Overview of Chemical EOR

Gary A. Pope

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

Casper EOR workshop
October 26, 2007
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
Polymer Flooding Overview
Polymer Flooding

The objective of polymer flooding as a mobility control agent is to provide better displacement and volumetric sweep efficiencies during a waterflood

- Polymer injection projects far outnumber chemical floods at a lower risk and for a wider range of reservoir conditions, but at the cost of relatively small incremental oil

- The range of recovery with polymer is 5 to 30% of OOIP (Courtenay, France)

- Polymer flood efficiency is in the range of 0.7 to 1.75 lb of polymer per bbl of incremental oil production
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 cost about $1.75/lb and can be used up to at least 210 F.
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 220 F
Structure and Behavior of Partially Hydrolyzed Polyacrylamide (HPAM)

\[ \left( \begin{array}{l}
\text{H}_2\text{C} - \text{CH} - \\
\text{C} = \text{O} \\
\text{NH}_2
\end{array} \right)_x \quad \left( \begin{array}{l}
\text{H}_2\text{C} - \text{CH} - \\
\text{C} = \text{O} \\
\text{O}^-
\end{array} \right)_y \]

(i) LOW SALT

(ii) HIGH SALT

\[ \frac{y}{x+y} \]
Selected Papers on Successful Polymer Floods

- Christopher et al. SPE 17395 (1988)
  - Good example of quality control process
- Koning et al. SPE 18092 (1988)
  - High viscosity oil
- Maitin SPE 24118 (1992)
  - Incremental recovery of 8 to 22% OOIP reported
  - Good example of individual well responses
- Takagi et al. SPE 24931 (1992)
  - History match of polymer flood pilot
- Putz et al. SPE 28601 (1994)
  - Very good performance in high perm sand
  - Example of good data on produced polymer
- Wang et al. SPE 77872 (2002)
- Chang et al. SPE 89175 (2006)
  - World's largest polymer flood at Daqing-235 MMBbls (2004) with incremental recovery of 12% OOIP
Laboratory Program Overview

- Laboratory experiments are essential and should be done at an early stage of the evaluation
- A systematic laboratory plan is needed
  - Screening studies are needed for polymer selection and performance evaluation
  - Look for problems or surprises early in study before extensive lab work is undertaken
  - Reservoir condition tests are needed early on
  - Correct interpretation of data can be difficult and uncertain so best strategy is recognize uncertainty from the start
  - Explore new ideas and exploit opportunities rather than just feed the simulator and explore wide range of conditions early on
- Laboratory program needs to be based upon realistic field program
Initial Phase of Lab Program

• Polymer Selection
  ➢ Economics of reducing salinity

• Polymer Screening
  ➢ Viscosity and cost for feasible salinity options
  ➢ Filtration and quality control
  ➢ Thermal stability

• Core flooding
  ➢ Reservoir conditions and fluids
  ➢ Pressure taps on core
  ➢ Wide range of variables
Polymer Selection

• Hydrolyzed polyacrylamide polymers most likely choice, especially if salinity reduced
  ➢ Probably only 3 manufacturers that currently make HPAM for EOR applications
  ➢ Need to work closely with one or two of them to select best HPAM

• Alternatives to HPAM
  ➢ Modified versions of polyacrylamide only practical alternative in short run
HPAM Mixing Procedure
Important for Repeatability

- Mix brine and stir at 300-400 rpm
- Add dried polymer slowly to shoulder of vortex (2-3 min)
- After 30 minutes-1 hour, reduce speed to 100-200 rpm
- Allow at least 24 hours for hydration
Filtration Testing

Filtration Ratio (F.R.) \[ = \frac{t_{200mL} - t_{180mL}}{t_{80mL} - t_{60mL}} \]
Flopaam Series Filtration Tests

- Flopaam 3230S
- Flopaam 2330S
- Flopaam 3330S

1.2 micron filter
23 C
Pressure drop: 10 psi
$C_{\text{polymer}}$: 5000 ppm
Polymer Viscosity

Temperature: 25°C
Polymer: Amps
Concentration: 750 g/m³

Fig. 8-6
Example of Viscosity of High Molecular Weight Polymer (SNF FP3630S)

Viscosity [cp] vs. Electrolyte Concentration [TDS, ppm]

