L WaterCut 204: 2,425 mg/L WaterCut 684 or 250 mg/L Cr^{+3}) was dissolved in 1% NaCl. Gel composition is listed in Table 4. Gel injection was followed by a Na_2CO_3 alkaline-surfactant-polymer solution and a NaOH alkaline-surfactant-polymer solution in separate corefloods.
- Chromium-xanthan gum system was the third chromium acetate gel system tested. Chromium-xanthan gum gel was a rigid gel - polyacrylamide:chromium ion 30:9.7 WaterCut 204: chromium trichloride hexahydrate (5,000 mg/L Flocon 4800C: 3,250 mg/L WaterCut 684 or 335 mg/L Cr^{+3}) dissolved in 1% NaCl. Injected gel composition is listed in Table 4. Gel injection was followed by a Na_2CO_3 alkaline-surfactant-polymer solution and a NaOH alkaline-surfactant-polymer solution in separate corefloods.
- Silicate based gels were mixed according to Lakatos et.al.⁵ Polyacrylamide was Flopaam AN 923. Colloidal silicate was Ludox SM from Grace Davison. Calcium (II) was calcium dichloride dihydrate. 500 mg/L polyacrylamide and 60,000 mg/L Ludox SM were mixed as separate solutions. Both components were dissolved in 1.0 wt% NaCl plus 100 mg/L calcium chloride (148 mg/L as calcium chloride dihydrate). Equal volumes of chemical solutions were injected and mixed in-line just prior to entering the core. Net concentration of chemicals injected was 250 mg/L Flopaam AN 923, 30,000 mg/L Ludox SM, and 100 mg/L calcium chloride. Table 4 again lists gel composition. Gel injection was followed by a Na_2CO_3 alkaline-surfactant-polymer solution and a NaOH alkaline-surfactant-polymer solution in separate corefloods.
- Resorcinol-formaldehyde solutions were also mixed a 1.0 wt% NaCl solution in an injection tank as a single solution just prior to injection. Table 4 lists gel

composition. Gel injection was followed by a Na_2CO_3 alkaline-surfactant-polymer solution and a NaOH alkaline-surfactant-polymer solution in separate corefloods.

Fractured Linear Core Linear Corefloods

- Chromium acetate-polyacrylamide system tested was a rigid tonguing gel mixed as defined for the single linear corefloods. Gel injection was followed by a NaOH alkaline-surfactant-polymer solution in separate corefloods.

Dual Individual Core, Common Manifold Radial Corefloods

- Colloidal dispersion gel, aluminum citrate-polyacrylamide solutions were mixed as defined for the single linear corefloods. Multiple tanks of gelant solution were used during gel injection. Gel injection was followed by a Na_2CO_3 alkaline-surfactant-polymer solutions and a NaOH alkaline-surfactant-polymer solution in separate corefloods.
- Rigid-tonguing chromium acetate-polyacrylamide solutions as defined for the single linear corefloods. Gel injection was followed by a Na_2CO_3 alkaline-surfactant-polymer solutions and a NaOH alkaline-surfactant-polymer solution in separate corefloods.

Dual Stacked Core, Common Well Bore Stacked Radial Corefloods

- Rigid-tonguing chromium acetate-polyacrylamide solutions were mixed as defined as defined for the single linear corefloods. Gel injection was followed by a Na_2CO_3 alkaline-surfactant-polymer solutions and a NaOH alkaline-surfactant-polymer solution in separate corefloods.

Gel chemical compositions are listed in Table 4.

Table 4
Gel Chemical Compositions

<u>Gel</u>	<u>Polymer</u> <u>Type</u>	<u>mg/L</u>	<u>Cross Linking Agent (Bulk)</u> <u>Type</u>	<u>mg/L</u>
72°F Corefloods				
Al citrate - PHPA	HiVis 350	400	Watercut 677N	415
Cr^{+3} -PHPA flowing	Watercut 204	3000	Watercut 684	970
Cr^{+3} -PHPA rigid tonguing	Watercut 204	7,500	Watercut 684	2,425
Cr^{+3} -Xanthan Gum	Flocon 4800	5,000	Watercut 684	3,250
Si-PHPA	Flopaam AN923	250	Ludox SM	30,000
Resorcinol	analytical grade	20,000	Formaldehyde	17,100
125°F Corefloods				
Cr^{+3} -PHPA rigid tonguing	Watercut 204	5,000	Watercut 684	1,590
Cr^{+3} -Xanthan Gum	Flocon 4800	5,000	Watercut 684	3,250
175°F Corefloods				
Cr^{+3} -PHPA rigid tonguing	Watercut 204	3,000	Watercut 684	1,430
Cr^{+3} -Xanthan Gum	Flocon 4800	2,000	Watercut 684	950

Sodium carbonate and sodium hydroxide alkaline-surfactant-polymer solutions were injected into corefloods following gel treatment. Sodium carbonate solution was 0.885 wt% Na_2CO_3 plus 0.06 wt% ORS-46HF plus 1300 mg/L Alcoflood 1275A. Sodium hydroxide solution was 1.0 wt% NaOH plus 0.06 wt% ORS-46HF plus 1300 mg/L Alcoflood 1275A. ORS-46HF was supplied by OCT, Inc. Interfacial tension between the two alkaline-surfactant-polymer solutions and Big Sinking crude oil was 0.207 and 0.191 dyne/cm, respectively. Injected alkaline-surfactant-polymer solutions were chosen for two reasons. First, interfacial tension between crude oil and the NaOH and Na_2CO_3 solutions are similar. Second, a high interfacial tension solution was injected to minimize potential effect on gel of an ultra low interfacial tension solution and to minimize oil saturation change with the Big Sinking crude oil. Reduced oil saturation change presumably facilitates direct pressure comparison between different steps in the corefloods.

Corefloods at 125°F and 175°F used the same 1.0 wt% NaOH plus 0.06 wt% ORS-60HF plus 1300 mg/L Alcoflood 1275A solution as did the 72°F coreflood but switched to a 19.4° API gravity crude oil. Interfacial tension between the alkaline-surfactant-polymer solution and 19.4° API crude oil was 0.001 dyne/cm, a low enough interfacial tension to expect significant crude oil production with injection of an alkaline-surfactant-polymer solution.

Linear corefloods were performed using 1 inch diameter by 5 inches long, unfired Berea sandstone. Radial corefloods used 6 inches diameter by 2 inches high, unfired Berea sandstone. Table 5 lists core properties.

Table 5
Berea Core Properties
100% NaCl Brine Saturated

Coreflood	Permeability	Porosity(%)	---Oil Saturation---	
	$K_{T,abs}(md)$		$S_{oi}(V_p)$	$S_{or}(V_p)$
Linear Corefloods				
NaOH no gel	130	22.6	0.682	0.303
Na ₂ CO ₃ no gel	220	22.9	0.702	0.314
Al-PHPA-NaOH	515	22.4	0.727	0.346
Al-PHPH-Na ₂ CO ₃	410	22.9	0.628	0.309
Cr-PHPA flowing – NaOH	200	20.7	0.503	0.347
Cr-PHPA flowing - Na ₂ CO ₃	100	20.0	0.590	0.392
Cr-PHPA rigid tonguing – NaOH	315	23.3	0.564	0.319
Cr-PHPA rigid tonguing - Na ₂ CO ₃	330	22.5	0.525	0.328
Si-PHPA-NaOH	350	22.1	0.529	0.281
Si-PHPA-Na ₂ CO ₃	410	22.9	0.573	0.272
Cr ⁺³ -XG flowing – NaOH	518	23.0	0.628	0.367
Cr ⁺³ -XG flowing - Na ₂ CO ₃	349	22.4	0.613	0.364
Resorcinol-				
Formaldehyde rigid – NaOH	625	23.3	0.549	0.307
Resorcinol-				
Formaldehyde rigid –Na ₂ CO ₃	467	22.3	0.579	0.307

100% NaCl Brine Saturated				
<u>Coreflood</u>	Permeability	<u>Porosity(%)</u>	---Oil Saturation---	
	<u>K_{T,abs}(md)</u>		<u>S_{oi}(V_p)</u>	<u>S_{or}(V_p)</u>
Fractured Core Linear Coreflood				
Cr ⁺³ - PHPA rigid – NaOH (prior to cutting fracture)	595	22.8	0.562	0.349
125°F Linear Corefloods				
Cr ⁺³ - PHPA rigid - NaOH	555	23.3	0.712	0.336
Cr ⁺³ -XG rigid - NaOH	502	22.8	0.791	0.382
175°F Linear Corefloods				
Cr ⁺³ - PHPA rigid - NaOH	425	23.1	0.582	0.211
Cr ⁺³ -XG rigid - NaOH	290	22.6	0.609	0.236
Radial Corefloods				
dual core, common manifold, separate coreholders				
Al ⁺³ -PHPA- Na ₂ CO ₃	622	22.1	0.502	0.314
Al ⁺³ -PPPH-Na ₂ CO ₃	53	17.5	0.545	0.399
Cr ⁺³ -PHPA rigid tonguing – NaOH	435	22.0	0.545	0.353
Cr ⁺³ -PHPA rigid tonguing – NaOH	33	19.1	0.540	0.404
dual core, common well bore, same coreholder				
Cr ⁺³ -PHPA rigid tonguing – NaOH	631	22.5	0.581	0.251
Cr ⁺³ -PHPA rigid tonguing - Na ₂ CO ₃	58	18.5	0.494	-----
175°F Radial Corefloods				
dual core, common well bore, same core holder				
Cr ⁺³ -PHPA rigid tonguing – NaOH	511	23.0	0.541	0.286
Cr ⁺³ -PHPA rigid tonguing - Na ₂ CO ₃	52	17.9	0.510	0.355

S_{oi} and S_{or} are initial and waterflood residual oil saturation, respectively. PHPA is partially hydrolyzed polyacrylamide, and XG is xanthan gum.

Single Core Coreflood - injected fluid sequence is listed below. Corefloods were performed at 72, 125, and 175°F.

1. Saturate core with 1.0 wt% NaCl by evacuation and determine porosity and pore volume
2. Inject 1.0 wt% NaCl and determine the absolute permeability to water (k_{abs}).
3. Inject crude oil to immobile water and determine the effective permeability to oil at immobile water (k_{orw}).
4. Inject 1.0 wt% NaCl at 12 ft/day fluid frontal advance rate to residual oil and determine the effective permeability to water at residual oil (k_{orw}).
5. Inject gel fluids at 12 ft/day.
6. Stop injection. Pull coreholder apart, clean gel out of injection and production lines. Fill injection lines with 1.0 wt% NaCl before assembling coreholder.
7. Re-assemble coreholder and allow gel to form overnight with no flow.
8. Inject 1.0 wt% NaCl at 12 ft/day to stable pressures.
9. Inject ASP solution at 12 ft/day. Inject 5 to 10 pore volumes.
10. Shut-in overnight.

11. Resume ASP solution injection at 12 ft/day. Inject 1 to 2 pore volumes.
12. Inject 1.0 wt% NaCl at 12 ft/day for 5 to 10 pore volumes to get stable pressures and determine permeability change from step 8.

Differential pressures were measured from the core injection face to one inch from the injection face, and from injection face to production face. Differential pressure from one inch behind the injection face to production face of the core was calculated by difference between the two measured values. Produced oil and water were collected in graduated cylinders with each step.

Single fractured core linear coreflood - injected fluid sequence at 72 °F is:

1. Repeat steps 1 through 3 of the single linear coreflood procedure.
2. Remove core from core holder and fracture core along its length.
3. Place fractured core into core holder. Put overburden pressure on core and inject Big Sinking crude oil and determine k_{orw} .
4. Inject crude oil to immobile water at 30 ft/day and determine the effective permeability to oil at immobile water (k_{orw}).
5. Inject 1.7 pore volumes of 1.0 wt% NaCl at 4 ft/day fluid frontal advance rate to residual oil and determine k_{wro} .
6. Inject at 4 ft/day 0.5 pore volumes of chromium acetate:polyacrylamide gel (7500 mg/L WaterCut 204: 2425 mg/L WaterCut 684 or 250 mg/L Cr^{+3}).
7. Inject 0.05 pore volume of 1.0 wt% NaCl. Stop injection. Clean out injection and production lines. Fill injection lines with 1.0 wt% NaCl. Do not take the core holder apart.
8. Shut-in for two days.
9. Inject 1.0 wt% NaCl at 4 ft/day for 7.4 pore volumes to get stable pressures, flush gel from core, and get resistance factor.
10. Inject 7.1 pore volumes 1.0 wt% NaOH plus 0.06 wt% active ORS-46HF plus 1300 mg/L Alcoflood 1275A at 4 ft/day.
11. Inject 1.0 wt% NaCl at 4 ft/day for 6.5 pore volumes to get stable pressures and flush ASP-gel from core.

Differential pressures were measured from the core injection face to production face.

Dual Core Coreflood- individual radial coreholders connected to a common injection manifold - injected fluid sequence is listed below. Corefloods were performed at 72 and 175°F. Individual Core holder Injection Manifold steps 1 - 3

1. Saturate core with 1.0 wt% NaCl and determine porosity and pore volume
2. Inject 1.0 wt% NaCl and determine the absolute permeability to water (k_{abs}).
3. Inject crude oil to immobile water and determine the effective permeability to oil at immobile water (k_{orw}).

Common Core holder Injection Manifold steps 4 - 10 - fluid frontal advance rates are average for two cores - calculate individual core rates and add the volumes to be injected.

4. Connect the two individual cores to a common injection manifold.
5. Inject 1.0 wt% NaCl at 5 ft/day fluid frontal advance rate to residual oil and determine k_{orw} for each core.
6. Inject 1 pore volumes (sum of two cores) of gel solution at 5 ft/day.

7. Stop injection. Pull coreholders apart and clean gel out of injection and production lines. Fill injection lines with 1.0 wt% NaCl before assembling coreholder.
8. Re-assemble coreholder and allow gel to form for two days.
9. Inject 1.0 wt% NaCl at 5 ft/day and determine resistance factor.
10. Inject ASP solutions at 5ft/day and determine resistance factor.
11. Inject 1.0 wt% NaCl at 5 ft/day and determine residual resistance factor. Produced oil and water were collected in graduated cylinders with each step. Differential pressures were measured from injection well bore to production annulus port of each core.

Dual Core Corefloods - stacked radial core in the same coreholder with a common well bore - injected fluid sequence is listed below. Corefloods were run at 72 and 175°F.

Individual Injection Manifold in separate radial core holders in steps 1 - 3

1. Saturate core with 1.0 wt% NaCl and determine porosity and pore volume.
2. Inject 1.0 wt% NaCl and determine the absolute permeability to water (k_{abs}).
3. Inject crude oil to immobile water and determine k_{orw} .

Place core in stacked core radial core holder. A piece of cellulose paper was placed between cores to facilitate capillary continuity. An O-ring was placed on the outer edge of the cores at their junction that sealed to the annulus edge to facilitate separate collection of fluids from each core. Place an overburden of 1000 psi was placed on cores. Stacked core injection steps 4 - 10 - fluid frontal advance rates are summed height, average porosity, and average diameter for two cores.

