A SQUEEZEABLE ASPHALTENE INHIBITOR FOR CO$_2$ FLOODED OIL FIELDS

July 11$^{th}$ 2013
Casper, Wyoming
Geoffrey Leonard - Research Engineer Baker Hughes Upstream Chemicals
Outline

• Background of Asphaltenes
• History
• First generation product performance
• New ‘Squeeze’ product’s developmental strategy
• Application and action
• Performance
• Coreflood Testing
• 100% Oil Coreflood Results
• Carbonate Formation Tests
• Future & Current Work
Background

Asphaltenes precipitate and deposit when destabilized
  – Natural pressure depletion in system
  – Acid
  – High gravity crude blending
  – CO₂ and NGL flooding

Asphaltene Inhibitor Applications
  – Continuous Injection systems via Capillaries
  – Current Squeeze Injections use conventional AI chemistries

Current Squeeze Applications
  – Some success stories (Italy, Coral Field, US Land)
  – Longer retention times are needed
  – An AI Squeeze chemistry can be applied inside formation where asphaltene onset pressure (AOP) maybe occurring
Pressure, Temperature, Composition Effects

Solubility is a minimum at the bubble point so deposition is highest at the bubble point.
**HP Test Method Product Development**

- Quantify deposits left in cell
- Quantify precipitates left in oil

![Graph showing asphaltenes (g) for Blank 1, Blank 2, Inhibitor A, and Inhibitor B](image)

- 15,000 psi, 390°F
- NIR laser solids detection
- Mercury free
- Variable volume
- High pressure deposition and filtration

![Equipment setup showing piston, gas, oil, and laser](image)
Polar Fractions Distribution

West Texas Samples

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Asph from solid deposit</th>
<th>Asph from pentane ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>F^40/60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F^30/70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F^20/80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F^10/50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supernatant</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Percent weight fraction

© 2012 BAKER HUGHES INCORPORATED. ALL RIGHTS RESERVED. TERMS AND CONDITIONS OF USE: BY ACCEPTING THIS DOCUMENT, THE RECIPIENT AGREES THAT THE DOCUMENT TOGETHER WITH ALL INFORMATION INCLUDED THEREIN IS THE CONFIDENTIAL AND PROPRIETARY PROPERTY OF BAKER HUGHES INCORPORATED AND INCLUDES VALUABLE TRADE SECRETS AND/OR PROPRIETARY INFORMATION OF BAKER HUGHES (COLLECTIVELY "INFORMATION"). BAKER HUGHES RETAINS ALL RIGHTS UNDER COPYRIGHT LAWS AND TRADE SECRET LAWS OF THE UNITED STATES OF AMERICA AND OTHER COUNTRIES. THE RECIPIENT FURTHER AGREES THAT THE DOCUMENT MAY NOT BE DISTRIBUTED, TRANSMITTED, COPIED OR REPRODUCED IN WHOLE OR IN PART BY ANY MEANS, ELECTRONIC, MECHANICAL, OR OTHERWISE, WITHOUT THE EXPRESS PRIOR WRITTEN CONSENT OF BAKER HUGHES, AND MAY NOT BE USED DIRECTLY OR INDIRECTLY IN ANY WAY DETRIMENTAL TO BAKER HUGHES' INTEREST.
History

• Baker Hughes has been active in the investigation of asphaltene problems for over 30 years

• First to develop an Asphaltene Inhibitor for deepwater application & suite of Asphaltene Dispersant products

• Successful use histories with PAO3042 and PAO3080 in deepwater, land, and unconventional environments
Why ‘Squeeze’ to control asphaltene deposition?

Oil Field Depletion

Secondary oil recovery

Tertiary oil recovery

Localized Asphaltene Treatment

Asphaltene deposition at near wellbore:

- Reduces production
- Requires frequent solvent wash interventions
- Permanent wettability effects
Baker Hughes’ PAO 3080 increased oil production & reduced well interventions

- A field with CO₂ injector wells
- Asphaltene Inhibitor applied as a squeeze treatment
- 60% decrease frequency in well interventions
- 48% decrease of chemical cost
- Annual chemical cost savings of $2.5MM for 10,000bbl/d

+40° API Gravity
4500-5500ft depth wells
Approx. field production 10,000bbl/d
PAO 3080 – Improved performance [cont.]