- Blue square: NaCl only
- Red circle: 9:1 NaCl/CaCl₂

1500 ppm polymer, 23 C, 11 s⁻¹
Laboratory Core Flood Data

• Variables
  ➢ Permeability and other core properties
  ➢ Polymer concentration and slug size
  ➢ Flow rate
  ➢ Electrolytes
  ➢ Initial water saturation
  ➢ Crude oil

• Measurements
  ➢ Polymer retention
  ➢ Viscosity of effluent over wide range of shear rate
  ➢ Resistance Factor and Residual Resistance Factor
  ➢ Oil recovery
Lab Uncertainties and Problems

• Unrepresentative or altered cores
  ➢ Wettability of cores may be altered
  ➢ Clay may be altered
  ➢ Crude may be altered
  ➢ Surrogate cores and fluids

• Length of cores
  ➢ Pressure taps along core
  ➢ Polymer behavior not uniform along core
  ➢ Steady state never reached
Potential Implementation Problems

- Polymer supplier or product changes
  - Make stringent quality control specifications and stick to them
  - Make sure lab and field polymer are same
  - Polymer vendor inflexible and unable to make adjustments after injection starts
- Unknown thief zones
- Injectivity lower than expected
- Production problems
How to fail--it's easy

• Don't inject enough polymer
• Open up high mobility paths by injecting water for a long time before polymer
• Shear degrade the polymer
• Plug the rock with low quality solution or polymer too large for small pores
• Use biodegradable polymer such as xanthan gum without effective biocide
• Inject polymer in wells without geological continuity
How to be successful

- Set clear goals
- Clear technical leadership
- Adequate resources
- Continuity
- Documentation
- Partner with polymer experts
- Good plan
- Facilities planning for polymer flooding starts early
Daqing Polymer Injection

Project Description:
- Over 2000 wells now injecting polymer at Daqing
- Typical slug size is 0.6 PV
- Most well patterns are 5-spot
- about 30-50% of injected polymer is produced
- maximum produced polymer conc. is approx. 2/3 of injected

Lessons Learned:
- Higher initial water cut results in lower incremental gains in recovery (see figure to left)
- The total cost of polymer flooding ($6.60/bbl inc. oil) is actually less than for waterflooding ($7.85/bbl inc. oil) due to decreased water production and increased oil production.
- More heterogeneous reservoir:
  - larger increase in sweep efficiency
  - shorter response time to polymer flooding
  - strongest influence on recovery is connectivity of pay zones
- To obtain higher recovery with polymer flooding:
  - lower producer WHP
  - stimulate producers
  - increase polymer concentration
  - increase polymer molecular weight
Surfactant-Polymer Flooding Overview
Surfactant Flooding

• Many technically successful pilots have been done
• Several small commercial projects have been completed and several more are in progress
• The problems encountered with some of the old pilots are well understood and have been solved
• 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
Favorable Characteristics for Surfactant Flooding

- High permeability and porosity
- High remaining oil saturation (>25%)
- Light oil less than 50 cp--but recent trend is to apply to viscous oils up to 200 cp or even higher viscosity
- 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
- Reservoir temperatures less than 300 F for surfactant and less than 220 F if polymer is used for mobility control
Background

• Many surfactants will reduce the interfacial tension to ultra low values--this is not hard to achieve
• The limitations of most surfactants is usually related to high viscosity emulsions or microemulsions and high retention, so the emphasis in this introduction will be on how to select the exceptional surfactants that do not have this problem
• Once a good surfactant is selected, then surfactant modeling is relatively simple with only a few well designed experiments needed to provide the most important simulation parameters
• The remaining challenge is then one of good reservoir characterization, reservoir engineering and optimization
Surfactants

• Anionic surfactants preferred
  – Low adsorption at neutral to high pH on both sandstones and carbonates
  – Can be tailored to a wide range of conditions
  – Widely available at low cost in special cases
  – Sulfates for low temperature applications
  – Sulfonates for high temperature applications
  – Cationics can be used as co-surfactants

• Non-ionic surfactants have not performed as well for EOR as anionic surfactants
Surfactant Selection Criteria

- High solubilization ratio at optimum (ultra low IFT)
- Commercially available at low cost
- Feasible to tailor to specific crude oil, temperature and salinity
- Highly branched hydrophobe needed for low viscosity micelles and microemulsions
- Low adsorption/retention on reservoir rock
- Insensitive to surfactant concentration above CMC and low CMC
Surfactant Selection Criteria