4. Stack cores so that a common well bore is present.
5. Inject 1.0 wt% NaCl at 5 ft/day fluid frontal advance rate to residual oil saturation and determine k_{orw} for each core.
6. Inject approximately 0.6 pore volumes (sum of two core) gel fluids at 5 ft/day and monitor injection pressure.
7. Inject 0.1 pore volume of 1.0 wt% NaCl at 5 ft/day.
8. Stop injection. Pull coreholders apart and clean out gel from injection and production lines. Fill injection lines with 1.0 wt% NaCl before assembling coreholder.
9. Re-assemble coreholder and allow gel to form for two days.
10. Inject 1.0 wt% NaCl at 5 ft/day for 5 pore volumes and determine resistance factor.
11. Inject 1 to 2 pore volumes of ASP solution at 5ft/day and monitor injection pressure.
12. Inject 1.0 wt% NaCl at 5 ft/day for 5 pore volumes and determine residual resistance factor.

Produced fluids were collected in test tubes on a fraction collector. Differential pressures were measured from injection well bore to production annulus port of each core.

Resistance factor for all corefloods was calculated according to $RF_i = \frac{(\Delta P / q)_i}{(\Delta P / q)_{baseline}}$, where ΔP

is differential pressure, psi, and q is injection rate, ml/hr. Baseline values are after 1.0 wt% NaCl injection at S_{orw} and before initial gel chemical solution injection.

Oil saturation is determined by mass balance of injected and produced fluids. Final oil saturation was cross-checked by extraction of fluids from core by hot toluene.

Results and Discussion

Laboratory Evaluations

Base Case Alkaline-Surfactant-Polymer Linear Corefloods

Alkaline-surfactant-polymer solutions were injected into Berea core without a prior gel sequence to provide a basis for gel effect on core parameters. Figures 1 and 2 depict the resistance factor changes for the NaOH and Na₂CO₃ corefloods. Residual resistance factors of 1 to 2 were observed after injection of an alkaline-surfactant-polymer solution. Core permeability changes are listed in Table 6.

Table 6

Berea Sandstone Physical Parameters – Alkaline-Surfactant-Polymer Corefloods

	-----Permeability (md)-----		
	K_1	K_2	K_T
NaOH+ORS-46HF+Alcoflood 1275A – 22.6% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	78	150	130
Effective Perm to Oil at Immobile Water, K_{orw}	435	595	560
Effective Perm to Water at Residual Oil, K_{wro}	31	44	41
Gel Sequence	----	----	----
ASP Solution	64	25	28
Na ₂ CO ₃ +ORS-46HF+Alcoflood 1275A – 22.9% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	98	292	220
Effective Perm to Oil at Immobile Water, K_{orw}	390	730	635
Effective Perm to Water at Residual Oil, K_{wro}	28	47	42
Gel Sequence	----	----	----
ASP Solution	85	40	44

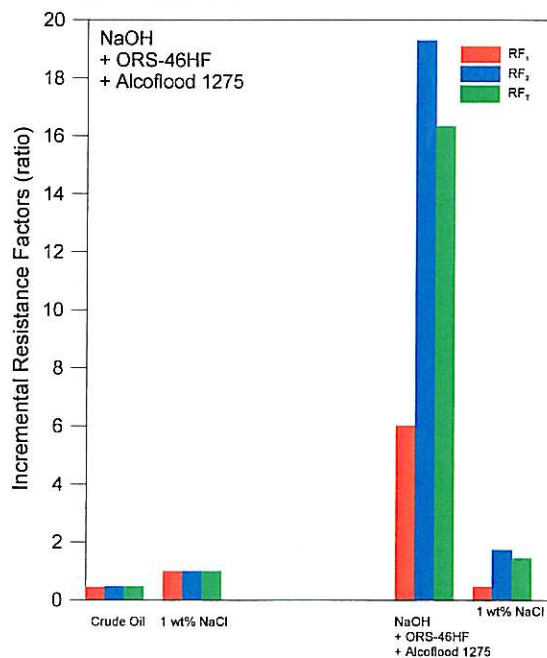


Figure 1 Ending Resistance Factors for the NaOH+ORS-46HF+Alcoflood 1275A Linear Coreflood, from left to right each set of histograms is RF₁(red), RF₂(blue), RF_T(green)

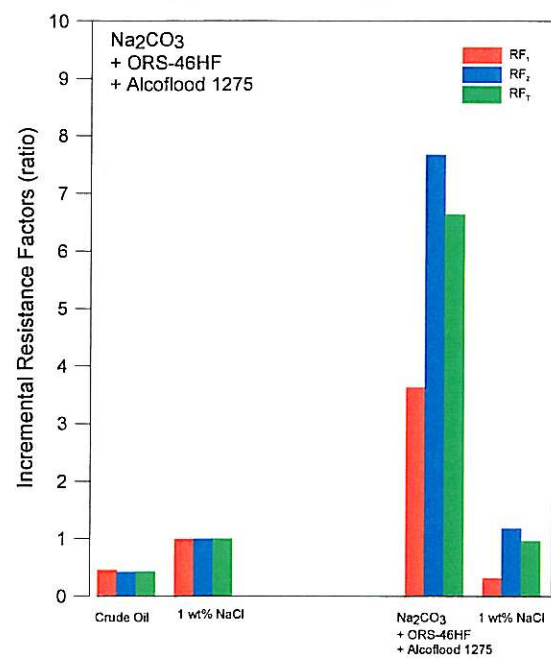


Figure 2 Ending Resistance Factors for the Na₂CO₃-OFS46HF+Alcoflood 1275A Linear Coreflood, from the left to right each set of histograms is RF₁(red), RF₂(blue), RF_T(green)

Oil saturation changes of the two corefloods are depicted in Figures 3 and 4.

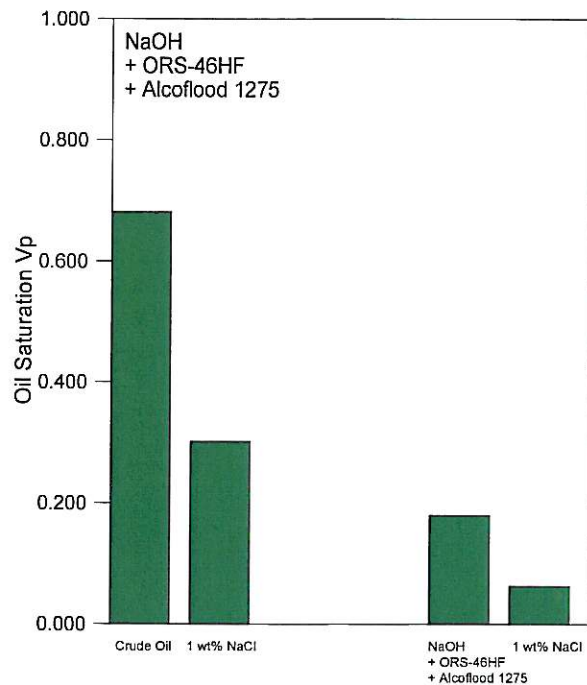


Figure 3 Ending Oil Saturation for the NaOH+ORS-46HF+Alcoflood 1275A Linear Coreflood

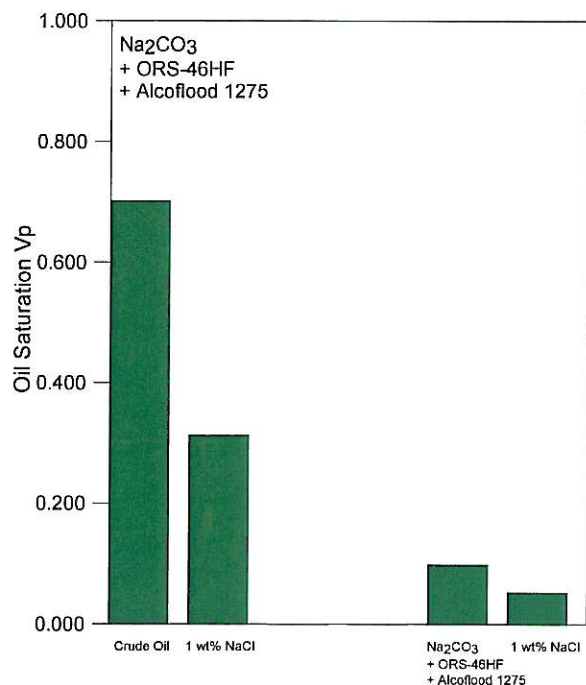


Figure 4 Ending Oil Saturation for the Na₂CO₃-OFS46HF+Alcoflood 1275A Linear Coreflood

Oil recoveries are summarized in Table 7.

Table 7

Oil Recovery of Alkaline-Surfactant-Polymer Linear Corefloods

Injected Solution	-----Cumulative Oil Recovery, % OOIP-----	
	NaOH-Coreflood	Na ₂ CO ₃ -Coreflood
1 wt% NaCl - Waterflood	55.6	55.3
ASP Solution and NaCl flush	90.6	92.5
ASP Incremental recovery	35.0	37.2

Aluminum-Polyacrylamide Gel Formation

Colloid dispersion aluminum citrate-polyacrylamide gels were the first series of gels evaluated. HiVis 350 was mixed with aluminum citrate in ratios of 10:1, 20:1, 30:1, and 40:1 (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 after one week at all polymer concentrations. When dissolved in 0.1 wt% Na₂SO₄, tonguing gels formed after four weeks at the higher polymer concentration. Similar results were observed at 125 °F and 175 °F. Flowing gels were observed in the 1.0 wt% NaCl solutions at one day at both temperatures. When polymer and aluminum were dissolved in 1.0 wt% Na₂SO₄, flowing gels were observed after one day at 125 °F and after two days at 175 °F. Tonguing gels were not observed at the elevated temperatures.

A tonguing gel was developed with aluminum citrate with AN 905 when 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.

Aluminum-polyacrylamide gels were not stable to alkaline-surfactant-polymer solutions when in contact for 24 days at 72°F. This was true whether the gels were flowing colloidal dispersion, low polymer concentration gel or higher concentration polymer and aluminum tonguing gels. Figure 5 shows a flowing aluminum-polyacrylamide gel dissolved in 0.1% Na₂SO₄ stability when contacting alkaline-surfactant-polymer solutions with pH values from 9.2 to 12.9. 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 6. 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.

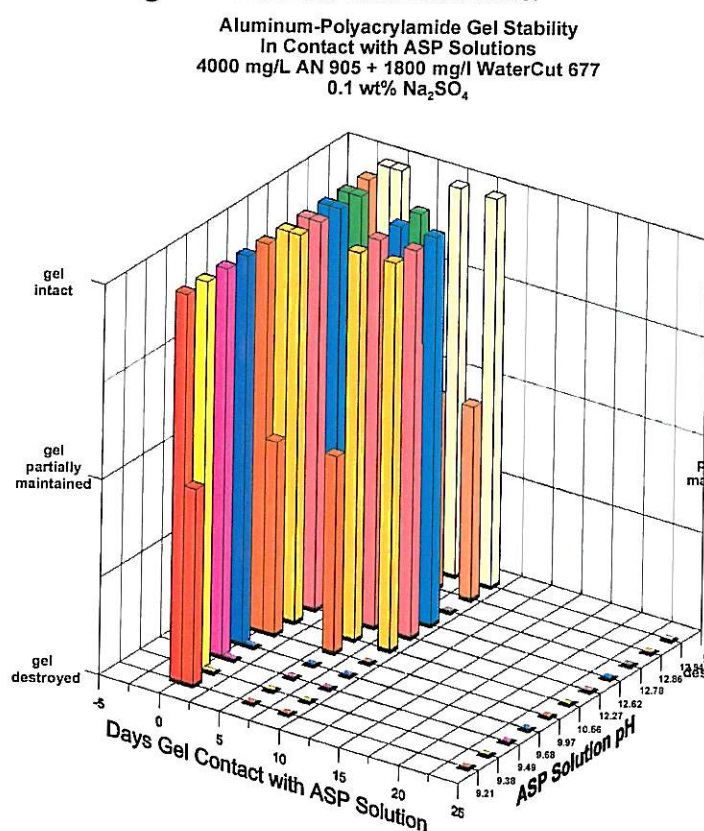


Figure 5 Aluminum-Polyacrylamide Gel in 0.1% Na₂SO₄ Stability with ASP Solutions

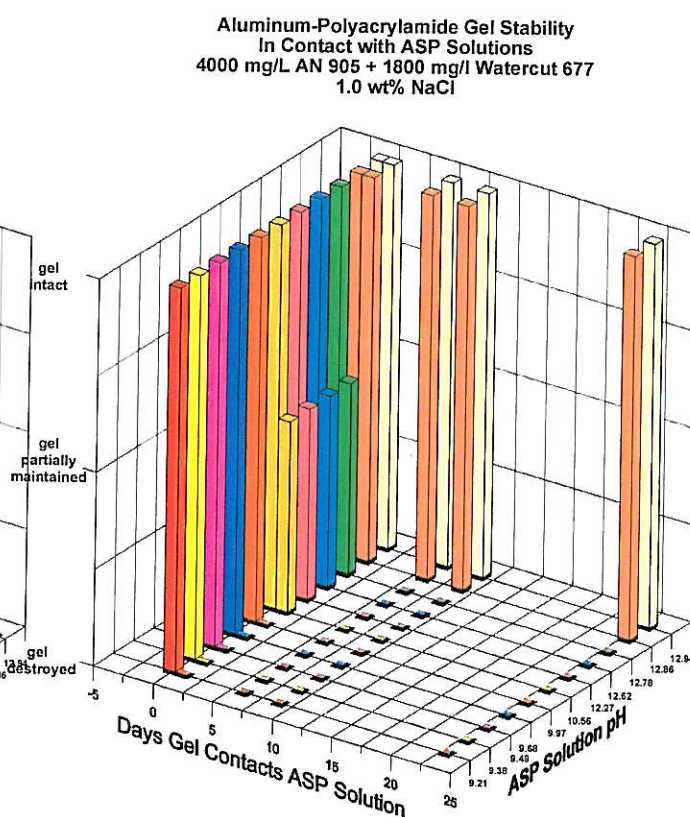


Figure 6 Aluminum-Polyacrylamide Gel in 1.0% NaCl Stability with ASP Solutions

When tested at 125°F and 175°F, aluminum-polyacrylamide gels were not stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9.

A pair of linear corefloods were performed to evaluate if the colloid dispersion, aluminum citrate-polyacrylamide gel technology is stable to subsequent injection of an alkaline-surfactant-

polymer solution. Injected gel mixture was 400 mg/L HiVis 350 plus 20 mg/L Watercut 677N as Al^{+3} . Figures 7 and 8 depict resistance factor changes for NaOH and Na_2CO_3 alkaline-surfactant-polymer corefloods. In both corefloods, pressures during gel injection exceeded pressure transducer limitation so reported resistance factors are limit values. Residual resistance factors after gel injection and before alkaline-surfactant-polymer solution indicated gel was placed uniformly through the core. Average permeability reduction of 13 was observed with the aluminum citrate-polyacrylamide gel.

