ASP Design for the Minnelusa Formation under Low-Salinity Conditions: Impact of Anhydrite Dissolution on ASP performance

By
Mahdi Kazempour
Casey S. Gregersen
Vladimir Alvarado

Chemical and Petroleum Engineering Department, University of Wyoming

Date
September 11th, 2012
Overview

• Introduction

• Objective
  • **ASP** design for X reservoir in the Minnelusa formation
    • **Under** low- salinity condition
    • **Presence** of anhydrite

• **Conclusions & Future Works**
Introduction

Basic concepts relevant to chemical EOR mechanisms:

**Alkaline**
- Generates in-situ soaps
- Regulates ionic strength
- Reduces the adsorption of anionic species
- Alters the wettability

**Surfactant**
- Lowers IFT between oil and brine
- Alters the wettability

**Polymer**
- Increases water viscosity
- Reduces water permeability
- Improves the viscoelastic behavior of displacing fluid

\[ S_{or} = f\left( CN = \frac{Viscous \; forces}{Capillary \; forces}\right) \]

\[ S_{or} \downarrow \quad CN \uparrow \]

Lake 89; Wyatt et al. 2002; Hirasaki et al. 2008; Kazempour et al. 2011
Introduction (cont’d)

Scheme representing basic interactions during alkaline flooding:

Alkali

- Alkali-aqueous species interactions
- Alkali-rock interactions
- Alkali-oil interaction (soap generation)

Water

Rock

- Sandstone (Berea)
- Sandstone (containing anhydrite (A))
- Sandstone (containing active clays (AC))
- Sandstone (containing both A & AC)

Crude Oil
Design an ASP Blend for Low-Salinity Minnelusa Conditions
Fresh injection water:

1,600 ppm NaCl

Low salinity Minnelusa formation water:

< 20,000 ppm of TDS

<table>
<thead>
<tr>
<th>Oil</th>
<th>$\mu_{oil}$ (cP)</th>
<th>$\rho_{oil}$ (gr/cc)</th>
<th>TAN (mg KOH/gr oil)</th>
<th>Asphaltene (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>83</td>
<td>0.91</td>
<td>0.43</td>
<td>5.41</td>
</tr>
</tbody>
</table>
Fluid-Fluid Interactions
Phase Behavior (Bottle Tests)

Parameter
- Salinity
- Surfactant blend ratio
- Soap/surfactant ratio

Initial interface
Brine + surfactant

Pipette (bottom sealed)

Varying parameter

Oil

Winsor Type - I
Winsor Type - II
Winsor Type - III

24 hr

Optimal parameter

Winsor Type - I
Winsor Type - II
Winsor Type - III
Phase behavior (cont’d)

Only 1 wt% Surfactant

Salinity \((\text{NaCl ppm})\) increases

<table>
<thead>
<tr>
<th>5000</th>
<th>10000</th>
<th>125000</th>
<th>15000</th>
<th>17500</th>
<th>20000</th>
<th>22500</th>
<th>25000</th>
<th>30000</th>
<th>35000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Phase behavior (cont’d)

Blend of 1wt% Surfactant + 1wt% Na₂CO₃

Salinity (NaCl ppm) increases

<table>
<thead>
<tr>
<th>Salinity (NaCl ppm)</th>
<th>1500</th>
<th>2500</th>
<th>3500</th>
<th>5000</th>
<th>7500</th>
<th>10000</th>
<th>15000</th>
<th>20000</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Ionic strength (Molal)</th>
<th>0.287</th>
<th>0.303</th>
<th>0.320</th>
<th>0.344</th>
<th>0.385</th>
<th>0.425</th>
<th>0.507</th>
<th>0.589</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺ conc. (Molal)</td>
<td>0.214</td>
<td>0.231</td>
<td>0.249</td>
<td>0.274</td>
<td>0.317</td>
<td>0.360</td>
<td>0.445</td>
<td>0.531</td>
</tr>
</tbody>
</table>
Phase behavior (cont’d)

Blend of 1wt% Surfactant + 1wt% NaOH

Salinity (NaCl ppm) increases

<table>
<thead>
<tr>
<th>Salinity (ppm)</th>
<th>Ionic strength (Molal)</th>
<th>Na⁺ conc. (Molal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>0.257</td>
<td>0.276</td>
</tr>
<tr>
<td>2500</td>
<td>0.273</td>
<td>0.293</td>
</tr>
<tr>
<td>3500</td>
<td>0.290</td>
<td>0.310</td>
</tr>
<tr>
<td>5000</td>
<td>0.314</td>
<td>0.336</td>
</tr>
<tr>
<td>7500</td>
<td>0.354</td>
<td>0.378</td>
</tr>
<tr>
<td>10000</td>
<td>0.395</td>
<td>0.421</td>
</tr>
<tr>
<td>15000</td>
<td>0.476</td>
<td></td>
</tr>
</tbody>
</table>
Phase Behavior (The Role of Alkali Type)