• Minimal propensity to form liquid crystals, gels, macroemulsions
  – Microemulsion viscosity < 10 cp
• Rapid coalescence to microemulsion
  – Undesirable if greater than a few days and preferably less than one day
  – Slow coalescence indicates problems with gels, liquid crystals or macroemulsions
Custom Designed Surfactant

Hydrophobic Tail

\[ \text{CH}_3(\text{CH}_2)_m \]

\[ \text{CHCH}_2 \text{O} \]

\[ \text{CH}_2 \text{CH} \text{O} \]

\[ \text{CH}_3 \text{CH}_2 \text{O} \]

\[ \text{CH}_3(\text{CH}_2)_n \]

Where \( m+n \) = Desirable hydrophobe tail

Hydrophillic Head

\[ \text{S} \text{O}^-\text{Na}^+ \]

\[ \text{O} \]

\[ \text{O} \]
Surfactant Phase Behavior

**Winsor Type I Behavior**

- Oil-in-water microemulsion
- Surfactant stays in the aqueous phase
- Difficult to achieve ultra-low interfacial tensions
Surfactant Phase Behavior

**Winsor Type II Behavior**

- Water-in-oil microemulsion
- Surfactant lost to the oil and observed as surfactant retention
- Should be avoided in EOR
Matching the Surfactant to the Oil

Surfactants with an equal attraction to the oil and water are optimum
Surfactant Phase Behavior

Winsor Type III Behavior

– Separate microemulsion phase
– Bicontinuous layers of water, dissolved hydrocarbons
– Ultra-low interfacial tensions ~ 0.001 dynes/cm
– Desirable for EOR
Surfactant Phase Behavior

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

- Effect of electrolyte
- Oil solubilization, IFT reduction
- Microemulsion densities
- Surfactant and microemulsion viscosities
- Coalescence times
- Identify optimal surfactant-cosolvent formulations
- Identify optimal formulation for coreflood experiments
Microemulsion phase behavior
Interface Fluidity

Increasing Electrolyte Concentration
**Solubilization ratios**

\[
\sigma_o = \frac{V_o}{V_s} \quad \sigma_w = \frac{V_w}{V_s}
\]

- \( \sigma_o \) = oil solubilization ratio
- \( V_o \) = volume of oil solubilized
- \( V_s \) = volume of surfactant
- \( V_w \) = volume of water solubilized
Microemulsion Phase Behavior

Optimum salinity: 4.9 wt% NaCl
Solubilization Ratio, $\sigma$: 16 cc/cc
interfacial tension = 0.3 / $\sigma^2$

0.625 wt% PetroStep B-110
0.375 wt% PetroStep IOS 1518
0.25 wt% sec-butanol
temp = 52 C

***After 21 days***

Oil
Water

Type I
Type III
Type II
Type II(-)
Microemulsion
Type II (+) Microemulsion
Type III Microemulsion
Pseudoternary or "Tent" Diagram

Fig. 9-7
Interfacial Tension Depends On...

- Surfactant type(s), concentration
- Co-surfactant (co-solvent) type(s), concentration
- Electrolyte type(s), concentration
- Oil characteristic
- Polymer type, concentration
- Temperature
Correlation of Solubilization Parameters with Interfacial Tension $\gamma$

$$\gamma = \frac{C}{\sigma^2}$$

Chun Huh equation
Solubilization Parameters and Phase Behavior

Type II (-)

Type II (+)
Interfacial Tension and Solubilization Parameters

![Graph showing interfacial tension and solubilization parameters against salinity.]
IFT and Retention and Oil recovery

Fig. 9-11
Highest Oil Recovery at Optimal Salinity...
Volume Fraction Diagrams

(a) WOR = 4

(b) WOR = 1

(c) WOR = 1/4
Microemulsion Viscosity

Total fluid composition
1.5 Vol. % TRS 10–410
1.5 Vol. % IBA
50.0 Vol. % N-decane

303K
Shear rate = 0.152 s⁻¹

Viscosity (mPa - s)

Salinity, wt. % NaCl
Volume Fraction Diagram

4% Sodium dihexyl sulfosuccinate, 8% 2-Propanol, 500 ppm xanthan gum, Sodium Chloride