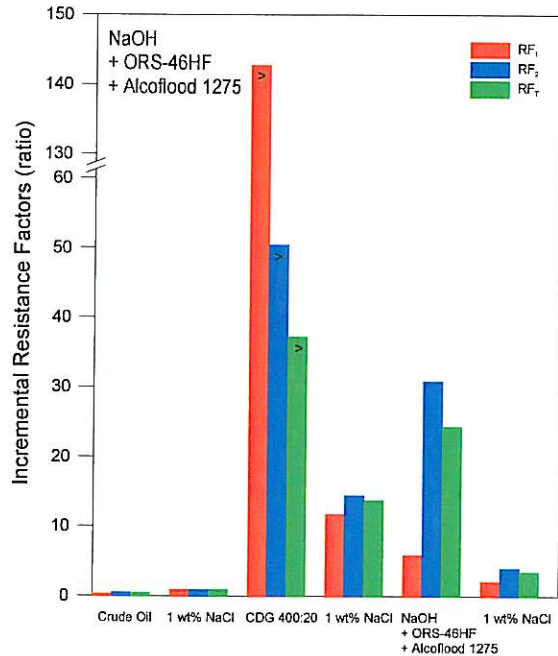


Figure 7 Ending Resistance Factors for the Aluminum Citrate-Polyacrylamide Colloidal Dispersion Gel followed by NaOH+ORS-46HF+Alcoflood 1275A Linear Coreflood, from left to right each set of histograms is RF₁(red), RF₂(blue), RF₃(green)

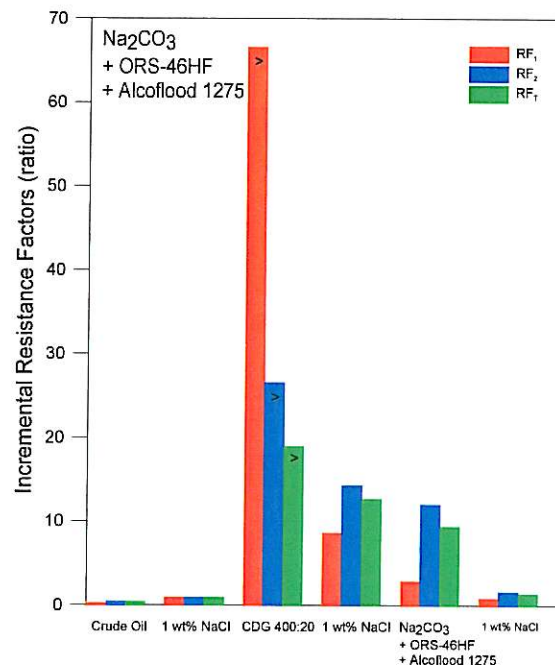


Figure 8 Ending Resistance Factors for the Aluminum Citrate-Polyacrylamide Colloidal Dispersion Gel followed by Na_2CO_3 +ORS-46HF+Alcoflood 1275A Linear Coreflood, from left to right each set of histograms is RF₁(red), RF₂(blue), RF₃(green)

Resistance factors during alkaline-surfactant-polymer injection were of the same order of magnitude as alkaline-surfactant-polymer solutions without prior gel injection, in the 10 to 20 range. Residual resistance factors after alkaline-surfactant-polymer injection were slightly greater than those after alkaline-surfactant-polymer solutions, 2 to 3 compared to 1 to 2. Aluminum citrate-polyacrylamide gels are not stable to either NaOH or Na_2CO_3 alkaline-surfactant-polymer solution injection. Permeability changes are summarized in Table 8.

Table 8
Berea Sandstone Physical Parameters – Aluminum Citrate - Polyacrylamide

	-----Permeability (md)-----		
	<u>K₁</u>	<u>K₂</u>	<u>K_T</u>
NaOH+ORS-46HF+Alcoflood 1275A – 22.4% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	380	550	515
Effective Perm to Oil at Immobile Water, K _{orw}	710	880	845
Effective Perm to Water at Residual Oil, K _{wro}	47	82	73
Gel Sequence	4	6	5
ASP Solution	22	20	20
Na ₂ CO ₃ +ORS-46HF+Alcoflood 1275A – 22.9% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	355	425	410
Effective Perm to Oil at Immobile Water, K _{orw}	440	555	530
Effective Perm to Water at Residual Oil, K _{wro}	22	43	37
Gel Sequence	3	3	3
ASP Solution	24	26	25

Oil recovery was not affected by aluminium citrate-polymer injection. Table 9 summarizes the oil production with each step.

Table 9
Oil Recovery of Aluminum Citrate – Polyacrylamide Gel Linear Corefloods

	-----Cumulative Oil Recovery, % OOIP-----	
<u>Injected Solution</u>	<u>NaOH-Coreflood</u>	<u>Na₂CO₃-Coreflood</u>
1wt% NaCl - Waterflood	52.4	46.0
Gel Sequence and NaCl flush	55.6	51.3
ASP Solution and NaCl flush	85.4	84.7
Gel Incremental Oil Recovery	3.2	5.3
Gel+ASP Incremental Recovery	33.0	38.7

Some incremental oil was produced by aluminum citrate – polyacrylamide gel injection with the majority being produced by subsequent alkaline-surfactant-polymer solutions. Waterflood and chemical flood (gel plus ASP solution) oil recoveries are similar to those observed without prior gel injection. Aluminum citrate – polyacrylamide gel injection does not produce significant matrix incremental oil and prior gel injection does not affect incremental oil production capacity of the subsequent alkaline-surfactant-polymer solution.

A dual individual core, common manifold radial coreflood was performed to determine if the colloidal dispersion, aluminum citrate-polyacrylamide gel technology is stable to subsequent injection of an alkaline-surfactant-polymer solution in a situation where a difference in permeability exists between two cores. Radial common manifold, dual core corefloods permit a gel system to be tested in a situation where once the gel is in place, the injected fluid flows into the core with the highest effective permeability. This is similar to an injection well that is perforated at multiple sand intervals, each with different permeability, separated by a vertical permeability barrier. Injected gel mixture was 400 mg/L HiVis 350 plus 20 mg/L Watercut 677N as Al⁺³. Injected alkaline-surfactant-polymer solution was 0.885 wt% Na₂CO₃ plus 0.06

wt% active ORS-46HF plus 1300 mg/L Alcoflood 1275A. Figures 9 and 10 depict resistance factor changes for the low and high permeability cores' corefloods. Residual resistance factors in the low permeability core, after gel injection and before alkaline-surfactant-polymer solution, indicated that gel was placed primarily near well bore. However, this is primarily due to the low volume of fluid injected into the core. High permeability core resistance factor distribution during gel placement suggest that gel was distributed through out the core.

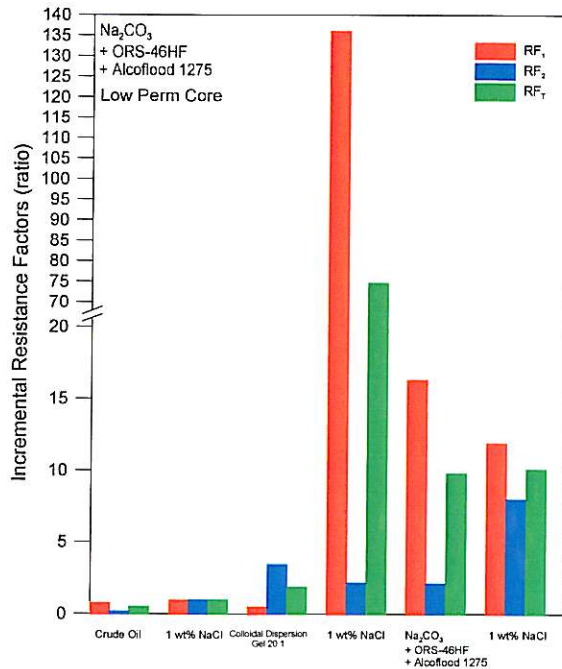


Figure 9 Low Permeability Core, Ending Resistance Factors for the Flowing Aluminum Citrate-Polyacrylamide Gel followed by Na₂CO₃+ORS-46HF+Alcoflood 1275A, from left to right each set of histograms is RF₁(red), RF₂(blue), RF₇(green)

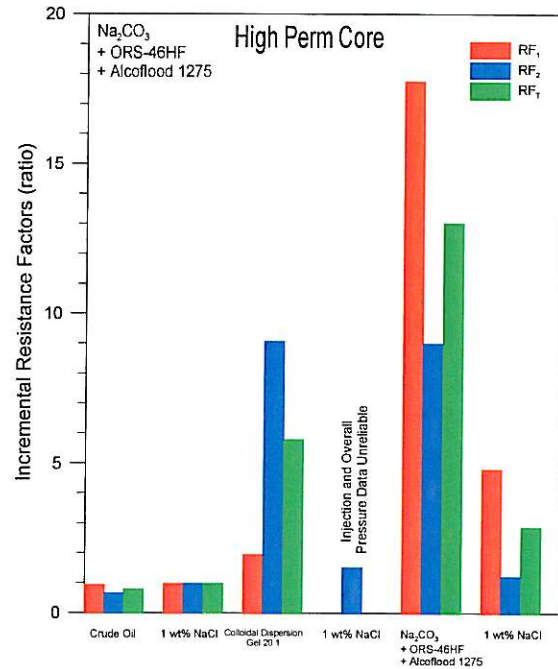
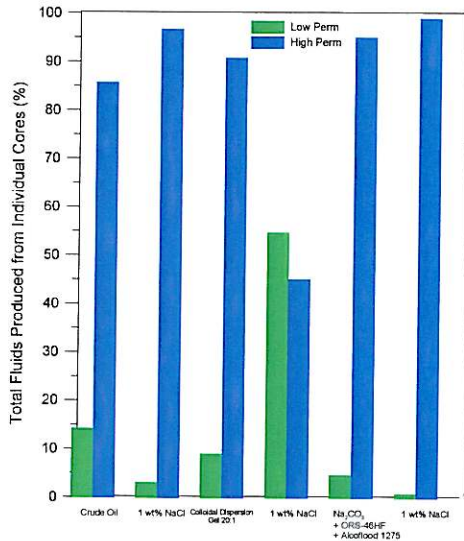


Figure 10 High Permeability Core, Ending Resistance Factors for the Flowing Aluminum Citrate-Polyacrylamide followed by Na₂CO₃+ORS-46HF+Alcoflood 1275A, from left to right each set of histograms is RF₁(red), RF₂(blue), RF₇(green)

Flow distribution change due to aluminum citrate-polyacrylamide gel injection is shown in Figure 11. Initial flow is distributed with 90% or greater flowing through the high permeability core during crude oil, initial waterflood, and gel injection. Flow distribution was essentially equalized during the water flush subsequent to gel placement, indicating gel was diverting injected water from the high permeability core into the low permeability core. Injection of the alkaline-surfactant-polymer solution resulted in destruction of the gel and reversion of the flow distribution back to the original pattern.



Core permeability changes during the aluminum citrate-polyacrylamide gel dual radial coreflood are summarized in Table 10.

Figure 11 Flow Distribution between High and Low Permeability Cores, Dual Radial Coreflood, Aluminum Citrate-Polyacrylamide Gel, green is low permeability core and blue is high permeability core

**Table 10
Berea Sandstone Physical Parameters
Common Manifold, Dual Radial Core
Aluminum Citrate-Polyacrylamide Gel Coreflood**

	-----Permeability (md)-----		
	<u>K_I</u>	<u>K₂</u>	<u>K_T</u>
Na ₂ CO ₃ +ORS-46HF+Alcoflood 1275A			
High Permeability Core – 22.1% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	651	566	622
Effective Perm to Oil at Immobile Water, K _{orw}	729	392	576
Effective Perm to Water at Residual Oil, K _{wro}	107	41	72
Post Gel Sequence, K _{wro}	---	---	---
Post ASP Solution, K _{wro}	22	33	25
Low Permeability Core – 17.5% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	55	49	53
Effective Perm to Oil at Immobile Water, K _{orw}	24	53	29
Effective Perm to Water at Residual Oil, K _{wro}	3	2	2
Post Gel Sequence, K _{wro}	---	---	---
Post ASP Solution, K _{wro}	0.3	0.2	0.2

Table 11 summarizes oil production of the aluminium citrate-polyacrylamide dual core radial coreflood.

Table 11
**Oil Recovery of Common Manifold, Dual Radial Core
Aluminum Citrate-Polyacrylamide Gel Corefloods**

<u>Injected Solution</u>	-----Cumulative Oil Recovery, % OOIP-----	
	<u>High K - Core</u>	<u>Low K - Core</u>
1.0 wt% NaCl - Waterflood	37.4	26.7
Gel Sequence and NaCl flush	40.0	28.4
ASP Solution and NaCl flush	65.3	28.6
	-----Incremental Oil Recovery, % OOIP-----	
Gel Incremental Oil Recovery	2.6	1.7
Gel+ASP Incremental Recovery	27.9	1.7

Failure of the alkaline-surfactant-polymer solution to divert and flow through the low permeability core is evident with the poor oil recovery. In the high permeability core where chemical solution was injected, the alkaline-surfactant-polymer solution mobilized incremental oil.

Chromium-Polyacrylamide Gel Formation

Chromium acetate-polyacrylamide gels formed tonguing to rigid gels. Table 12 lists how gel type varied with chemical concentration and dissolution water at 72°F.

Table 12
Chromium (III) – Polyacrylamide Gel Formation at 72°F

Watercut 204		Gel Description	
<u>Concentration</u>	<u>Ratio</u>		
<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 week period. Tonguing to rigid gel formation with 5000 and 7500 mg/L Watercut 204 plus WaterCut 684 at ratios between 30:1 and 50:1 was observed at 125°F and 175°F. Gel formation was accelerated at the evaluated temperatures.

Chromium acetate-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 polymer:chromium concentration ratio of 15 or less was stable to alkaline-surfactant-polymer pH up to 12.9. Figures 12 and 13 depict unstable and stable chromium:polyacrylamide gel systems. Figure 12 is a tonguing gel and Figure 13 is a rigid tonguing gel. Chromium acetate-polyacrylamide gels were stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9 at elevated temperature.

**Chromium-Polyacrylamide Gel Stability
In Contact with ASP Solutions
7500 mg/L Watercut 204 + 300 mg/l WaterCut 684
0.1 wt% Na₂SO₄**

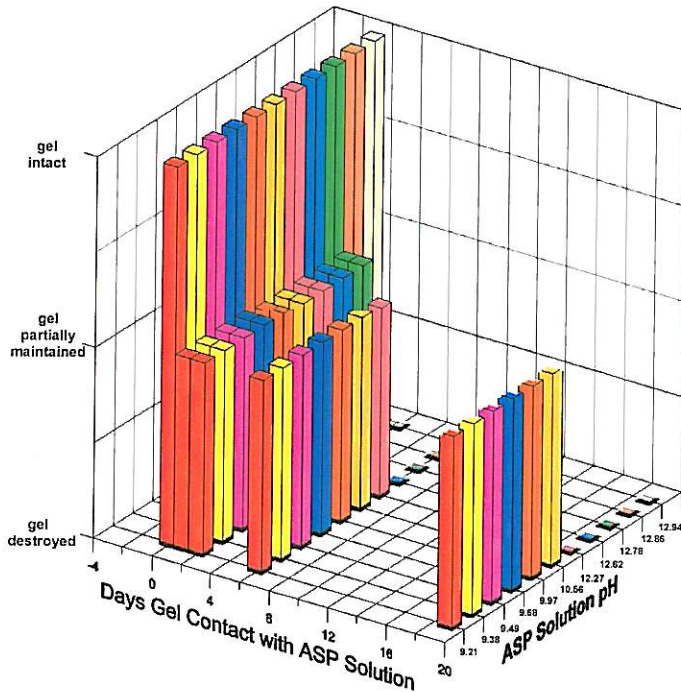


Figure 12 Chromium (III)-Polyacrylamide Gel in 0.1% Na₂SO₄ Stability with ASP Solutions

**Chromium-Polyacrylamide Gel Stability
In Contact with ASP Solutions
7500 mg/L Watercut 204 + 1500 mg/l WaterCut 684
0.1 wt% Na₂SO₄**

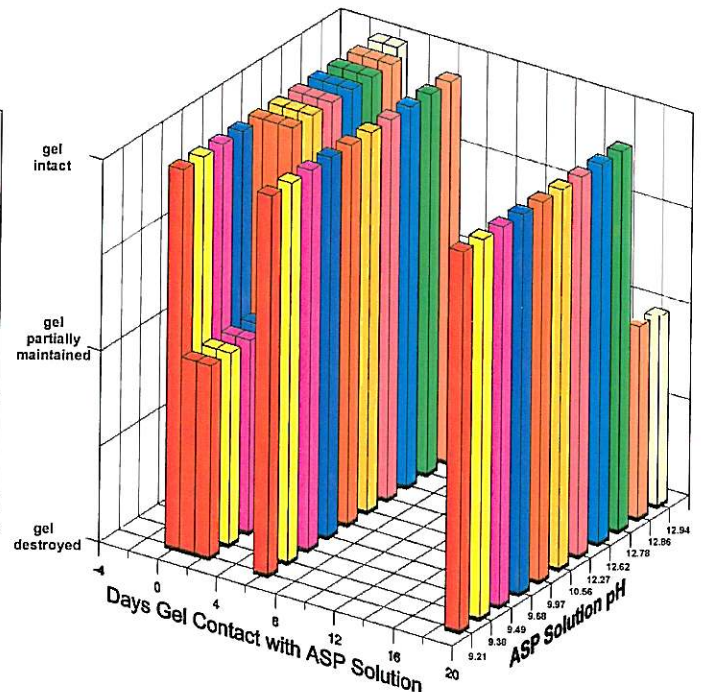


Figure 13 Chromium (III)-Polyacrylamide Gel in 0.1% Na₂SO₄ Stability with ASP Solutions

Two pairs of linear corefloods were performed to evaluate if chromium acetate-polyacrylamide gel technology is stable to subsequent injection of an alkaline-surfactant-polymer solution. A flowing chromium acetate – polyacrylamide gel was evaluated in the first pair of linear corefloods. Injected gel mixture was 3000 mg/L Watercut 204 plus 100 mg/L Watercut 684 as Cr⁺³. Figures 14 and 15 depict the resistance factor changes for the NaOH and Na₂CO₃ corefloods.