The opt. Salinity < 20,000 ppm

Only 1wt% Surfactant

1wt% Surfactant + 1wt% NaOH

Opt_Sal > 35,000 ppm

Opt_Sal =~ 11,500 ppm

1wt% Surfactant + 1wt% Na\textsubscript{2}CO\textsubscript{3}

Opt_Sal =~ 30,000 ppm
Phase Behavior (The Role of Alkali Type) cont’d

Gregersen et al. Fuel, 2012
Rock-Fluid Interactions
Introduction (cont’d)

Traditional point of view: *fluid-fluid impacts*

Exploration in this research: *rock-fluid impacts on EOR performance*
Thin section results after flooding

Inlet face condition after NaOH flood
  $\Phi = 4.89\%$
Outlet face condition after NaOH flood
  $\Phi = 1.58\%$
Inlet face condition after Na$_2$CO$_3$ flood
  $\Phi = 3.73\%$
Outlet face condition after Na$_2$CO$_3$ flood
  $\Phi = 2.82\%$
Forward Simulation - Radial Case

(\text{NaOH} \text{ flood after 1 Inj. PV})

Kazempour et al. Fuel, 2012
(Na$_2$CO$_3$ flood after 1 Inj. PV)
Forward Simulation- Radial Case cont’d

(\text{NaBO}_2\text{ flood after 1 Inj. PV})
Linear Coreflooding Experiments
Linear Coreflooding System

The coreflooding system schematics
### Material & methods (cont’d)

<table>
<thead>
<tr>
<th><strong>X</strong> Crude Oil</th>
<th><strong>Viscosity at 48°C = 83 cP</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surfactant</strong></td>
<td>0.75wt%PS13-D + 0.25wt%PS3B</td>
</tr>
<tr>
<td><strong>Polymer</strong></td>
<td>Flopaam-3330s</td>
</tr>
<tr>
<td></td>
<td>2000 ppm (ASP)</td>
</tr>
<tr>
<td></td>
<td>1000 ppm (P)</td>
</tr>
<tr>
<td><strong>Alkali</strong></td>
<td>1wt% NaOH</td>
</tr>
<tr>
<td><strong>Core</strong></td>
<td><strong>Berea:</strong></td>
</tr>
<tr>
<td></td>
<td>L= 7.904 cm</td>
</tr>
<tr>
<td></td>
<td>D= 3.73 cm</td>
</tr>
<tr>
<td></td>
<td>PV= 22.12 cc</td>
</tr>
<tr>
<td></td>
<td>Φ= 25.62%</td>
</tr>
<tr>
<td></td>
<td>K&lt;sub&gt;air&lt;/sub&gt;= 366.9 md</td>
</tr>
<tr>
<td></td>
<td><strong>Minnelusa:</strong></td>
</tr>
<tr>
<td></td>
<td>L= 7.017 cm</td>
</tr>
<tr>
<td></td>
<td>D= 3.728 cm</td>
</tr>
<tr>
<td></td>
<td>PV= 16.41 cc</td>
</tr>
<tr>
<td></td>
<td>Φ= 21.43%</td>
</tr>
<tr>
<td></td>
<td>K&lt;sub&gt;air&lt;/sub&gt;= 808.2 md</td>
</tr>
</tbody>
</table>
Comparison between ASP Flooding Results in Berea and Minnelusa Cores

The sequence and slug size of injected materials:

- 8 PVs WF
- 1 PV ASP
- 1 PV P
- 5 PV WF

**Berea**

**Minnelusa**

*Gregersen et al. Fuel, 2012*
As expected, secondary minerals were produced (calcite and sulfur imply anhydrite dissolution)
Anhydrite Distribution along the Core (After Flooding)

Gregersen et al. Fuel, 2012
The Effect of Ca\textsuperscript{2+} presence on ASP performance

1 wt% NaOH +
0.75% PS13-D & 0.25% PS3B +
1500ppm NaCl +
Various amounts of CaCl\textsubscript{2}