Oleic Phase

Microemulsion Phase

Aqueous Phase

NaCl Concentration (mg/L)

Volume Fraction

0.0, 0.2, 0.4, 0.6, 0.8, 1.0

4,000, 6,000, 8,000, 10,000, 12,000, 14,000
From Trapping Number to traditional definition of Capillary Number

\[
N_{Tr} = \left| \frac{\vec{k} \cdot (\nabla \Phi' + g\Delta \rho \nabla D)}{\sigma_{ll'}} \right|
\]

If the pressure gradient is small compared to buoyancy

\[
N_{Tr} \approx N_{Cl}
\]

\[
N_{Cl} = \left| \frac{\vec{k} \cdot \nabla \Phi'}{\sigma_{ll'}} \right|
\]
Capillary Desaturation Curve

![Graph showing Capillary Desaturation Curve with UTCHEM Model, Dwarakanath, 1997, and Pennell et al., 1996 data points.](image)

- UTCHEM Model
- Dwarakanath, 1997
- Pennell et al., 1996
Comparison of Model With Experimental Nonwetting Phase Residual Saturation

![Graph showing comparison of normalized nonwetting phase residual saturation with trapping number (NT) for reservoir core, heptane, Berea core, gas (C₈/nC₄), and Sandpack, gas (C₈/nC₄).]
Kamath SPE 71505--Remaining oil saturation is a function of capillary number but is insensitive to aging or displacement method (Unsteady state cleaned (■), unsteady state restored state (○), and steady state (●))
Residual Oil Saturation variation with **capillary number** -- core artifacts due to capillary end effects and non-uniform saturation have been accounted for-Kamath
Salinities from Representative Oilfield Brines...
Effect of Cosurfactant on Surfactant Retention

Fig. 9-28

Adsorption (µg-mole/g clay)

Equilibrium concentration (g-mole/m³)

0% 2% 6%

10% Isobutyl alcohol
Recovery Efficiencies from 21 MP field tests

\[ E_R = 0.09 + 0.27t_{DMB} \]

(omitting \( \Delta \))
Total Relative Mobilities

Fig. 9-34
# Example Field Application

<table>
<thead>
<tr>
<th>Specific reservoir</th>
<th>Salinity</th>
<th>160,000 mg/L (TDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>8000 mg/L (Ca++ + Mg++)</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>52 C</td>
<td></td>
</tr>
<tr>
<td>API gravity</td>
<td>45 API, light oil</td>
<td></td>
</tr>
<tr>
<td>Rock type</td>
<td>sandstone</td>
<td></td>
</tr>
</tbody>
</table>
Microemulsion Phase Behavior Test

Optimum salinity: 4.9 wt% NaCl
Solubilization Ratio, $\sigma$: 16 cc/cc
Interfacial tension = $0.3/\sigma^2$

After 21 days***

0.625 wt% PetroStep B-110
0.375 wt% PetroStep IOS 1518
0.25 wt% sec-butanol
temp = 52 C
Aqueous Solubility Test

0.625 wt% Petrostep® B-110
0.375 wt% Petrostep® IOS
0.25 wt% sec-butanol
2000 ppm Flopaam 3330S

Temperature = 22°C
(injection temperature)

NaCl Scan

<table>
<thead>
<tr>
<th>wt %</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Clear, Stable
Cloudy, Unstable

***Objective → Clear solution at optimal salinity (4.9 wt% NaCl)
Polymer Selection

NAME: Flopaam™ 3330S
PRODUCER: SNF Floerger
TYPE: HPAM

Flopaam™ 3330S works well for 50 - 500 md rock
- JIP Meeting 2006

***Need to consider***
- 160,000 mg/L TDS
- 8000 mg/L Ca++, Mg++
Chemical Flood Design

**SP Slug:**
- 0.625 wt% Petrostep® B-110
- 0.375 wt% Petrostep® IOS
- 0.25 wt% sec-butanol
- 2000 ppm Flopaam™ 3330S
- 4.9 wt% NaCl ***opt. salinity***

Injection volume: 0.3 PV
velocity: 2 ft/day

**AQUEOUS STABILITY**

<table>
<thead>
<tr>
<th>NaCl Scan wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