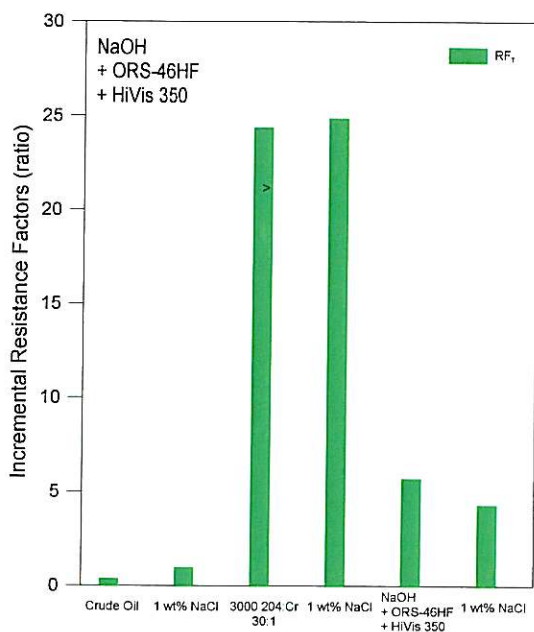


Figure 14 Ending Resistance Factors for the Flowing Chromium Acetate-Polyacrylamide Gel followed by NaOH+ORS-46HF+HiVis 350 Linear Coreflood, RF_T (green)

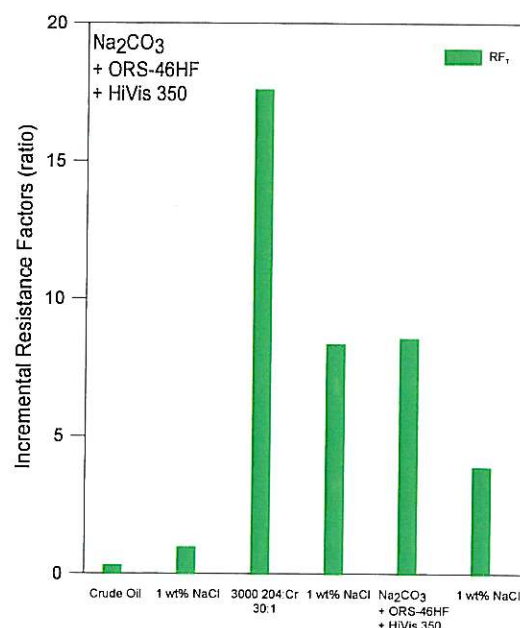


Figure 15 Ending Resistance Factors for the Flowing Chromium Acetate-Polyacrylamide Gel followed by Na₂CO₃+ORS-46HF+ HiVis 350 Linear Coreflood, F_T (green)

In both flowing chromium acetate-polyacrylamide corefloods, resistance factor after gel was reduced by alkaline-surfactant-polymer injection but not to levels of the base alkaline-surfactant-polymer injection. This suggests that flowing chromium acetate – polyacrylamide gels are somewhat stable to alkaline-surfactant-polymer solution injection. The fact that resistance factors generated by gel solutions are reduced when alkaline-surfactant-polymer solution is injected suggests that some destruction of gel does occur. Permeability changes are summarized in Table 13.

Table 13

Berea Sandstone Physical Parameters

- Flowing Chromium Acetate – Polyacrylamide –

	-----Permeability (md)-----		
	K_1	K_2	K_T
NaOH+ORS-46HF+ HiVis 350 – 20.7% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	---	---	200
Effective Perm to Oil at Immobile Water, K_{orw}	---	---	210
Effective Perm to Water at Residual Oil, K_{wro}	---	---	12
Gel Sequence	---	---	0.5
ASP Solution	---	---	3

	-----Permeability (md)-----		
	K_I	K_2	K_T
$\text{Na}_2\text{CO}_3 + \text{ORS-46HF} + \text{HiVis 350} - 20.0\% \text{ Porosity}$			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	---	---	100
Effective Perm to Oil at Immobile Water, K_{orw}	---	---	165
Effective Perm to Water at Residual Oil, K_{wro}	---	---	8
Gel Sequence	---	---	0.5
ASP Solution	---	---	2

Rigid tonguing gel chromium acetate – polyacrylamide gel system was tested in a second pair of linear corefloods. Injected gel mixture was 7500 mg/L Watercut 204 plus 250 mg/L Watercut 684 as Cr^{+3} . Figures 16 and 17 depict the resistance factor changes for the NaOH and Na_2CO_3 corefloods.

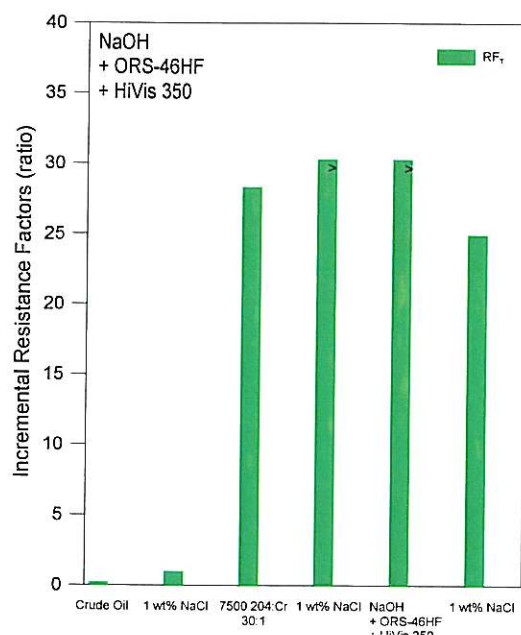


Figure 16 Ending Resistance Factors for the Rigid tonguing Chromium Acetate-Polyacrylamide Gel followed by NaOH+ORS-46HF + HiVis 350 Linear Coreflood, RF_T (green)

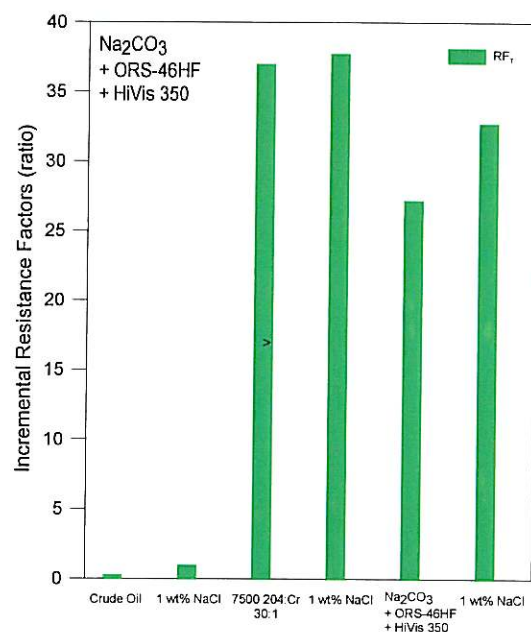


Figure 17 Ending Resistance Factors for the Rigid tonguing Chromium Acetate-Polyacrylamide Gel followed by $\text{Na}_2\text{CO}_3 + \text{ORS-46HF} + \text{HiVis 350}$ Coreflood, RF_T (green)

Rigid tonguing chromium acetate-polyacrylamide gel solutions maintained resistance factor after alkaline-surfactant-polymer solution was injected. Corefloods suggest that a rigid tonguing gel mixture is more stable to subsequent alkaline-surfactant-polymer injection. Permeability changes are summarized in Table 14.

Table 14
Berea Sandstone Physical Parameters
- Rigid tonguing Chromium Acetate – Polyacrylamide -

	-----Permeability (md)-----		
	<u>K_I</u>	<u>K₂</u>	<u>K_T</u>
NaOH+ORS-46HF+ HiVis 350– 23.3% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	---	---	315
Effective Perm to Oil at Immobile Water, K _{orw}	---	---	410
Effective Perm to Water at Residual Oil, K _{wro}	---	---	15
Gel Sequence	---	---	0.5
ASP Solution	---	---	0.6
Na ₂ CO ₃ +ORS-46HF+ HiVis 350 – 22.5% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	---	---	330
Effective Perm to Oil at Immobile Water, K _{orw}	---	---	400
Effective Perm to Water at Residual Oil, K _{wro}	---	---	18
Gel Sequence	---	---	0.5
ASP Solution	---	---	0.6

Table 15 summarizes oil production of the four chromium acetate – polyacrylamide corefloods.

Table 15
Oil Recovery of Chromium Acetate – Polyacrylamide Gel Linear Corefloods
-----Cumulative Oil Recovery, % OOIP-----

<u>Injected Solution</u>	<u>NaOH-Coreflood</u>	<u>Na₂CO₃-Coreflood</u>
Flowing Gels (3000 mg/L Watercut 204: 100 mg/L Cr⁺³)		
1wt% NaCl - Waterflood	31.0	33.5
Gel Sequence and NaCl flush	46.3	49.3
ASP Solution and NaCl flush	77.9	62.4
Gel Incremental Oil Recovery	15.3	15.8
Gel+ASP Incremental Recovery	31.9	13.1
Rigid tonguing Gels (7500 mg/L Watercut 204: 250 mg/L Cr⁺³)		
1wt% NaCl - Waterflood	43.4	37.5
Gel Sequence and NaCl flush	72.9	65.9
ASP Solution and NaCl flush	82.0	78.8
Gel Incremental Oil Recovery	29.4	28.4
Gel+ASP Incremental Recovery	9.1	12.9

Chromium acetate – polyacrylamide gel injection produced more incremental oil than did the aluminum citrate – polyacrylamide gel systems probably due to the higher differential pressures developed during gel placement and subsequent water flush. This trend is shown within chromium acetate-polyacrylamide gels in that more rigid gels produced more oil during gel placement and flush. Subsequent alkaline-surfactant-polymer solutions produced additional incremental oil with total recovery being slightly lower than either aluminum citrate – polyacrylamide gel or alkaline-surfactant-polymer corefloods. Oil recovery by an alkaline-

surfactant-polymer solution is not effected by prior chromium acetate – polyacrylamide gel injection.

A dual individual core, common manifold radial coreflood was performed to determine if the chromium acetate – polyacrylamide gel technology is stable to subsequent injection of an alkaline-surfactant-polymer solution. Injected gel mixture was 7500 mg/L Watercut 204 plus 250 mg/L Watercut 684 as Cr^{+3} . Injected alkaline-surfactant-polymer solutions was 1.0 wt% NaOH plus 0.06 wt% active ORS-46HF plus 1300 mg/L Alcoflood 1275A. Figures 18 and 19 depict resistance factor changes for the low and high permeability cores' corefloods. Chromium acetate-polyacrylamide gels reduced permeabilities significantly in both cores. Core permeability changes during the chromium acetate-polyacrylamide gel dual radial coreflood are summarized in Table 16.

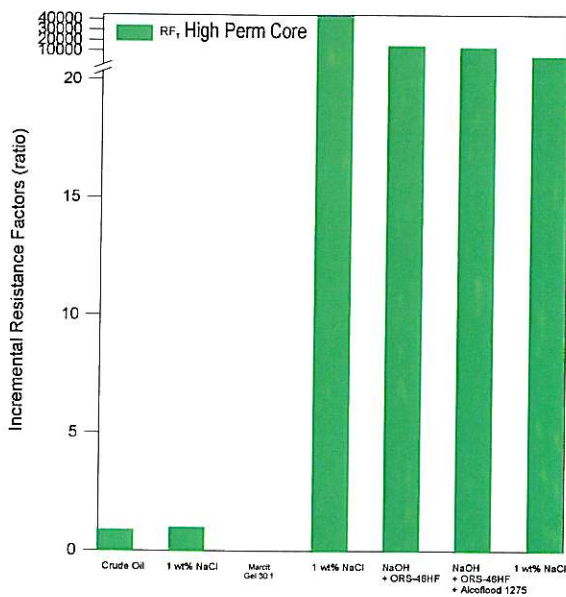


Figure 18 Low Permeability Core, Ending Resistance Factors for the Rigid Chromium Acetate-Polyacrylamide Gel followed by NaOH+ORS-46HF+Alcoflood 1275A, from left to right each set of histograms is RF_T (green)

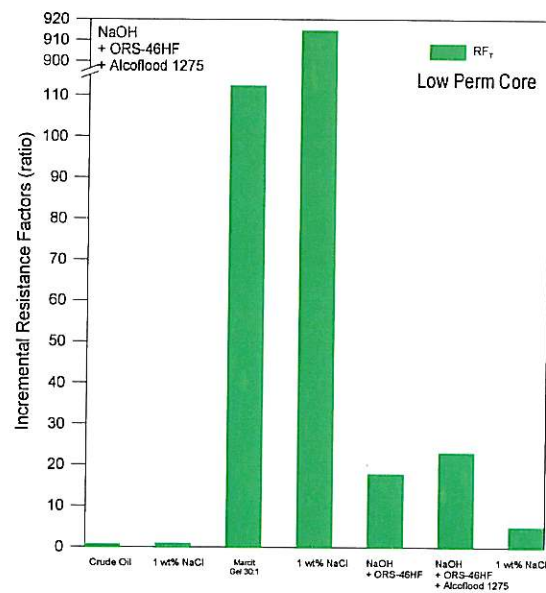


Figure 19 High Permeability Core, Ending Resistance Factors for the Rigid Chromium Acetate-Polyacrylamide Gel followed by NaOH+ORS-46HF+Alcoflood 1275A, from left to right each set of histograms is RF_T (green)