Asphaltene treating costs dropped:
$2.22/bbl ⇒ $1.53/bbl

Annual Chemical Cost Savings:
$2.5MM

Additional Cost Savings:
Deferred Production~10,000bbl/yr

Asphaltene Treating Cost Based On Usage

38% Fewer interventions per well

PAO 3080 treated wells: 100 ⇒ 120

Performance realized within 7 months
Development Objectives & Strategy

Develop a squeezable AI that has:

• a squeeze life at least 50% better than existing inhibitors
• performance at least 95% of existing inhibitors
• passes all deepwater compatibility and stability requirements

Prove it with coreflood testing and field trials
Squeeze Application of AI

STAGE 3

- Pre-flush – well clean-up with Xylene and an asphaltene dispersant
- Squeeze Asphaltene Inhibitor Solution
- Over-flush – Oil/produced fluids
  - May shut-in
  - Return to production
  - Monitor returns for inhibitor residuals

Over-flush ➔
Main Treatment ➔
Pre-flush ➔

Inhibitor placed in formation
Application of AI Squeeze

\[ K_{\text{desorb}} \]
\[ K_{\text{ads}} \]
\[ \text{AI} \]
\[ \text{Oil} \]

AI Squeeze

Chemical

Rock Affinity

FORMATION

© 2012 BAKER HUGHES INCORPORATED. ALL RIGHTS RESERVED. TERMS AND CONDITIONS OF USE: BY ACCEPTING THIS DOCUMENT, THE RECIPIENT AGREES THAT THE DOCUMENT TOGETHER WITH ALL INFORMATION INCLUDED THEREIN IS THE CONFIDENTIAL AND PROPRIETARY PROPERTY OF BAKER HUGHES INCORPORATED AND INCLUDES VALUABLE TRADE SECRETS AND/OR PROPRIETARY INFORMATION OF BAKER HUGHES (COLLECTIVELY "INFORMATION"). BAKER HUGHES RETAINS ALL RIGHTS UNDER COPYRIGHT LAWS AND TRADE SECRET LAWS OF THE UNITED STATES OF AMERICA AND OTHER COUNTRIES. THE RECIPIENT FURTHER AGREES THAT THE DOCUMENT MAY NOT BE DISTRIBUTED, TRANSMITTED, COPIED OR REPRODUCED IN WHOLE OR IN PART BY ANY MEANS, ELECTRONIC, MECHANICAL, OR OTHERWISE, WITHOUT THE EXPRESS PRIOR WRITTEN CONSENT OF BAKER HUGHES, AND MAY NOT BE USED DIRECTLY OR INDIRECTLY IN ANY WAY DETRIMENTAL TO BAKER HUGHES' INTEREST.
## Performance Testing

### Core-Flood Oil

<table>
<thead>
<tr>
<th>Test Samples</th>
<th>% Transmittance</th>
<th>% Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>20 - 50</td>
<td>-</td>
</tr>
<tr>
<td>PAO 3042</td>
<td>11.9</td>
<td>53.0</td>
</tr>
<tr>
<td>PAO 3080</td>
<td>11.1</td>
<td>55.9</td>
</tr>
<tr>
<td>AI Squeeze</td>
<td>11.0</td>
<td>56.5</td>
</tr>
<tr>
<td>AI Squeeze PP</td>
<td>10.9</td>
<td>56.7</td>
</tr>
</tbody>
</table>

