Chemical Flooding Overview

Gary A. Pope

Center for Petroleum and Geosystems Engineering
The University of Texas at Austin

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Chemical Methods of Enhanced Oil Recovery

- Surfactants to lower the interfacial tension between the oil and water or change the wettability of the rock
- Water soluble polymers to increase the viscosity of the water
- Surfactants to generate foams or emulsions
- Polymer gels for blocking or diverting flow
- Alkaline chemicals such as sodium carbonate to react with crude oil to generate soap and increase pH
- Combinations of chemicals and methods
What has changed since the 70s and 80s

- Surfactants and polymers with both higher performance and better characteristics are now available
- Detergent manufacturing has greatly improved so the quality of the commercial product is better
- The cost of HPAM polymer has actually decreased by a factor of 3 in real terms
- Low cost alkali such as sodium carbonate reduces surfactant adsorption and for this and other reasons alkaline-surfactant-polymer (ASP) flooding was developed as a lower cost alternative to traditional SP flooding
- Reservoir modeling is vastly better and faster
What has changed since the 70s and 80s

• Numerous commercial chemical floods have been done in recent years so we have a lot more field experience to guide us in terms of what works best
• Reservoir characterization and other enabling technologies have improved
• Polymer injectivity can be vastly increased by the use of horizontal wells and hydraulic fractures
• Recent laboratory results show high surfactant performance in dolomite reservoir rock using low cost anionic surfactant is just as high as in sandstones
Current Research

• New polymers and surfactants
• New ways of making and using foam for mobility control
• New chemical EOR methods for fractured reservoirs
• New reservoir simulators for full field models of chemical flooding
• Understanding and exploiting the role of low salinity on oil recovery in polymer floods
• Understanding and exploiting the role of viscoelasticity on polymer performance
• Understanding and modeling the role of alkali and in situ surfactant generation on phase behavior
Polymer Flooding

• Very mature method with 40 years of commercial applications
• Largest current polymer flood is in the Daqing field with about 220,000 B/D incremental oil production from polymer flooding and 12% OOIP incremental recovery as of 2005
• Best commercial projects have produced about 1 incremental STB of oil for each $1 or $2 of polymer injected and about 12% OOIP
• Applicable to light and medium gravity oils with viscosities up to at least 200 cp
• Limited to reservoirs with remaining oil saturation above residual oil saturation
Polymer Flooding

- Hydrolyzed polyacrylamide (HPAM) is the only commonly used polymer in the field and can be used up to about 185°F depending on the brine hardness.
- Molecular weights up to 30 million now available at the same cost as 8 million 30 years ago—about $1/lb.
- Quality has improved.
- Modified polyacrylamides such as HPAM-AMPS co-polymers are commercially available now for about $1.75/lb and are stable to higher temperatures.
Favorable Characteristics for Polymer Flooding

- High remaining oil saturation
- Low waterflood residual oil saturation
- High permeability and porosity
- Sufficient vertical permeability to allow polymer to induce crossflow in reservoir and good geological continuity
- High polymer concentration and slug size
- High injectivity due to favorable combination of high permeability, wells, or injection of parting pressure
- Fresh water and/or soft water
- Reservoir temperatures less than 250 F
Chateaurenard Field Polymerflood (Elf Aquitaine)

Comparison of the oil recovery for the final simulation (PF6) with the field oil recovery.
Example of Viscosity of High Molecular Weight Polymer (SNF FP3630S)

Electrolyte Concentration [TDS, ppm]

Viscosity [cP]

1500 ppm polymer, 23 C, 11 s⁻¹
Surfactant Flooding

- Many technically successful pilots and a few small scale commercial projects including some in WY have been done but profit potential low at $20/Bbl oil
- The problems encountered with some of the old pilots are well understood e.g. Exxon used xanthan gum biopolymer in its Loudon pilots and had problems with biodegradation
- New generation surfactants will tolerate high salinity and high hardness so there is no practical limit for high salinity reservoirs
- Sulfonates are stable to very high temperatures so good surfactants are available for both low and high temperature reservoirs
- Current high performance surfactants cost less than $2/lb of pure surfactant
- ASP is less expensive due to lower adsorption ....
Favorable Characteristics for Surfactant Flooding