Table 16
Berea Sandstone Physical Parameters
Common Manifold, Dual Radial Core
Chromium Acetate-Polyacrylamide Gel Coreflood

	-----Permeability (md)-----		
	K_1	K_2	K_T
NaOH+ORS-46HF+Alcoflood 1275A			
High Permeability Core – 22.0% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	502	535	435
Effective Perm to Oil at Immobile Water, K_{orw}	483	278	393
Effective Perm to Water at Residual Oil, K_{wro}	89	29	54
Post Gel Sequence, K_{wro}	---	---	---
Post ASP Solution, K_{wro}	---	---	0.1
Low Permeability Core – 19.1% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	26	70	33
Effective Perm to Oil at Immobile Water, K_{orw}	14	40	16
Effective Perm to Water at Residual Oil, K_{wro}	1	1	1
Post Gel Sequence, K_{wro}	---	---	---
Post ASP Solution, K_{wro}	0.3	0.3	0.3

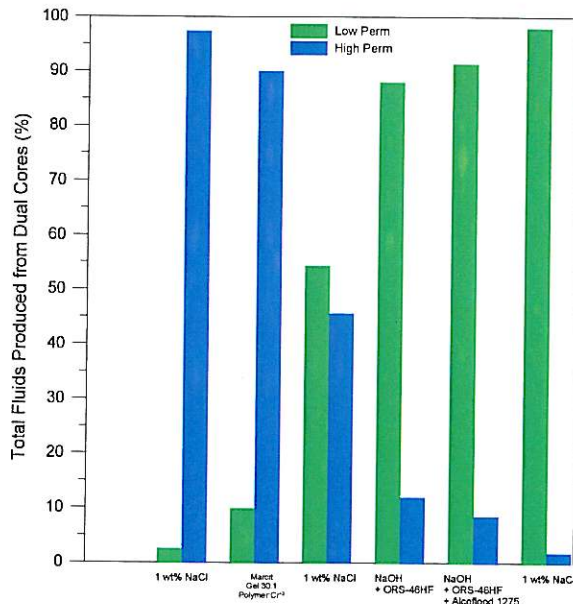


Figure 20 Flow Distribution between High and Low Permeability Cores, Dual Radial Coreflood, Chromium Acetate - Polyacrylamide Gel, green is low permeability and blue is high permeability

A change in flow distribution due to chromium acetate-polyacrylamide gel injection is shown in Figure 20. Initial flow is distributed with 90% or greater flowing through the high permeability core during crude oil, initial waterflood, and gel injection. Flow distribution was essentially equalized during the water flush subsequent gel placement, indicating gel was diverting injected water from the high permeability core into the low permeability core. Injection of the alkaline-surfactant-polymer solution resulted in even more diversion into the lower permeability core.

Table 17 summarizes oil production of the chromium acetate-polyacrylamide dual core radial coreflood.

Table 17
**Oil Recovery of Common Manifold, Dual Radial Core
 Chromium Acetate-Polyacrylamide Gel Coreflood**

<u>Injected Solution</u>	-----Cumulative Oil Recovery, % OOIP-----	
	<u>High K - Core</u>	<u>Low K - Core</u>
1.0 wt% NaCl - Waterflood	35.2	25.1
Gel Sequence and NaCl flush	51.0	28.0
ASP Solution and NaCl flush	51.7	52.6
	-----Incremental Oil Recovery, % OOIP-----	
Gel Incremental Oil Recovery	15.8	2.9
Gel+ASP Incremental Recovery	16.5	27.5

Alkaline-surfactant-polymer solution flow into the low permeability core recovered additional oil while the lack of flow into the high permeability core resulted in poor incremental oil recovery.

A dual stacked core pair with a common well bore coreflood evaluated the stability of a chromium acetate-polyacrylamide gel to subsequent alkaline-surfactant-polymer injection in a situation with fluid diversion. In this case, cross flow was possible. Injected gel mixture was 7500 mg/L Watercut 204 plus 250 mg/L Watercut 684 as Cr^{+3} . Injected alkaline-surfactant-polymer solution was 1.0 wt% NaOH plus 0.06 wt% active ORS-46HF plus 1300 mg/L Alcoflood 1275A. Figures 21 and 22 depict resistance factor changes for the both core. As in the separate manifold, dual individual coreflood, chromium acetate-polyacrylamide gel reduced the permeability of each core and that permeability change persisted with subsequent alkaline-surfactant-polymer injection. Permeability changes for dual, stacked core chromium acetate-polyacrylamide coreflood are summarized in Table 18.

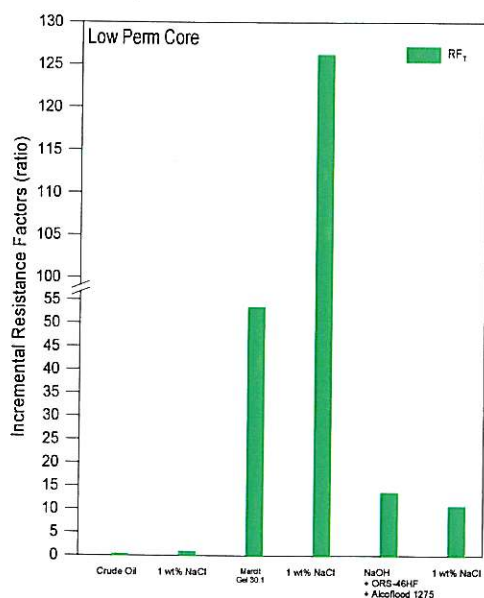


Figure 21 Low Permeability Core, Ending Resistance Factors for the Rigid Chromium Acetate-Polyacrylamide Gel followed by NaOH+ORS-46HF+Alcoflood 1275A, from left to right each set of histograms is RF_T (green)

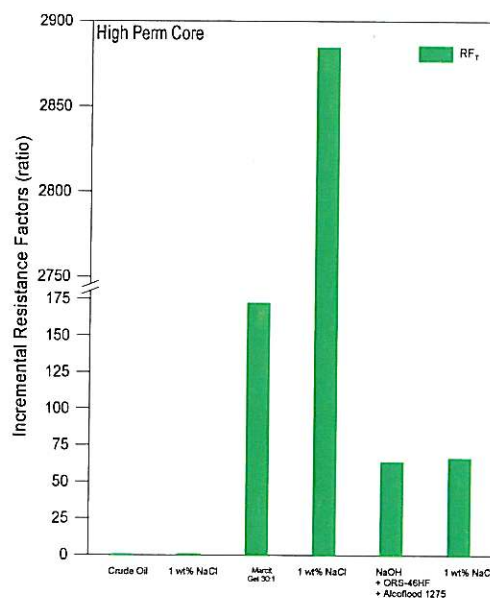


Figure 22 High Permeability Core, Ending Resistance Factors for the Rigid Chromium Acetate-Polyacrylamide Gel followed by NaOH+ORS-46HF+Alcoflood 1275A, from left to right each set of histograms is RF_T (green)

Table 18
**Berea Sandstone Physical Parameters – Chromium Acetate-Polyacrylamide
Dual Stacked, Same Well Bore Coreflood**

	-----Permeability (md)-----		
	K_1	K_2	K_T
NaOH+ORS-46HF+Alcoflood 1275A			
High Permeability Core – 22.5% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	850	400	628
Effective Perm to Oil at Immobile Water, K_{orw}	692	379	551
Effective Perm to Oil at Immobile Water, K_{orw} (after stacking core)	---	---	646
Effective Perm to Water at Residual Oil, K_{wro}	---	---	86
Post Gel Sequence, K_{wro}	---	---	0.03
Post ASP Solution, K_{wro}	---	---	1.3
Low Permeability Core – 18.5% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	58	59	58
Effective Perm to Oil at Immobile Water, K_{orw}	41	50	41
Effective Perm to Oil at Immobile Water, K_{orw} (after stacking core)	---	---	51
Effective Perm to Water at Residual Oil, K_{wro}	---	---	3.1
Post Gel Sequence, K_{wro}	---	---	0.02
Post ASP Solution, K_{wro}	---	---	4.0

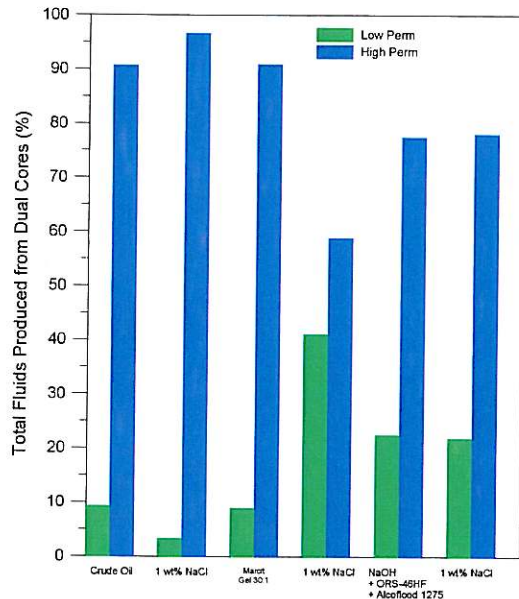


Figure 23 Flow Distribution between High and Low Permeability Cores, Dual Stacked Radial Coreflood, Chromium Acetate-Polyacrylamide Gel, green is low permeability and blue is high permeability

Change in flow distribution due to chromium acetate-polyacrylamide gel injection into the stacked radial core configuration is shown in Figure 23. Initial flow is distributed with 90% or greater flowing through the high permeability core during crude oil, initial waterflood, and gel injection. Flow distribution was equalized during the water flush subsequent to gel placement, indicating gel was diverting injected water from the high permeability core into the low permeability core. Injection of the alkaline-surfactant-polymer solution resulted in some reversion of injected fluid back to the high permeability core with approximately half of the diverted injection volume being maintained.

Oil recoveries from the chromium acetate-polyacrylamide gel stacked radial flood are summarized in Table 19. A significant volume of incremental oil was produced during gel injection from the high permeability core but not the low permeability core. Alkaline-surfactant-polymer injection produced a significant volume of

incremental oil from both core as well. It is possible that some oil mobilized from the low permeability core was produced by the high permeability core due to vertical communication.

Table 19
Oil Recovery of Chromium Acetate -- Polyacrylamide Gel
Dual Stacked, Same Well Bore Radial Coreflood

Injected Solution	-----Cumulative Oil Recovery, % OOIP-----	
	High K - Core	Low K - Core
1.0 wt% NaCl - Waterflood	56.7	5.4
Gel Sequence and NaCl flush	76.0	7.4
ASP Solution and NaCl flush	83.1	20.8
	-----Incremental Oil Recovery, % OOIP-----	
	High K - Core	Low K - Core
Gel Incremental Oil Recovery	19.3	3.0
Gel+ASP Incremental Recovery	26.4	13.4

Linear corefloods evaluating the polyacrylamide-chromium acetate gel were evaluated at 125°F and 175°F to determine if the gels were stable to an alkaline-surfactant-polymer solution at elevated temperatures. Two pairs of linear corefloods were performed to evaluate if the polyacrylamide-chromium acetate gel and the xanthan gum-chromium acetate gel were stable to alkaline-surfactant-polymer solutions at elevated temperatures in core. Figures 24 and 25 depict the resistance factor changes for the polyacrylamide-chromium acetate gel at 125°F and 175°F, respectively. Table 20 summarizes core permeability changes.

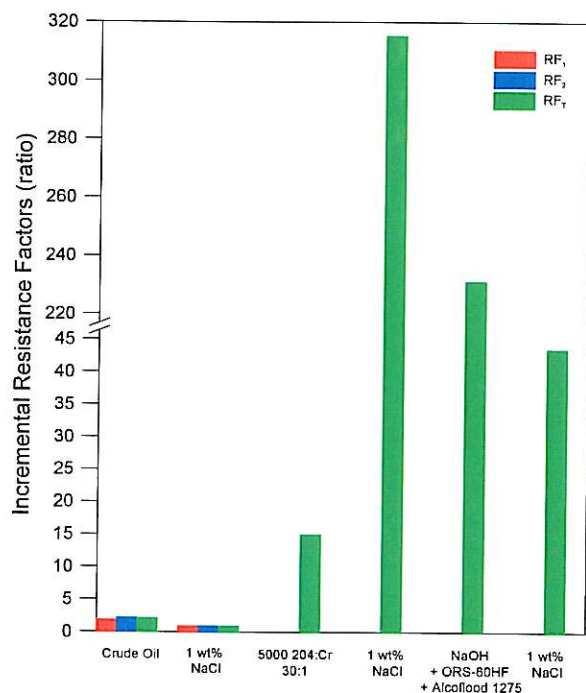


Figure 24 Ending Resistance Factors for Polyacrylamide-Chromium Acetate Gel followed by NaOH+ORS-60HF+Alcoflood 1275A Linear Coreflood at 125°F, from left to right each set of histograms is RF₁(red), RF₂(blue), RF_T(green)

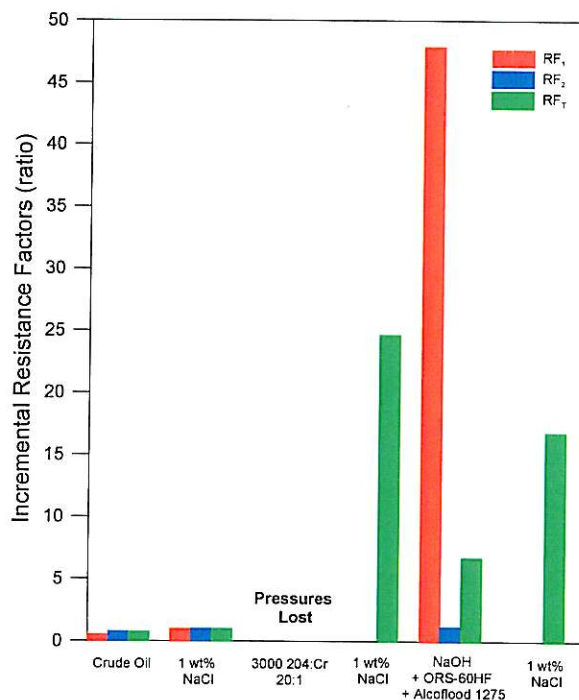


Figure 25 Ending Resistance Factors for Polyacrylamide-Chromium Acetate Gel followed by NaOH+ORS-60HF+Alcoflood 1275A Linear Coreflood at 175°F, from left to right each set of histograms is RF₁(red), RF₂(blue), RF_T(green)

Polyacrylamide-chromium acetate gels were stable to subsequent injection of a 1.0 wt% NaOH plus 0.10 wt% active ORS-60HF plus 1300 mg/L Alcoflood 1275A solution at 125 and 175°F.

Table 20
Berea Sandstone Physical Parameters
Polyacrylamide - Chromium Acetate Gel Linear Corefloods at 125 °F and 175°F

	-----Permeability (md)-----		
	<u>K₁</u>	<u>K₂</u>	<u>K_T</u>
NaOH+ORS-60HF+Alcoflood 1275A – 23.1% Porosity – 125°F			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	473	414	424
Effective Perm to Oil at Immobile Water, K _{orw}	646	320	353
Effective Perm to Water at Residual Oil, K _{wro}	13	6	7
Post Gel Sequence, K _{wro}	--	--	0.2
Post ASP Solution, K _{wro}	--	--	0.3
NaOH+ORS-60HF+Alcoflood 1275A – 23.3% Porosity – 175°F			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	282	772	555
Effective Perm to Oil at Immobile Water, K _{orw}	547	267	300
Effective Perm to Water at Residual Oil, K _{wro}	17	40	24
Post Gel Sequence, K _{wro}	--	--	<0.1
Post ASP Solution, K _{wro}	--	--	0.3

Gel sequence and alkaline-surfactant-polymer injection recovered additional oil. Table 21 summarizes oil production with each step. Oil recovery with the 19.4° API crude oil that had ultra low interfacial tension values between the alkaline-surfactant-polymer solution and the crude oil are significantly greater than those with the Big Sinking oil with relatively high interfacial tension values.