**Polymer Drive:**
- 2000 ppm Flopaam™ 3330S
- 3.0 wt% NaCl

Injection volume: 2.3 PV --> excess
velocity: 2 ft/day
SP Coreflood Setup

**Berea Sandstone**

<table>
<thead>
<tr>
<th>Parameter</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>$k_{\text{brine}}$</td>
<td>603 md</td>
</tr>
<tr>
<td>$k_{\text{o}_\text{rw}}$</td>
<td>0.12</td>
</tr>
<tr>
<td>$k_{\text{o}_\text{ro}}$</td>
<td>0.62</td>
</tr>
<tr>
<td>$S_{\text{or}}$</td>
<td>0.29</td>
</tr>
<tr>
<td>$S_{\text{w}}$</td>
<td>0.71</td>
</tr>
</tbody>
</table>

**Fluid viscosity (cp)**

<table>
<thead>
<tr>
<th>Fluid Type</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>

**Objective**

Less than 2 psi/ft at 1 ft/day

Transducer array

- In
- Out

- 0 – 5 psi
- 0 – 10 psi
- 0 – 20 psi
Coreflood Recovery

97% residual oil recovery, 0.009 final oil saturation
$v = 2.1 \text{ ft/day} \Rightarrow \Delta P_{\text{max}} = 1.2 \text{ psi/ft at 1 ft/d}$
Salinity Gradient

Surfactant retention
~ 0.24 mg / g rock

Total Dissolved Solids

Surfactant Concentration

Type I
Type II
Type III

Reservoir Brine
Surfactant Slug
Polymer Drive

Surfactant retention
~ 0.24 mg / g rock
Summary and Conclusions

• Phase behavior, aqueous solubility methods
  – led to successful coreflood

• Changing surfactant : co-surfactant ratio changed
  – optimal salinity
  – necessary co-solvent

• Coreflood achieved
  – 97% cumulative residual oil recovery
  – 1.2 psi/ft at 1 ft/day
  – 0.24 mg / g rock surfactant retention

• PetroStep® surfactants and Flopaam™ polymer
  – withstood high salinity and hardness
Simulation of Dolomite Oil Reservoir

- Using field and laboratory data
  - ¼ 5-spot symmetry element
  - 1.8 PV waterflood was simulated to obtain initial conditions

Permeability (md) vs Post-Waterflood Oil Saturation

**Injector**

**Producer**

[Images of permeability and oil saturation maps]
Simulation Results

Oil Saturation at 0.35 PV Injected

Surfactant Concentration (vol frac) at 0.35 PV Injected

Oil Saturation at 1.75 PV Injected (Final)

Surfactant Concentration (vol frac) at 1.75 PV Injected (Final)
Surfactant Concentration Sensitivity

- Surfactant concentration varied from 0.5 to 1.5 vol%.
- Average economic limit = 16 years.
Surfactant Slug Size Sensitivity

- Surfactant slug size varied from 0.15 to 0.5 PV
- Average economic limit = 16 years
Polymer Concentration Sensitivity

- Polymer concentration varied from 500 to 2500 ppm
- Average economic limit = 15 years
Surfactant Adsorption Sensitivity

- Surfactant adsorption varied from 0.1 to 0.6 mg surfactant/g rock
- Most recent laboratory data suggest 0.1 mg/g
Permeability distribution in md for offshore reservoir screened for surfactant-polymer flooding EOR
ASP Flooding Overview
High pH and/or ASP Flooding

• Surfactant adsorption is reduced on both sandstones and carbonates at high pH
• Alkali is inexpensive, so the potential for cost reduction is large
• Carbonate formations are usually positively charged at neutral pH, which favors adsorption of anionic surfactants. However, when Na$_2$CO$_3$ is present, carbonate surfaces (calcite, dolomite) become negatively charged and adsorption decreases several fold
• Alkali reacts with acid in oil to form soap, but not all crude oils are reactive with alkaline chemicals
• High pH also improves microemulsion phase behavior
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
• 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
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
Soap Extraction by NaOH

3 grams oil with 9 grams 0.1 M NaOH and ~1.3 gram IPA

<table>
<thead>
<tr>
<th>Midland Farm</th>
<th>Minas</th>
<th>Yates</th>
<th>White Castle</th>
<th>PBB</th>
</tr>
</thead>
<tbody>
<tr>
<td>~0</td>
<td>0.02</td>
<td>0.14</td>
<td>0.65</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Acid Number (mg KOH/gram oil) by surfactant titration

| ~0           | 0.16  | 0.75* | 2.2**        | 4.8 |

Acid numbers (mg KOH/gram oil) by non-aqueous phase titration

*0.2 mg KOH/gram oil by New Mexico group,  ** 1.5 mg KOH/ gram oil SPE 24117
Optimal salinity is a function of water oil ratio (WOR) and surfactant concentration, Yates oil.