- High permeability and porosity
- High remaining oil saturation (>25%)
- Light oil with viscosities less than 100 cp?
- Short project life due to favorable combination of small well spacing and/or high injectivity
- Onshore
- Good geological continuity
- Good source of high quality water and soft water if alkali is used
- Reservoir temperatures less than 250 F due to need for polymer for mobility control
Examples of high performance surfactants (N67-7PO-Sulfate vs. N67-7PO-Sulfonate)
Surfactant Phase Behavior

Transition from Type I-III-II
- Increase electrolyte
- Alcohol concentration
- Temperature
- Surfactant tail length
- EACN
- Pressure

Type I

Type II

Type III
Microemulsion phase behavior
**Microemulsion Phase Behavior Test**

**Optimum salinity:** 4.9 wt% NaCl

**Solubilization Ratio, \( \sigma \):** 16 cc/cc

**Interfacial tension:** \( 0.3 / \sigma^2 \)

**Types of Phase Behavior:***
- **Type I**
- **Type II**
- **Type III**

- 0.625 wt% PetroStep B-110
- 0.375 wt% PetroStep IOS 1518
- 0.25 wt% sec-butanol

Temp = 52°C

***After 21 days***
# Example Coreflood Setup

## Berea Sandstone

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>1 ft</td>
</tr>
<tr>
<td>Diameter</td>
<td>2 in</td>
</tr>
<tr>
<td>Temp</td>
<td>52 °C</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.20</td>
</tr>
<tr>
<td>$k_{brine}$</td>
<td>603 md</td>
</tr>
<tr>
<td>$k^{o}_{rw}$</td>
<td>0.12</td>
</tr>
<tr>
<td>$k^{o}_{ro}$</td>
<td>0.62</td>
</tr>
<tr>
<td>$S_{or}$</td>
<td>0.29</td>
</tr>
<tr>
<td>$S_{w}$</td>
<td>0.71</td>
</tr>
</tbody>
</table>

## Objective

Less than 2 psi/ft at 1 ft/day

## Fluid viscosity (cp)

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>2</td>
</tr>
<tr>
<td>Surfactant slug</td>
<td>10.5</td>
</tr>
<tr>
<td>Polymer Drive</td>
<td>9</td>
</tr>
</tbody>
</table>
Oil Recovery for SP Core Flood

97% residual oil recovery, 0.009 final oil saturation
Salinity Gradient

Surfactant retention ~ 0.24 mg / g rock

- Type I
- Type II
- Type III

Total Dissolved Solids, mg/L
Surfactant Concentration, mg/L
Pore Volumes

CPGE
Example of SP Field Study

- West Texas Field (Permian Basin)
  - Mixed-wet dolomite within Grayburg
  - Highly heterogeneous with layering
  - Primary recovery – 10% OOIP
  - Secondary recovery – 15% OOIP
  - Depth of 4,700 ft
  - Low reservoir pressure (~750-1000 psi)
  - High residual oil saturation (~40%)
  - Currently waterflooding 40-acre 5-spot patterns and producing at 1-2% oil cut
Surfactant Selection for Core Flood

- **Surfactant Selection Criteria**
  - Good solubilization ratio (ultra low IFT) at optimum salinity
  - Optimum salinity within the desired range of 2% to 6%
  - Microemulsion viscosity not too high
  - Good dilution behavior with formation brine
  - Compatible with HPAM polymer and stable aqueous phase at injected salinities

- **Polymer Selection Criteria**
  - HPAM polymer used for mobility control
  - Compatible with surfactant at slug and drive salinities
Interface Fluidity

Increasing Electrolyte Concentration
Optimal Salinity for N67-7PO and IOS-1518 with Midland Farms Crude

Electrolyte concentration (wt%)

Solubilization Ratio

0.75% C_{16-17}(PO)_7 SO_4, 0.25% C_{15-18} IOS, 2% SBA, 0.02% Na_2CO_3

MF3 Crude Oil
Temp. = 38 C
21 days after mixing
Oil Recovery From Reservoir Cores