Table 21
Oil Recovery of Polyacrylamide-Chromium Acetate Gel Corefloods at 125 °F and 175°F

	-----Cumulative Oil Recovery, % OOIP-----	
<u>Injected Solution</u>	<u>125°F-Coreflood</u>	<u>175°F-Coreflood</u>
1.0 wt% NaCl - Waterflood	52.8	63.7
Gel Sequence and NaCl flush	75.2	74.0
ASP Solution and NaCl flush	95.6	98.4
	-----Incremental Oil Recovery, % OOIP-----	
Gel Incremental Oil Recovery	22.4	10.3
Gel+ASP Incremental Recovery	20.4	24.4

A dual stacked core pair with a common well bore coreflood in which cross flow was possible evaluated the stability of a chromium acetate-polyacrylamide gel to subsequent alkaline-surfactant-polymer injection at 175°F. Injected gel mixture was 3000 mg/L Watercut 204 plus 150 mg/L Watercut 684 as Cr⁺³. Polymer and chromium ion concentrations were lower than previously reported 72°F coreflood to permit gel to be injected prior to becoming rigid. Injected alkaline-surfactant-polymer solution was 1.0 wt% NaOH plus 0.06 wt% active ORS-60HF plus 1300 mg/L Alcoflood 1275A. Crude oil was the 19.4° API gravity crude oil. Figures 26 and 27 depict resistance factor changes for both core. Chromium acetate-polyacrylamide gel reduced

the permeability of each core with the high permeability core permeability reduction being slightly greater during and after gel injection. Permeability changes were maintained after alkaline-surfactant-polymer injection but not to the same degree as previously reported possibly due to injection of a more fluid gel and gel syneresis. Permeability changes for dual, stacked core chromium acetate-polyacrylamide coreflood are summarized in Table 22.

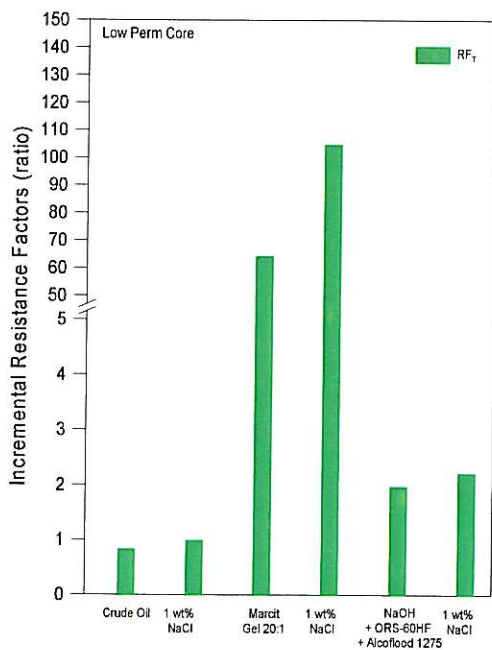


Figure 26 Low Permeability Core, Ending Resistance Factors for the Rigid Chromium Acetate-Polyacrylamide Gel followed by NaOH+ORS-60HF+Alcoflood 1275A at 175°F, from left to right each set of histograms is RF_T (green)

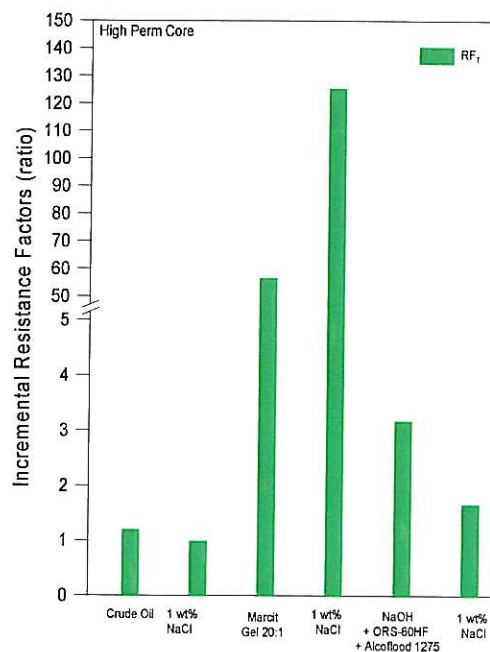


Figure 27 High Permeability Core, Ending Resistance Factors for the Rigid Chromium Acetate-Polyacrylamide Gel followed by NaOH+ORS-60HF+Alcoflood 1275A at 175°F, from left to right each set of histograms is RF_T (green)

Table 22
**Berea Sandstone Physical Parameters – Chromium Acetate-Polyacrylamide
Dual Stacked, Same Well Bore 175°F Radial Coreflood**

	-----Permeability (md)-----		
	K_1	K_2	K_T
NaOH+ORS-60HF+Alcoflood 1275A			
High Permeability Core – 23.0% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	535	458	508
Effective Perm to Oil at Immobile Water, K_{orw}	105	90	90
Effective Perm to Oil at Immobile Water, K_{orw} (after stacking core)	---	---	108
Effective Perm to Water at Residual Oil, K_{wro}	---	---	3.7
Post Gel Sequence, K_{wro}	---	---	0.03
Post ASP Solution, K_{wro}	---	---	2.2
Low Permeability Core – 18.5% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	45	82	52
Effective Perm to Oil at Immobile Water, K_{orw}	28	18	23
Effective Perm to Oil at Immobile Water, K_{orw} (after stacking core)	---	---	26
Effective Perm to Water at Residual Oil, K_{wro}	---	---	0.6
Post Gel Sequence, K_{wro}	---	---	0.01
Post ASP Solution, K_{wro}	---	---	0.3

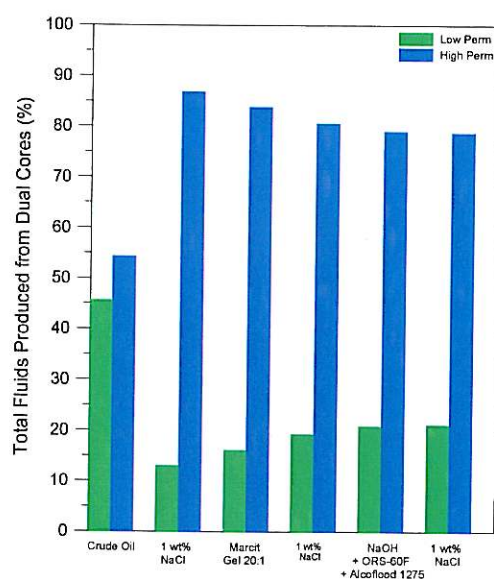


Figure 28 Flow Distribution between High and Low Permeability Cores, Dual Stacked Radial Coreflood at 175°F, Chromium Acetate -Polyacrylamide Gel, green is low permeability and blue is high permeability

Change in flow distribution due to chromium acetate-polyacrylamide gel injection into the stacked radial core configuration is shown in Figure 28. Flow distribution was 87% flow through the high permeability core during initial waterflood. Flow distribution was reduced to 80% through the high permeability core during the water flush subsequent to gel placement, indicating gel was diverting injected water from the high permeability core into the low permeability core. Injected alkaline-surfactant-polymer solution did not alter the flow distribution.

Oil recoveries from the chromium acetate-polyacrylamide gel stacked radial flood are summarized in Table 23. Incremental oil was produced during gel injection from each core. Alkaline-surfactant-polymer injection produced a significant volume of incremental oil from both core.

Table 23

**Oil Recovery of Chromium Acetate -- Polyacrylamide Gel
Dual Stacked, Same Well Bore, 175°F Radial Coreflood**

<u>Injected Solution</u>	-----Cumulative Oil Recovery, % OOIP-----	
	<u>High K - Core</u>	<u>Low K - Core</u>
1.0 wt% NaCl - Waterflood	47.5	30.4
Gel Sequence and NaCl flush	59.1	38.0
ASP Solution and NaCl flush	93.0	52.1
-----Incremental Oil Recovery, % OOIP-----		
Gel Incremental Oil Recovery	11.6	6.6
Gel+ASP Incremental Recovery	33.9	14.1

The final coreflood in the polyacrylamide-chromium acetate gel series was a fractured core linear coreflood at 72°F. Coreflood was performed to determine if gel solutions placed in a fracture are stable to subsequent injection of an alkaline-surfactant-polymer solution. Injected gel mixture was 7500 mg/L Flocon 4800C plus 250 mg/L Watercut 684 as Cr⁺³. Alkaline-surfactant-polymer solution injected was 1.0 wt% NaOH plus 0.06 wt% active ORS-46HF plus 1300 mg/L Alcoflood 1275A.

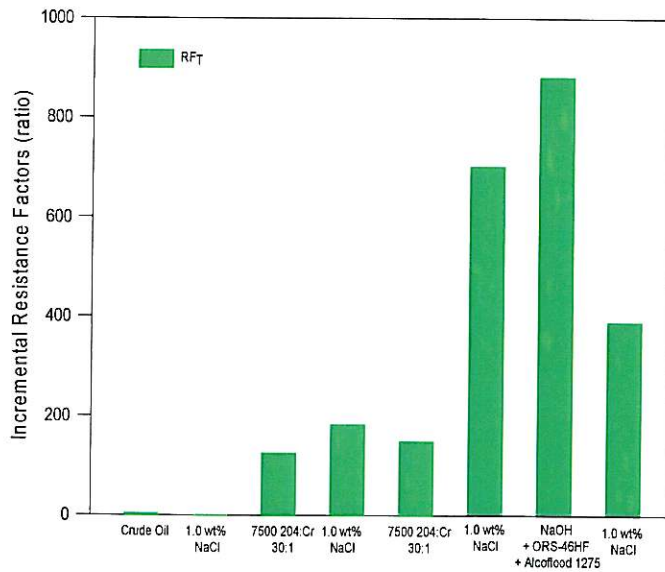


Figure 29 Ending Resistance Factors for a Rigid Polyacrylamide-Chromium Acetate Gel followed by NaOH+ORS-46HF+Alcoflood 1275A in a Fractured Core Linear Coreflood, R_FT(green)

Figure 29 depicts resistance factor changes measured from the injection face to the production face of the core. Residual resistance factors after gel injection and before alkaline-surfactant-polymer solution indicated gel was placed uniformly in the fracture as well as in the core. Residual resistance factors after alkaline-surfactant-polymer injection following gel injection were maintained and were of the same order of magnitude as prior to alkaline-surfactant-polymer injection. Polyacrylamide-chromium acetate gels used to plug fractures are stable to subsequent NaOH alkaline-surfactant-polymer solution injection. Permeability changes are summarized in Table 24.

Table 24
Berea Sandstone Physical Parameters
Chromium Acetate – Polyacrylamide Fracture Core Linear Coreflood
Permeability (md)

	<u>K_T</u>
NaOH+ORS-46HF+Alcoflood 1275A – 22.8% Porosity	
Pre-Fracture Absolute Permeability to 1.0 wt% NaCl, K _{abs}	630
Pre-Fracture Effective Perm to Oil at Immobile Water, K _{orw}	355
Post-Fracture Effective Perm to Oil at Immobile Water, K _{orw}	33,500
Post-Fracture Effective Perm to Water at Residual Oil, K _{wro}	23,000
Post-Fracture, Post-Gel Sequence, K _{wro}	33
Post-ASP Solution, K _{wro}	60

Chromium-Xanthan Gum Gel Formation

Chromium acetate-xanthan gum gels either did not form a gel or formed flowing to hard gels as listed in Table 25.

Table 25
Chromium Acetate – Xanthan Gum Gel Formation

Flocon 4800C		Gel Description	
Concentration	Ratio		
<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% Na_2SO_4 , high concentration polymer and chromium ion gels showed little syneresis and low concentration gels did not shrink.

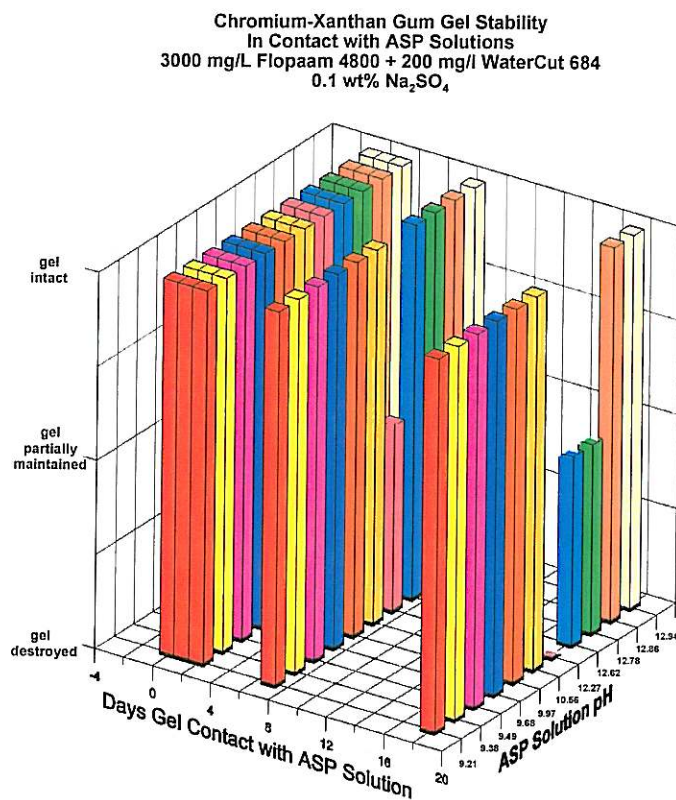


Figure 30 Chromium (III)-Xanthan Gum Gel in 0.1% Na_2SO_4 Stability with ASP Solutions

injection and before alkaline-surfactant-polymer solution indicated gel was placed uniformly through the core. Average permeability reduction of 5 was observed with the xanthan gum-chromium acetate gel.

Chromium acetate:xanthan gum gels were stable when in contact with up to pH 12.9 alkaline-surfactant-polymer solutions dissolved in either 0.1% Na_2SO_4 or 1.0% NaCl for 19 days at 72, 125, and 175°F. Gels were either tonguing or rigid tonguing gels (3,000 and 5,000 mg/L xanthan gum, respectively). Figure 30 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.