After 1hr at 48 °C

Using 0.45 micron filter

Taking 6cc water sample from the top

Adding 6cc of the DC crude oil

Calcium precipitate (Here Ca(OH)\textsubscript{2})

Gregersen et al. Fuel, 2012
### The Effect of Ca$^{2+}$ presence on ASP performance cont’d

<table>
<thead>
<tr>
<th>TDS (mg/l)</th>
<th>11,500</th>
<th>12,500</th>
<th>13,500</th>
<th>15,000</th>
<th>17,500</th>
<th>20,000</th>
<th>25,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$ (mg/l)</td>
<td>0</td>
<td>35.7</td>
<td>40.8</td>
<td>49.1</td>
<td>74.7</td>
<td>132.7</td>
<td>728.3</td>
</tr>
<tr>
<td>pH (at 48 °C)</td>
<td>12.52</td>
<td>12.49</td>
<td>12.46</td>
<td>12.4</td>
<td>12.3</td>
<td>12.13</td>
<td>11.72</td>
</tr>
</tbody>
</table>
History Matching & Forward Simulation
HM Process

- Schematic figure
- $K_r$ at different CN
Two scenarios for HM:

- HM just RF (%OOIP)

- HM both RF (%OOIP) & pressure drop (ΔP) data
  - Monitoring surfactant concentration
HM Process (cont’d)

First scenario

Second scenario
Forward Simulation

Forward simulation: Hypothetical 3D case
Forward Simulation

First scenario

Second scenario
Closing Remarks

- The proposed ASP formulation, resulting from blending a surfactant with the appropriate cosurfactant, turns out to be effective under low salinity conditions. This was demonstrated in phase behavior and coreflooding experiments.

- Secondary mineral precipitation during ASP treatment is inferred from our observation, most likely as a result of anhydrite dissolution. This can lead to permeability reduction (injectivity loss), particularly in low-permeable formations and also fine accumulation in production facilities.

- The type of alkali agent and its initial concentration are paramount to achieve optimum phase behavior in the surfactant-soap system.
Future works

- Find additional chemical candidates for different conditions in other Wyoming’s formations.
- Complete numerical simulation part using the real geological model of that specific field.
- Perform a pilot test.
Acknowledgement

- My Colleagues:
  - Dr. V. Alvarado
  - Casey S. Gregersen

- TIORCO LLC.
  - Dr. E. J. Manrique

- Merit Company

- Enhanced Oil Recovery Institute
  - Dr. G. Murrell
  - Dr. R. Barati
  - David Mohrbacker

- The School of Energy Resources (SER)
Geochemical modeling and experimental evaluation of high-pH floods: Impact of Water–Rock interactions in sandstone

Mahdi Kazempour, Eric Sundstrom, Vladimir Alvarado

Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 82071, USA

Fuel xxx (2012) xxx–xxx

Role of active clays on alkaline–surfactant–polymer formulation performance in sandstone formations

Mahdi Kazempour a, Eduardo J. Manrique b,*, Vladimir Alvarado a,*, Jieyuan Zhang b, Michael Lantz b

a Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 82071, USA
b TNOCO LLC, 2452 S. Trenton Way, Suite M, Denver, CO 80231, USA

Fuel xxx (2012) xxx–xxx

ASP design for the Minnelusa formation under low-salinity conditions: Impacts of anhydrite on ASP performance

Casey S. Gregersen, Mahdi Kazempour, Vladimir Alvarado

Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 82071, USA

Fuel xxx (2012) xxx–xxx
THANK YOU!

Please ask your interesting questions
Backup Slides
I-76 (two-phase flow experiment)

CT-scanning results before flooding
Observed permeability damage (after flooding)
ASP Design for the Minnelusa Formation under Low-Salinity Conditions
ASP Design for the Minnelusa Formation under Low-Salinity Conditions
Results (ASP#Berea) (cont’d)
Results (ASP#2 Minnelusa)

pH and surfactant concentration at effluent:

Stable W/O emulsion
Find more economical solution (lowering the concentration of surfactant and alkali agents)
Phase behavior (cont’d) (Find more economical composition)