### Turbiscan Results

- Untreated
- 500 ppm Al Squeeze

---

© 2012 BAKER HUGHES INCORPORATED. ALL RIGHTS RESERVED. TERMS AND CONDITIONS OF USE: BY ACCEPTING THIS DOCUMENT, THE RECIPENT AGREES THAT THE DOCUMENT TOGETHER WITH ALL INFORMATION INCLUDED THEREIN IS THE CONFIDENTIAL AND PROPRIETARY PROPERTY OF BAKER HUGHES INCORPORATED AND INCLUDES VALUABLE TRADE SECRETS AND/OR PROPRIETARY INFORMATION OF BAKER HUGHES (COLLECTIVELY "INFORMATION"). BAKER HUGHES RETAINS ALL RIGHTS UNDER COPYRIGHT LAWS AND TRADE SECRET LAWS OF THE UNITED STATES OF AMERICA AND OTHER COUNTRIES. THE RECIPENT FURTHER AGREES THAT THE DOCUMENT MAY NOT BE DISTRIBUTED, TRANSMITTED, COPIED OR REPRODUCED IN WHOLE OR IN PART BY ANY MEANS, ELECTRONIC, MECHANICAL, OR OTHERWISE, WITHOUT THE EXPRESS PRIOR WRITTEN CONSENT OF BAKER HUGHES, AND MAY NOT BE USED DIRECTLY OR INDIRECTLY IN ANY WAY DETRIMENTAL TO BAKER HUGHES' INTEREST.
Chemical Monitoring in a Coreflood

**Chemical Monitoring in a Coreflood**

- **C. (ppm)**: AI for ‘Squeeze’
- **MEC** (Minimum Effective Concentration)
- **‘Squeeze Life’ ‘Longer Squeeze Life’**
- **Pore Volumes**
- **Δ Pressure (PSI)**
- **Transmittance**
- **%Transmittance**
- **Squeeze Life**
- **Oil Production**
- **Asphaltene Deposits/Blockages**
- **Initial Chemical Depletion Equilibration**
- **Reliable and continuous chemical desorption**
- **Insufficient chemical depletion/blocking**
- **K_{fow} = 25 mD after total ### PV passed**
- **ADT %T for PV**
- **Δ Pressure**
- **K_{fow} = 100 mD after ### PV passed**
- **AI for ‘Squeeze’**
- **Chemistry**
- **Desorbed**

© 2012 BAKER HUGHES INCORPORATED. ALL RIGHTS RESERVED. TERMS AND CONDITIONS OF USE: BY ACCEPTING THIS DOCUMENT, THE RECIPIENT AGREES THAT THE DOCUMENT TOGETHER WITH ALL INFORMATION INCLUDED THEREIN IS THE CONFIDENTIAL AND PROPRIETARY PROPERTY OF BAKER HUGHES INCORPORATED AND INCLUDES VALUABLE TRADE SECRETS AND/OR PROPRIETARY INFORMATION OF BAKER HUGHES (COLLECTIVELY "INFORMATION"). BAKER HUGHES RETAINS ALL RIGHTS UNDER COPYRIGHT LAWS AND TRADE SECRET LAWS OF THE UNITED STATES OF AMERICA AND OTHER COUNTRIES. THE RECIPIENT FURTHER AGREES THAT THE DOCUMENT MAY NOT BE DISTRIBUTED, TRANSMITTED, COPIED OR REPRODUCED IN WHOLE OR IN PART BY ANY MEANS, ELECTRONIC, MECHANICAL, OR OTHERWISE, WITHOUT THE EXPRESS PRIOR WRITTEN CONSENT OF BAKER HUGHES, AND MAY NOT BE USED DIRECTLY OR INDIRECTLY IN ANY WAY DETRIMENTAL TO BAKER HUGHES' INTEREST.
Coreflood Unit Overview

• Hassler type core holder
  – Pressure Rating = 5000 PSI
  – Core Diameters for study = 1” & 2”
• Pulse-less pumping system
  – Constant flow syringe pumps
  – Piston Cylinders for Reservoir Fluids, Chemicals, & Brines
• System of pressure and differential pressure transducers
• Computer data acquisition & control system
Coreflood Results: I