72°F linear corefloods were performed to determine if chromium acetate-xanthan gum gel solutions are stable to subsequent injection of an alkaline-surfactant-polymer solution. Injected gel mixture was 7500 mg/L Flocon 4800C plus 335 mg/L Watercut 684 as Cr^{+3} . Figures 31 and 32 depict resistance factor changes for NaOH and Na_2CO_3 alkaline-surfactant-polymer corefloods. Residual resistance factors after gel

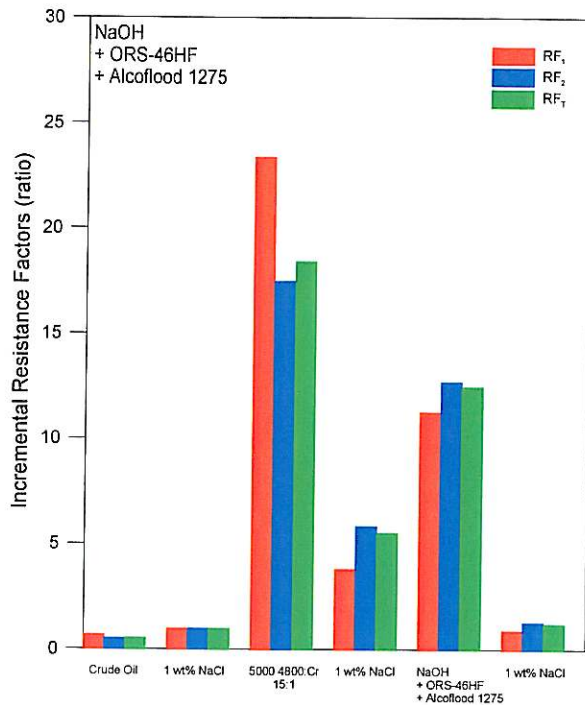


Figure 31 Ending Resistance Factors for Chromium Acetate-Xanthan Gum Gel followed by NaOH+ORS-46HF+Alcoflood 1275A Linear Coreflood, from left to right each set of histograms is RF₁(red), RF₂(blue), RF_T(green)

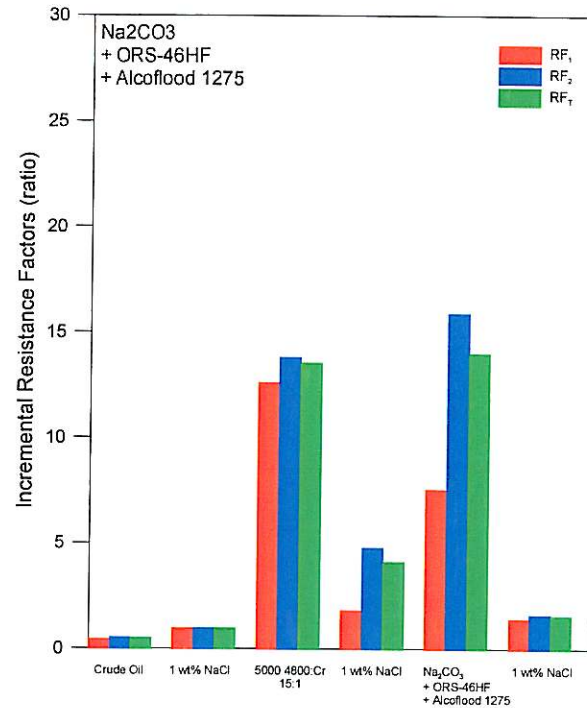


Figure 32 Ending Resistance Factors for Chromium Acetate-Xanthan Gum Gel followed by Na₂CO₃+ORS-46HF+Alcoflood 1275A Linear Coreflood, from left to right each set of histograms is RF₁(red), RF₂(blue), RF_T(green)

Resistance factors during alkaline-surfactant-polymer solution injection were of the same order of magnitude as alkaline-surfactant-polymer solutions without prior gel injection, in the 5 to 20 range. Residual resistance factors after alkaline-surfactant-polymer injection following gel injection were approximately the same as those after just alkaline-surfactant-polymer solution injection, 1.6 after the Na₂CO₃ solution and 1.2 after the NaOH solution compared to 1.5 and 1.0, respectively. Xanthan gum-chromium acetate gels are not stable to either NaOH or Na₂CO₃ alkaline-surfactant-polymer solution injection. Table 26 summarizes permeability changes.

Table 26

Berea Sandstone Physical Parameters			
Chromium Acetate – Xanthan Gum Linear Corefloods			
	-----Permeability (md)-----		
	<u>K₁</u>	<u>K₂</u>	<u>K_T</u>
NaOH+ORS-46HF+Alcoflood 1275A – 23.0% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	450	538	517
Effective Perm to Oil at Immobile Water, K _{orw}	522	528	527
Effective Perm to Water at Residual Oil, K _{wro}	56	43	45
Post Gel Sequence, K _{wro}	15	7	8
Post ASP Solution, K _{wro}	61	33	36

Na₂CO₃+ORS-46HF+Alcoflood 1275A – 22.9% Porosity

Absolute Permeability to 1.0 wt% NaCl, K _{abs}	298	366	349
Effective Perm to Oil at Immobile Water, K _{orw}	383	381	381
Effective Perm to Water at Residual Oil, K _{wro}	27	32	31
Post Gel Sequence, K _{wro}	15	7	8
Post ASP Solution, K _{wro}	18	19	19

Xanthan gum-chromium acetate gel injection produced some incremental oil, as did alkaline-surfactant-polymer injection. Waterflood and chemical flood (gel plus ASP solution) oil recoveries are lower than those observed without prior gel injection. Prior gel injection does not affect subsequent alkaline-surfactant-polymer solution ability to produce incremental oil. Table 27 summarizes the oil production with each step.

Table 27

Oil Recovery of Chromium Acetate – Xanthan Gum Gel Linear Corefloods

<u>Injected Solution</u>	-----Cumulative Oil Recovery, % OOIP-----	
	<u>NaOH-Coreflood</u>	<u>Na₂CO₃-Coreflood</u>
1.0 wt% NaCl - Waterflood	41.5	40.6
Gel Sequence and NaCl flush	51.9	50.7
ASP Solution and NaCl flush	65.3	59.0
	-----Incremental Oil Recovery, % OOIP-----	
Gel Incremental Oil Recovery	10.4	10.1
Gel+ASP Incremental Recovery	23.8	18.4

Xanthan gum-chromium acetate gel system linear corefloods at 125°F and 175°F were performed to evaluate if gels were stable to an alkaline-surfactant-polymer solution at elevated temperatures. Figures 33 and 34 depict the resistance factor changes for the xanthan gum-chromium acetate gels at 125°F and 175°F, respectively. Xanthan gum-chromium acetate gel was not stable to subsequent injection of a 1.0 wt% NaOH plus 0.06 wt% active ORS-60HF plus 1300 mg/L Alcoflood 1275A solution either at 125°F or at 175°F. The latter is due primarily to the instability of the gel at the higher temperature. Table 28 summarizes core permeability changes.

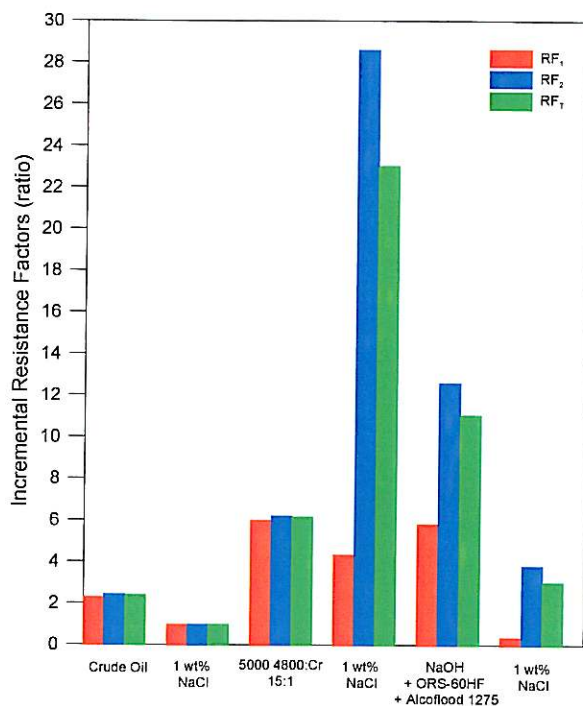


Figure 33 Ending Resistance Factors for Xanthan Gum-Chromium Acetate Gel followed by NaOH+ORS-60HF+Alcoflood 1275A Linear Coreflood at 125°F, from left to right each set of histograms is RF₁(red), RF₂(blue), RF_T(green)

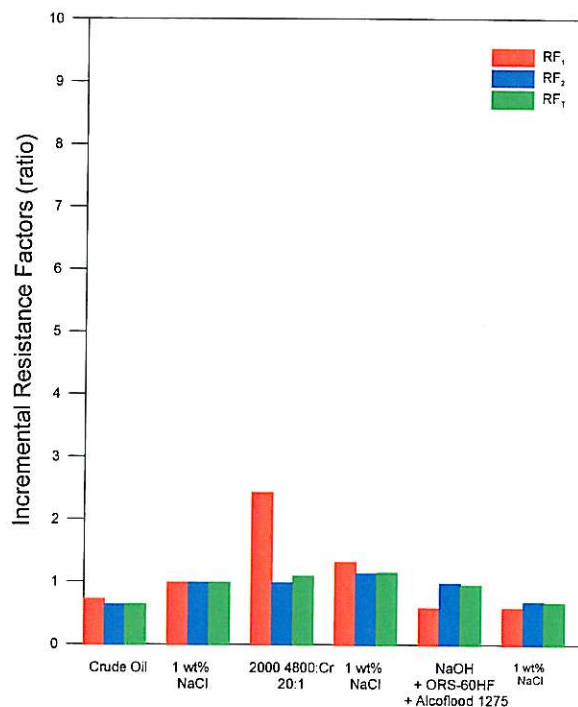


Figure 34 Ending Resistance Factors for Xanthan Gum-Chromium Acetate Gel followed by NaOH+ORS-60HF+Alcoflood 1275A Linear Coreflood at 175°F, from left to right each set of histograms is RF₁(red), RF₂(blue), RF_T(green)

Table 28

Berea Sandstone Physical Parameters

Xanthan Gum-Chromium Acetate Gel Linear Corefloods at 125°F and 175°F

	-----Permeability (md)-----		
	K_1	K_2	K_T
NaOH+ORS-60HF+Alcoflood 1275A – 22.8% Porosity – 175°F			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	346	280	291
Effective Perm to Oil at Immobile Water, K_{orw}	528	262	288
Effective Perm to Water at Residual Oil, K_{wro}	15	4	5
Post Gel Sequence, K_{wro}	8	2	3
Post ASP Solution, K_{wro}	18	5	6
NaOH+ORS-60HF+Alcoflood 1275A – 22.6% Porosity – 125°F			
Absolute Permeability to 1.0 wt% NaCl, K_{abs}	514	499	502
Effective Perm to Oil at Immobile Water, K_{orw}	535	535	535
Effective Perm to Water at Residual Oil, K_{wro}	32	21	22
Post Gel Sequence, K_{wro}	8	2	3
Post ASP Solution, K_{wro}	32	6	8

Gel sequence and alkaline-surfactant-polymer injection recovered additional oil. Table 29 summarizes oil production with each step.

Table 29
Oil Recovery of Xanthan Gum-Chromium Acetate Gel Corefloods at 125°F and 175°F

<u>Injected Solution</u>	-----Cumulative Oil Recovery, % OOIP-----	
	<u>125°F-Coreflood</u>	<u>175°F-Coreflood</u>
1.0 wt% NaCl - Waterflood	51.7	61.2
Gel Sequence and NaCl flush	69.4	68.4
ASP Solution and NaCl flush	92.4	92.2
	-----Incremental Oil Recovery, % OOIP-----	
Gel Incremental Oil Recovery	17.7	7.2
Gel+ASP Incremental Recovery	23.0	23.8

Significant incremental oil was produced by gel injection and subsequent alkaline-surfactant-polymer solutions with the 19.4° API gravity crude oil.

Resorcinol-Formaldehyde Gel Formation

Resorcinol-formaldehyde gels formed hard gels when dissolved in 1.0 wt% NaCl and in 0.1 wt% Na₂SO₄ at 72, 125, and 175°F. Gels formed at pH 9. Resorcinol concentrations of 1.0% or greater and formaldehyde concentrations of 0.85 wt% or greater were required. 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 the sulfomethylated resorcinol-formaldehyde gels.

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 at 72, 125, and 175°F. Gels were dissolved in 0.1 wt% Na₂SO₄ and 1.0 wt% NaCl. Gels were classified as hard. Figures 35 and 36 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 when in contact with any of the alkaline-surfactant-polymer solutions.

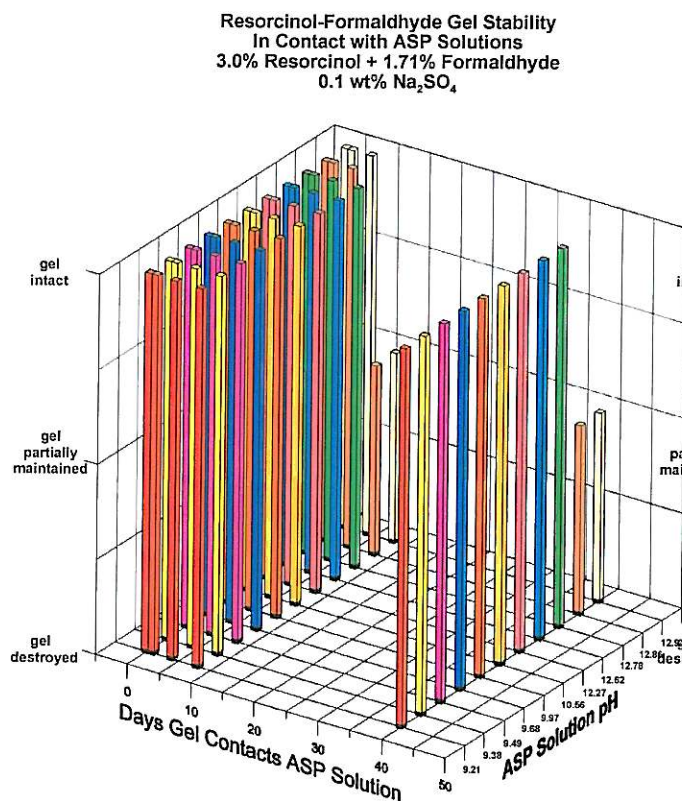


Figure 35 Resorcinol-Formaldehyde Gel in 0.1% Na₂SO₄ Stability with ASP Solutions

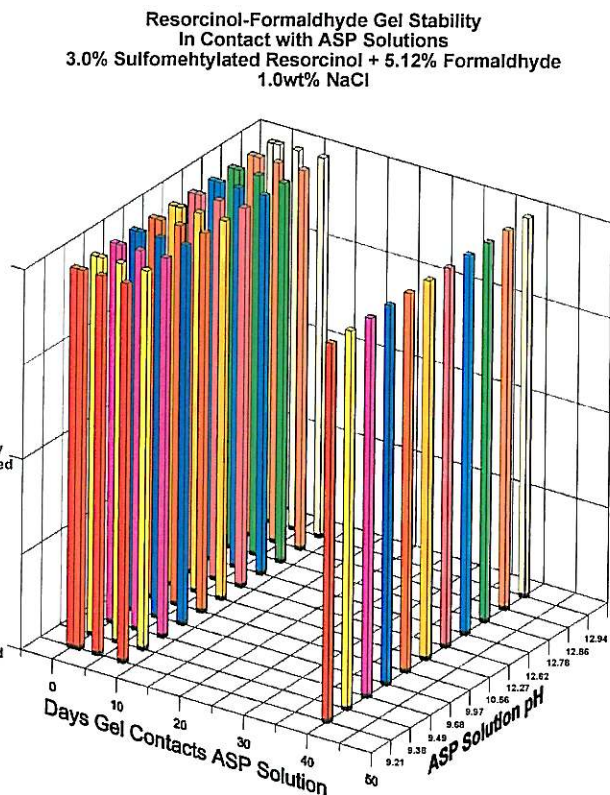


Figure 36 Sulfomethylated Resorcinol-Formaldehyde Gel in 0.1% NaCl Stability with ASP

Two pairs of linear core floods were performed to evaluate if the resorcinol-formaldehyde gel technology is stable to subsequent injection of an alkaline-surfactant-polymer solution. A rigid resorcinol-formaldehyde gel was evaluated in linear corefloods. Injected gel mixture was 20,000 mg/L resorcinol plus 17,100 mg/L formaldehyde at pH 9. Figures 37 and 38 depict the resistance factor changes for the NaOH and Na₂CO₃ corefloods.