Surfactant: TC Blend
1% Na2CO3
x% NaCl

Surfactant Concentration, %
Optimal NaCl Conc, %
WOR=1
WOR=3
WOR=10
Acid number of crude oil: 0.2 KOH mg/g oil

Optimal Salinity Correlates with Soap/Synthetic Surfactant Ratio

With 1% Na₂CO₃

Optimal NaCl Conc., %

Yates crude oil

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

Soap/Synthetic Surfactant Mole Ratio
ASP Core Flood Schematic
Aqueous Phase Behavior
Microemulsion Phase Behavior
Polymer Viscosity

Shear Rate, s⁻¹

Viscosity, cP

Polymer Drive
Effluent
(2.02 PV)
Effluent

Oil breakthrough at 0.35 PV

Surfactant breakthrough at 0.95 PV
Summary of coreflood Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core length, cm</td>
<td>27.79</td>
</tr>
<tr>
<td>Permeability, md</td>
<td>448</td>
</tr>
<tr>
<td>Porosity, fraction</td>
<td>0.19</td>
</tr>
<tr>
<td>Oil viscosity, cp</td>
<td>3</td>
</tr>
</tbody>
</table>

**ASP flooding:**

The core was originally saturated with (3wt %) NaCl brine

0.1 PV Surfactant slug - 3% surfactant (IOS C\textsubscript{20-24}), 2500 ppm polymer (AN125), 1.0% Na\textsubscript{2}CO\textsubscript{3} + 1.9% NaCl

Polymer drive - 2500 ppm polymer, 1.0% Na2CO3 + 1.0% NaCl
Cumulative oil recovery
Oil Cut

![Graph showing Oil Cut percentage over pore volumes. The graph compares Frac Oil and simulation data.]
Pressure drop

- Temp = 85 °C
- q = 0.5 ml/min
- front adv. = 8.3 ft/day

Graph showing pressure drop over pore volumes for different conditions.
## List of Elements and Reactive Species

<table>
<thead>
<tr>
<th>Elements or pseudo-elements</th>
<th>Hydrogen (reactive), Sodium, Calcium, Aluminum, Silicon, Oxygen, Carbonate, Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Independent aqueous or oleic species</td>
<td>$H^+$, $Na^+$, $Ca^{2+}$, $Al^{3+}$, $CO_3^{2-}$, $Cl^-$, $H_4SiO_4$, $H_2O$</td>
</tr>
<tr>
<td>Dependent aqueous or oleic species</td>
<td>$Ca(OH)^+$, $Al(OH)^{2-}$, $Al(OH)_2^-$, $Ca(HCO_3)^+$, $OH^-$, $HCO_3^-$, $H_2CO_3$, $H_3SiO_4^-$, $H_2SiO_4^{2-}$, $HSi_2O_6^{3-}$, $Si_2O_5^{2-}$, $Al(OH)_4^-$</td>
</tr>
<tr>
<td>Adsorbed cations on clay</td>
<td>$H^+$, $Na^+$, $Ca^{2+}$</td>
</tr>
<tr>
<td>Solid species</td>
<td>$CaCO_3$ (Calcite), $SiO_2$ (Silica), $Al_2Si_2O_5(OH)_4$ (Kaolinite), $NaAlSi_2O_6.H_2O$ (Analcite)</td>
</tr>
</tbody>
</table>
Effluent pH for Berea Core During ASP Flood

- Experimental Data
- UTCHEM Simulation
Well Pattern and Spacing for ASP Simulation

Producer

Injector
Permeability Field

Layer 1

Layer 2

Permeability, md
Injection Scheme for Base Case ASP Simulation

1.5% Sodium Chloride

0.2 PV

0.3 PV

0.15 PV

0.79 PV

2% Surfactant

0.15% Polymer

1.6% Sodium Carbonate

0.15% Polymer

Water
Oil Recovery as a Function of Injected Surfactant Amount

Cumulative Oil Recovered (fraction of ROIP)

Amount of Surfactant Injected (tons)
Summary and Conclusions

• Laboratory and simulation studies show that the ASP flood is a viable process for the Karamay reservoir.