NO CHEMICAL COREFLOOD

$K_{fo} = 66.4 \text{ mD after 88 PV passed}$

$K_{fo} = 12.6 \text{ mD after total 170PV passed}$

$+80\%$ reduction in permeability

Conditions

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Overburden Pressure</td>
<td>1500 PSI</td>
<td>Flow rate</td>
<td>0.25 mL/min</td>
</tr>
<tr>
<td>Oven Temperature</td>
<td>150 F</td>
<td>Chemical Shut-in</td>
<td>15hrs</td>
</tr>
</tbody>
</table>
Coreflood Results: II

PAO 3080 COREFLOOD

K_{fo} = 26.6 mD after 108PV passed

K_{fo} = 12.9 mD 185 after total PV passed

Coreflood Results:

Conditions

Overburden Pressure 1500 PSI
Oven Temperature 150 F
Flow rate 0.25 mL/min
Chemical Shut-in 15hrs
Coreflood Results: III

Conditions
- Overburden Pressure: 1500 PSI
- Oven Temperature: 150 F
- Flow rate: 0.25 mL/min
- Chemical Shut-in: 15hrs

K\text{io} = 7.14 \text{ mD}
After 97 PV passed

K\text{fo} = 2.1 \text{ mD}
after total 220 PV passed

AI SQUEEZE COREFLOOD

% Transmittance

Pore Volumes
Coreflood Results: IV

K_\text{io} = 5.33 \, \text{mD} 
\text{after 125PV passed}

K_\text{fo} = 3.36 \, \text{mD} 
285 after total PV passed

Conditions

- Overburden Pressure: 1500 PSI
- Oven Temperature: 150 F
- Flow rate: 0.25 mL/min
- Chemical Shut-in: 15hrs
Comparison of Corefloods

+130% Squeeze Life Extension

New AI Squeeze: 54% (avg) Reduction after 200+ PV
PAO 3080 Tests: 52% Reduction after 180 PV
Changing formations does not change performance

All test data shown so far featured:

Sandstone Formations

Now, we will look at performance within:

Carbonate Formations
Gravel Pack Testing

Carbonate-Dolomite Gravel <20mesh (850 microns)
Conducted at 200F
Flow rate = 2 mL/min
Nominal $\Delta P$ developed (100-250PSI)

Test Procedure:
- Flood with 5 PV of Brine
- Flood with 10 PV of Crude Oil
- Flood with 2 PV of Chemical
- Shut-in the column for 12 hours
- Flood with 40 PV of Crude Oil & Collect Residuals
Gravel Pack Test Results

Carbonate Gravel Pack Tests

% Transmittance

Pore Volumes

PAO 3080
Al Squeeze
Contact Angle Measurements

\[ \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \]

\( \gamma_{SV} \) represents the solid surface free energy.
## Contact Angle Results

### Combined Contact Angles

<table>
<thead>
<tr>
<th>Chemical Treatment</th>
<th>Tangent Method</th>
<th>Circular Fit Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>91.9 +/- 9.69</td>
</tr>
<tr>
<td>PAO 3080</td>
<td>56.8 +/- 16.84</td>
<td>54.5 +/- 13.37</td>
</tr>
<tr>
<td>AI Squeeze</td>
<td>69.1 +/- 16.61</td>
<td>64.2 +/- 12.23</td>
</tr>
</tbody>
</table>

### Blank

![Blank Contact Angle](image1)

### PAO 3080

![PAO 3080 Contact Angle](image2)

### AI Squeeze

![AI Squeeze Contact Angle](image3)
Takeaways

- **Longer Squeeze Life**
  - New AI composition has improved adsorption and desorption kinetics to sandstone formation and thus yields a **longer squeeze life** than PAO 3080

- **Equal Inhibition**
  - Inhibitor performance is **unaffected** by changes to composition designed to achieve longer squeeze life

- **Permeability Effects**
  - Application of chemical to core did **not** result in increased permeability damage relative to PAO 3080

- **Performance within Carbonates**
  - AI Squeeze chemistry remains within carbonate gravel pack longer and at higher inhibiting concentrations than PAO 3080
  - Contact Angle measurements show no residual surface damage
Future & Current Work

- Evaluate technology within carbonate system via coreflood testing
- Deploy in a Field Trial
Questions

Thank you for listening