1 wt% surfactant vary NaOH concentration in 1600 ppm NaCl solution

Alkalinity (NaOH ppm) increases

<table>
<thead>
<tr>
<th>pH</th>
<th>Alkalinity (NaOH ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.35</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>500</td>
</tr>
<tr>
<td>12.3</td>
<td>1K</td>
</tr>
<tr>
<td>12.57</td>
<td>2K</td>
</tr>
<tr>
<td>12.73</td>
<td>3K</td>
</tr>
<tr>
<td>12.85</td>
<td>4K</td>
</tr>
<tr>
<td>12.93</td>
<td>5K</td>
</tr>
<tr>
<td>13</td>
<td>6K</td>
</tr>
<tr>
<td>13.06</td>
<td>7K</td>
</tr>
<tr>
<td>13.11</td>
<td>8K</td>
</tr>
<tr>
<td>13.16</td>
<td>9K</td>
</tr>
<tr>
<td>13.2</td>
<td>10K</td>
</tr>
<tr>
<td>13.46</td>
<td>20K</td>
</tr>
</tbody>
</table>
Phase behavior (cont’d) (find more economical composition)

0.5wt% surfactant vary NaOH concentration in 1600 ppm NaCl solution

Alkalinity (NaOH ppm) increases

<table>
<thead>
<tr>
<th>pH</th>
<th>Concentration (NaOH ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.35</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>500</td>
</tr>
<tr>
<td>12.3</td>
<td>1K</td>
</tr>
<tr>
<td>12.57</td>
<td>2K</td>
</tr>
<tr>
<td>12.73</td>
<td>3K</td>
</tr>
<tr>
<td>12.85</td>
<td>4K</td>
</tr>
<tr>
<td>12.93</td>
<td>5K</td>
</tr>
<tr>
<td>13</td>
<td>6K</td>
</tr>
<tr>
<td>13.06</td>
<td>7K</td>
</tr>
<tr>
<td>13.11</td>
<td>8K</td>
</tr>
<tr>
<td>13.16</td>
<td>9K</td>
</tr>
<tr>
<td>13.2</td>
<td>10K</td>
</tr>
<tr>
<td>13.46</td>
<td>20K</td>
</tr>
</tbody>
</table>

pH values: 7.35, 12, 12.3, 12.57, 12.73, 12.85, 12.93, 13, 13.06, 13.11, 13.16, 13.2, 13.46
Phase behavior (cont’d) (find more economical composition)

Regards to the phase behavior results:

It seems 0.5wt% surfactant and 0.5wt% NaOH can work too
Material & methods for ASP#3

<table>
<thead>
<tr>
<th>Dead man Creek Crude Oil</th>
<th>Viscosity at 48°C = 83 cP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surfactant</strong></td>
<td>0.375wt%PS13-D + 0.125wt%PS3B</td>
</tr>
<tr>
<td><strong>Polymer</strong></td>
<td>Flopaam-3330s</td>
</tr>
<tr>
<td></td>
<td>2000 ppm (ASP)</td>
</tr>
<tr>
<td></td>
<td>1000 ppm (P)</td>
</tr>
<tr>
<td><strong>Alkali</strong></td>
<td>0.5wt% NaOH</td>
</tr>
<tr>
<td><strong>Core</strong></td>
<td>Minnelusa:</td>
</tr>
<tr>
<td></td>
<td>L= 6.77 cm</td>
</tr>
<tr>
<td></td>
<td>D= 3.69 cm</td>
</tr>
<tr>
<td></td>
<td>PV= 13.33 cc</td>
</tr>
<tr>
<td></td>
<td>Φ= 18.41%</td>
</tr>
<tr>
<td></td>
<td>K_{air}= 280 md</td>
</tr>
</tbody>
</table>
Results (ASP#3)
### Y formation brine composition (25°C)

<table>
<thead>
<tr>
<th>Ions</th>
<th>Concentration (mg/lit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>35,545</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1,124</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>328</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3,309</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>54,200</td>
</tr>
<tr>
<td>pH</td>
<td>7</td>
</tr>
<tr>
<td>TDS</td>
<td>94,506</td>
</tr>
</tbody>
</table>
Surf. 4 (1 wt%) - at 71° C

NaCl increases (ppm)

Initial interface

Opt. salinity range ($\sigma > 10$)
Effect of hardness (Ca\textsuperscript{2+} and Mg\textsuperscript{2+})

Surf. 4 (1wt%) - at 71 C

NaCl conc. = 70K ppm
- Sample 1
  - Ca\textsuperscript{2+} = 600 ppm
  - Mg\textsuperscript{2+} = 200 ppm
- Sample 2
  - Ca\textsuperscript{2+} = 1200 ppm
  - Mg\textsuperscript{2+} = 400 ppm

Initial interface
Core 104-b (anhydrite distribution)
Primary results of first coreflood

WF → SP flood → P flood → Post-WF

Looks very promising
RF and Pressure Drop data of First Coreflooding (104-b)