In both flowing rigid resorcinol-formaldehyde gel corefloods, resistance factor after gel was reduced by alkaline-surfactant-polymer injection but not to levels of the base alkaline-surfactant-polymer injection. Gel coreflood resistance factors are 3.5 after the Na₂CO₃ solution and 6.2 after the NaOH solution compared to 1.5 and 1.0 for just alkaline-surfactant-polymer solutions, respectively. This suggests that resorcinol-formaldehyde gel permeability reduction was reduced but not eliminated by alkaline-surfactant-polymer solution injection. Permeability changes are summarized in Table 30.

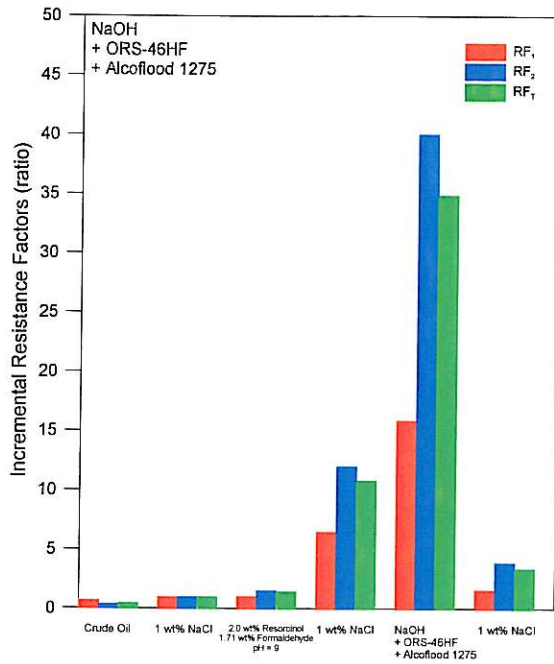


Figure 37 Ending Resistance Factors for the Rigid Resorcinol-Formaldehyde Gel followed by NaOH+ORS-46HF+Alcoflood 1275A Linear Coreflood, from left to right each set of histograms is RF₁(red), RF₂(blue), RF₃(green)

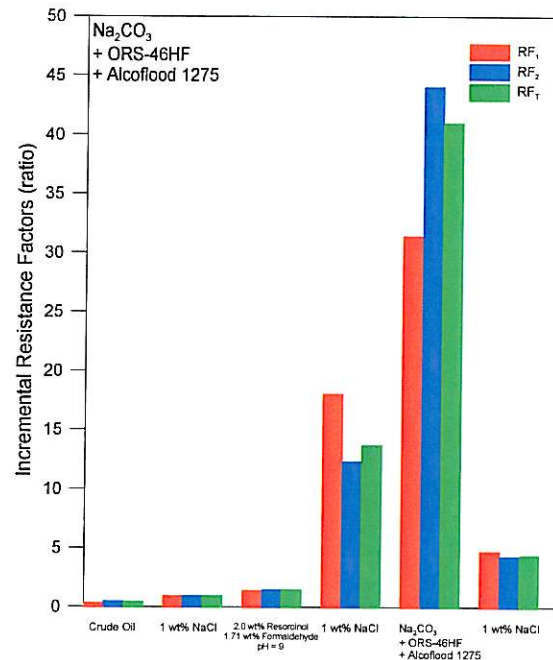


Figure 38 Ending Resistance Factors for the Rigid Resorcinol-Formaldehyde Gel followed by Na₂CO₃+ORS-46HF+Alcoflood 1275A Linear Coreflood, from left to right each set of histograms is RF₁(red), RF₂(blue), RF₃(green)

Table 30
Berea Sandstone Physical Parameters
Rigid Resorcinol-Formaldehyde Gel Linear Corefloods

	-----Permeability (md)-----		
	<u>K₁</u>	<u>K₂</u>	<u>K_T</u>
NaOH+ORS-46HF+Alcoflood 1275A – 20.7% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	621	626	625
Effective Perm to Oil at Immobile Water, K _{orw}	369	681	589
Effective Perm to Water at Residual Oil, K _{wro}	42	43	42
Post Gel Sequence, K _{wro}	6	4	4
Post ASP Solution, K _{wro}	26	11	12
Na ₂ CO ₃ +ORS-46HF+Alcoflood 1275A – 20.0% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	316	530	467
Effective Perm to Oil at Immobile Water, K _{orw}	386	370	373
Effective Perm to Water at Residual Oil, K _{wro}	23	30	28
Post Gel Sequence, K _{wro}	1	3	2
Post ASP Solution, K _{wro}	5	4	4

Oil recovery was not affected by resorcinol-formaldehyde injection. Table 31 summarizes the oil production with each step.

Table 31

Oil Recovery of Rigid Resorcinol-Formaldehyde Gel Linear Corefloods

<u>Injected Solution</u>	-----Cumulative Oil Recovery, % OOIP-----	
	<u>NaOH-Coreflood</u>	<u>Na₂CO₃-Coreflood</u>
1.0 wt% NaCl - Waterflood	44.0	47.1
Gel Sequence and NaCl flush	45.2	47.2
ASP Solution and NaCl flush	53.9	51.8
	-----Incremental Oil Recovery, % OOIP-----	
	Gel Incremental Oil Recovery	1.2
	Gel+ASP Incremental Recovery	9.9

Little incremental oil was produced by either resorcinol-formaldehyde gel injection or the subsequent alkaline-surfactant-polymer solutions. Chemical flood (gel plus ASP solution) oil recoveries are lower than those observed without prior gel injection. Prior resorcinol-formaldehyde gel injection appears to reduce subsequent alkaline-surfactant-polymer solution incremental oil production.

Silicate-Polyacrylamide Gel Formation

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 100 mg/l. Gels were hard gels and no syneresis was observed.

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 39 shows the 40,000 mg/l Ludox SM data.

The final pair of linear corefloods evaluated stability of the silicate-polyacrylamide gel technology to subsequent alkaline-surfactant-polymer injection. A rigid gel

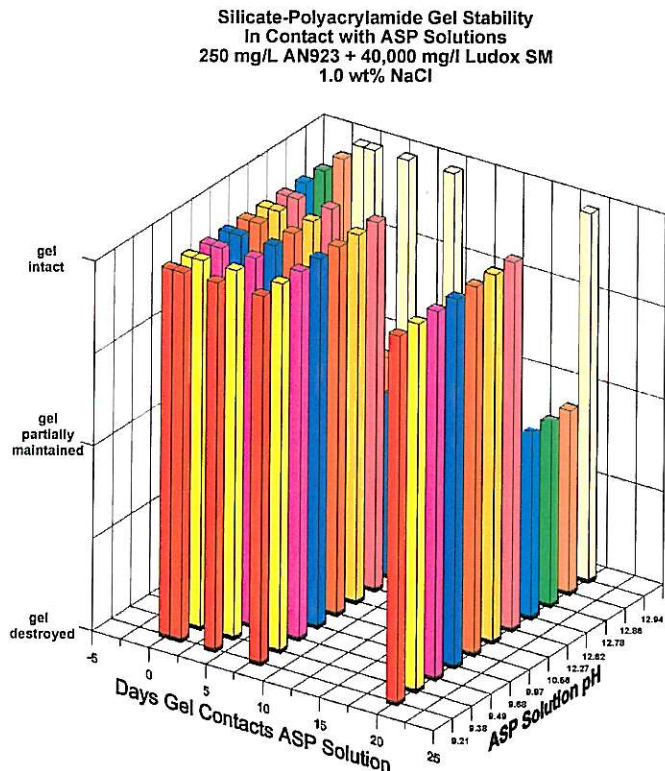


Figure 39 Silicate-Polyacrylamide Gel in 0.1% Na₂SO₄ Stability with ASP Solutions

composed of 250 mg/L Flopaam 923, 100 mg/L CaCl_2 , and 30,000 mg/L Ludox SM was injected prior to alkaline-surfactant-polymer solutions. Figures 40 and 41 depict resistance factor changes for NaOH and Na_2CO_3 alkaline-surfactant-polymer corefloods. Gel injection reduced permeability with NaCl flush resistance factors of approximately 10. Injection of either NaOH or Na_2CO_3 alkaline-surfactant-polymer solutions resulted in loss of permeability reduction. Residual resistance factors were 1.5 to 2.0. Na_2CO_3 coreflood front-end resistance factor showed plugging. Front-end data was ignored. Silicate-polyacrylamide gels are not stable to subsequent injection of alkaline-surfactant-polymer solutions.

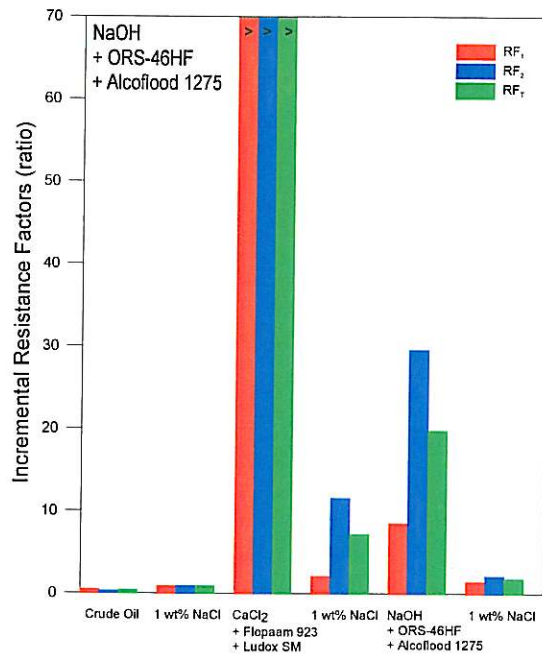


Figure 40 Ending Resistance Factors for the Silicate-Polyacrylamide Gel followed by NaOH+ORS-46HF-Alcoflood 1275A Linear Coreflood, from left to right each set of histograms is RF₁(red), RF₂(blue), RF_r(green)

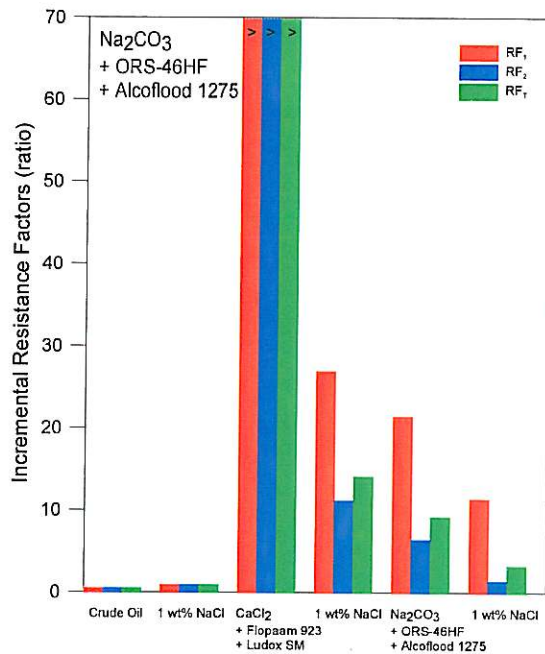


Figure 41 Ending Resistance Factors for the Silicate-Polyacrylamide Gel followed by Na_2CO_3 +ORS-46HF+Alcoflood 1275A Linear Coreflood, from left to right each set of histograms is RF₁(red), RF₂(blue), RF_r(green)

Permeability changes for silicate-polyacrylamide corefloods are summarized in Table 32.

Table 32
Berea Sandstone Physical Parameters – Silicate - Polyacrylamide

	-----Permeability (md)-----		
	<u>K₁</u>	<u>K₂</u>	<u>K_T</u>
NaOH+ORS-46HF+Alcoflood 1275A – 22.1% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	100	900	350
Effective Perm to Oil at Immobile Water, K _{orw}	250	1300	710
Effective Perm to Water at Residual Oil, K _{wro}	22	76	50
Gel Sequence	10	7	7
ASP Solution	14	34	27

	-----Permeability (md)-----		
	<u>K₁</u>	<u>K₂</u>	<u>K_T</u>
Na ₂ CO ₃ +ORS-46HF+Alcoflood 1275A – 22.9% Porosity			
Absolute Permeability to 1.0 wt% NaCl, K _{abs}	485	395	410
Effective Perm to Oil at Immobile Water, K _{orw}	685	605	620
Effective Perm to Water at Residual Oil, K _{wro}	58	52	53
Gel Sequence	2	5	4
ASP Solution	5	35	16

Oil recoveries from the silicate-polyacrylamide gel floods are summarized in Table 33. Oil recoveries were similar to the aluminum citrate-polyacrylamide corefloods with little incremental oil being produced during gel injection. Alkaline-surfactant-polymer injection produced a significant volume of incremental oil and total oil recovery was in the same range as prior corefloods.

Table 33
Oil Recovery of Silicate – Polyacrylamide Gel Linear Corefloods

<u>Injected Solution</u>	-----Cumulative Oil Recovery, % OOIP-----	
	<u>NaOH-Coreflood</u>	<u>Na₂CO₃-Coreflood</u>
1.0 wt% NaCl - Waterflood	46.9	52.5
Gel Sequence and NaCl flush	49.7	57.6
ASP Solution and NaCl flush	87.5	89.2
Gel Incremental Oil Recovery	3.2	5.1
Gel+ASP Incremental Recovery	37.8	31.6

Iron-Polyacrylamide Gel Formation

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.

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.

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. Aluminum citrate-polyacrylamide gels were not stable to subsequent injection of either a NaOH or a Na₂CO₃ alkaline-surfactant-polymer solution.
3. 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.
4. Chromium-polyacrylamide gels are stable to injection of either a NaOH or a Na₂CO₃ alkaline-surfactant-polymer solution. from 72°F to 175°F.
5. Flowing and rigid tonguing chromium-polyacrylamide gels were stable to injection of both NaOH and Na₂CO₃ alkaline-surfactant-polymer solutions. Rigid tonguing gels maintained permeability reduction after an alkaline-surfactant-polymer solution was injected while flowing gels permeability increased but not to either pre-gel or alkaline-surfactant-polymer flush values.
6. 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.
7. Chromium-xanthan gum gels are not stable to injection of either a NaOH or a Na₂CO₃ alkaline-surfactant-polymer solution.
8. Silicate-polyacrylamide gels were stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9.
9. Silicate-polyacrylamide gels were not stable to subsequent injection of either a NaOH or a Na₂CO₃ alkaline-surfactant-polymer solution.
10. Resorcinol-formaldehyde and sulfomethylated resorcinol-formaldehyde gels were stable to alkaline-surfactant-polymer solutions with pH values ranging from 9.2 to 12.9.
11. Iron-polyacrylamide gels were not stable to alkaline-surfactant-polymer solutions regardless of pH.
12. Prior gel sequence injection did not reduce the total oil recovered by a waterflood plus alkaline-surfactant-polymer solution with the exception of the resorcinol-formaldehyde gel.
13. Gel injection followed by alkaline-surfactant-polymer injection will improve oil recovery by diverting alkaline-surfactant-polymer solution into lower permeability rock.
14. Gels used to seal fractures are stable to subsequent alkaline-surfactant-polymer solution injection, if gels are stable to alkaline-surfactant-polymer solutions in other applications.

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