95% oil recovery or final oil saturation 1%
Economic Optimization of Polymer Concentration

- Polymer concentration varied from 500 to 2500 ppm
- Average economic limit = 15 years
Summary of Field Study in Dolomite Reservoir

• A reservoir model for a mixed wet, very heterogeneous Permian basin dolomite reservoir was developed for an SP optimization study
• SP design was developed using field and laboratory data and UTCHEM simulator
  - High polymer concentration makes more profit
• At $50/bbl oil and low surfactant adsorption, an SP flood in one 5-spot pattern could have an IRR of ~40%
• SWCTT shows high Sor
• Injectivity is very good for 80 md formation
ASP Flooding

- High potential for substantial recovery at reasonable cost (alkali is inexpensive, surfactant requirement is decreased)
- Surfactant adsorption is reduced
- Process is complex due to reactions with the crude oil to form soap and geochemical reactions--design and optimization are more complicated and uncertain
- Not all crude oils are reactive with alkaline chemicals
- Potential practical problems (e.g., precipitation, corrosion at wells)
- More work is needed for carbonate reservoirs, which contain roughly half of the oil in the world.
ASP: TWO SURFACTANTS FROM DIFFERENT SOURCES

Two Surfactants

Natural Soap (Naphthenic Acid+Alkali)
A hydrophobic surfactant
Generated in situ

Synthetic surfactant
A hydrophilic surfactant
Injected as the surfactant slug
Optimal Salinity Correlates with Soap/Synthetic Surfactant Ratio

With 1% Na$_2$CO$_3$

Acid number of crude oil:
0.2 KOH mg/g oil

Optimal Salinity Correlates with Soap/Synthetic Surfactant Ratio

With 1% Na$_2$CO$_3$

Optimal NaCl Conc., %

Yates crude oil
Acid number of crude oil:
0.2 KOH mg/g oil

Soap/Synthetic Surfactant Mole Ratio

WOR=1
WOR=3
WOR=10
ASP Flooding

- Mobility control is critical. According to Malcolm Pitts, 99% of floods will fail without mobility control
- Floods can start at any time in the life of the field
- Good engineering design is vital to success
- Laboratory tests must be done with crude and reservoir rock under reservoir conditions and are essential for each reservoir condition
- Floods must be done right or not at all
- Oil companies are in the business of making money and are risk adverse so....
  - Process design must be robust
  - Project life must be short
  - Chemicals must not be too expensive
Summary and Conclusions

- Chemical EOR technology is dramatically better than 30 years ago due to more experience, better understanding, better modeling, better enabling technologies and better chemicals at lower cost adjusted for inflation.

- Chemical EOR, especially ASP, is a complex technology requiring a high level of expertise and experience to successfully implement in the field.

- At current oil prices, oil companies operating in WY can make a high rate of return using chemical EOR methods.

- Many of the mature oil fields in WY appear to be suitable candidates for chemical flooding but operators should:
  - Screen reservoirs by doing SWCTT to measure SOR and test process in-situ.
  - Get expert advice.
Summary and Conclusions

- Many ASP floods made money even at $20/Bbl oil but were under designed for current oil prices
- Operators can both increase oil recovery and make more profit by using
  - larger amounts of surfactant and polymer than used in projects designed in the 90s
  - better geological characterization
  - better reservoir modeling and engineering design
  - better well technologies
  - better monitoring and control similar to what evolved over many decades with steam drives and CO2 floods
Recommendations for EOR

• Build good chemical EOR laboratories and hire experienced staff to work with the students
• Use the laboratories to support small independent operators as well as do research
  - Study reservoir data to identify good candidates
  - Ask for crude oil samples to do chemical screening
• Simulations must be done by students and/or staff who have done chemical EOR experiments and who will integrate geology, petrophysics, process engineering and reservoir engineering with the simulation and design
• Send the students to the field to work with the operators during the summer
• Form a working team with the field engineers for each specific field after doing the screening studies