• A simple formulation of Na$_2$CO$_3$, surfactant manufactured by Xinjiang refinery, and polyacrylamide polymer provided reasonable oil recovery efficiency.

• Simulation results indicated that oil recovery in the Karamay reservoir is very sensitive to the amount of polymer injected.
Courtenay Polymer Flood
Polymerflood Field Tests

• The most successful polymerflood field tests had the following characteristics in common
  – High permeability reservoirs
  – High permeability contrast
  – High oil saturations
  – High oil/water viscosity ratio (15 to 114)
  – High concentration of polymer (1000 to 2000 ppm)
  – Large quantity of polymer injected (162 to 520 lbs polymer /acre-ft)
  – Low temperature (30 to 57 C)
Polymer Flood in Courtenay Field

- OOIP = 1335 ktons
- Permeability of 500 md to 4 darcy
- Initial water saturation of 30% with residual oil saturation of 30%
- Viscous oil of 40 cp at reservoir temperature of 30 C
- Fresh formation water
- A successful pilot study conducted in 1985 to 1989
- Full field injection began in 1989
  - 18 production and 4 injection wells
  - Polymer concentration grading design (1000 ppm to 100 ppm)
  - 0.84 PV polymer
Polymer Grading (Courtenay, France)
Polymer Flood Oil Production (Courtenay, France)
Polymer Flood Cumulative Oil Production (Courtenay, France)
Alkaline/ Surfactant /Polymer Flood Field Tests
Alkaline Surfactant Polymer Field Projects Since 1980

Surfactant Enhanced Water Floods

Alkaline Surfactant Polymer Projects Completed or Underway Since About 1980

<table>
<thead>
<tr>
<th>Field</th>
<th>Owner</th>
<th>Technical Region</th>
<th>Start</th>
<th>API</th>
<th>Oil Viscosity cp</th>
<th>Type</th>
<th>Pore Volume Chemical</th>
<th>Oil Recovered % OOIP</th>
<th>Chemicals US Cost/bbl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adena Babcock &amp; Brown Surtek Colorado</td>
<td>2001</td>
<td>43</td>
<td>0.42</td>
<td>Tertiary</td>
<td>In progress</td>
<td>$2.45</td>
<td>Na2CO3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cambridge Barrett Surtek Wyoming</td>
<td>1993</td>
<td>20</td>
<td>25</td>
<td>Secondary</td>
<td>60.4% 28.07%</td>
<td>$2.42</td>
<td>Na2CO3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crossford Dome Surtek Alberta</td>
<td>1987</td>
<td></td>
<td></td>
<td>Secondary</td>
<td></td>
<td>$2.25</td>
<td>Alkali and Polymer Only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daqing BS Sinopac Surtek China</td>
<td>1996</td>
<td>36</td>
<td>3</td>
<td>Tertiary</td>
<td>82.1% 23.00%</td>
<td>$7.88</td>
<td>NaOH - Biosurfactant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daqing NW Sinopac Surtek China</td>
<td>1995</td>
<td>36</td>
<td>3</td>
<td>Tertiary</td>
<td>65.0% 20.00%</td>
<td>$7.80</td>
<td>NaOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daqing PO Sinopac Surtek China</td>
<td>1994</td>
<td>26</td>
<td>11.5</td>
<td>Tertiary</td>
<td>42.0% 22.00%</td>
<td>$5.51</td>
<td>Na2CO3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daqing XV Sinopac Surtek China</td>
<td>1995</td>
<td>36</td>
<td>3</td>
<td>Tertiary</td>
<td>48.0% 17.00%</td>
<td>$9.26</td>
<td>NaOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daqing XF Sinopac Surtek China</td>
<td>1995</td>
<td>36</td>
<td>3</td>
<td>Tertiary</td>
<td>55.0% 25.00%</td>
<td>$7.14</td>
<td>NaOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daqing Foam Sinopac Surtek China</td>
<td>1997</td>
<td>NA</td>
<td>NA</td>
<td>Tertiary</td>
<td>54.8% 22.32%</td>
<td>$8.01</td>
<td>ASPFoam Flood following WAG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daqing Scale Up Sinopac Surtek China</td>
<td>??</td>
<td></td>
<td></td>
<td>Tertiary</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>David</td>
<td>Surtek Alberta</td>
<td>1985</td>
<td>23</td>
<td>Tertiary</td>
<td>In progress</td>
<td>$0.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Driscoll Creek TRUE Surtek Wyoming</td>
<td>1998</td>
<td></td>
<td></td>
<td>Tertiary</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enigma Citation Surtek Wyoming</td>
<td>2001</td>
<td>24</td>
<td>43</td>
<td>Secondary</td>
<td>In progress</td>
<td>$2.49</td>
<td>Na2CO3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Etzikorn Renaissance/Husky Surtek Alberta</td>
<td>Current</td>
<td></td>
<td></td>
<td>Tertiary</td>
<td>In progress - Information not released</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gudong CNPC Shenli China</td>
<td>1992</td>
<td>17.4</td>
<td>41.3</td>
<td>Tertiary</td>
<td>55.0% 26.51%</td>
<td>$3.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isenhaur Enron Tiorco Wyoming</td>
<td>1980</td>
<td>43.1</td>
<td>2.8</td>
<td>Secondary</td>
<td>57.7% 11.58%</td>
<td>$0.83</td>
<td>Alkali and Polymer Only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Karmay CNPC UTNIPER China</td>
<td>1995</td>
<td>30.3</td>
<td>52.6</td>
<td>Tertiary</td>
<td>60.0% 24.00%</td>
<td>$4.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lagomar PDVSA Surtek Venezuela</td>
<td>2000</td>
<td>24.8</td>
<td>14.7</td>
<td>Tertiary</td>
<td>45.0% 20.11%</td>
<td>$4.80</td>
<td>Single Well Test</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mellot Ranch West Surtek Wyoming</td>
<td>2000</td>
<td>22</td>
<td>23</td>
<td>Tertiary</td>
<td>In progress</td>
<td>$2.51</td>
<td>NaOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minas I Chevron Texaco Indonesia</td>
<td>1999</td>
<td></td>
<td></td>
<td>Tertiary</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minas II Texaco Texaco Indonesia</td>
<td>Current</td>
<td></td>
<td></td>
<td>Tertiary</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sho Vel Tum LeNorman DOE Oklahoma</td>
<td>1998</td>
<td>26.4</td>
<td>41.3</td>
<td>Tertiary</td>
<td>60.0% 16.22%</td>
<td>$6.40</td>
<td>Low Acid Number - Viscous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beverly Hills Stocker Tiorco California</td>
<td>Surfactant Injectivity Test</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tanner Citation Surtek Wyoming</td>
<td>2000</td>
<td>21</td>
<td>11</td>
<td>Secondary</td>
<td>In progress</td>
<td>$2.82</td>
<td>NaOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>West Kiehl Barrett Surtek Wyoming</td>
<td>1987</td>
<td>24</td>
<td>17</td>
<td>Secondary</td>
<td>26.5% 20.68%</td>
<td>$2.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>West Moorcroft KSL Tiorco Wyoming</td>
<td>1991</td>
<td>22.3</td>
<td>20</td>
<td>Secondary</td>
<td>20.0% 15.00%</td>
<td>$1.46</td>
<td>Alkali and Polymer Only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>White Castle Shell Shell Louisiana</td>
<td>1987</td>
<td>29</td>
<td>2.8</td>
<td>Tertiary</td>
<td>26.9% 10.10%</td>
<td>$8.18</td>
<td>No Polymer</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Example Field Cases of ASP EOR Reported by Malcolm Pitts

<table>
<thead>
<tr>
<th>Field, Location, Year</th>
<th>Chemical Cost (dollars/barrel of incremental oil)</th>
<th>Concentration</th>
<th>Pore Volume (thousands of barrels)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alkali (wt%)</td>
<td>Surfactant (wt%)</td>
<td>Polymer (mg/l)</td>
</tr>
<tr>
<td>Pownall Ranch, WY, 1995</td>
<td>0.31</td>
<td>1.25</td>
<td>0.2</td>
</tr>
<tr>
<td>Tanner, WY, 2000</td>
<td>2.82</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Enigma, WY, 2000</td>
<td>2.49</td>
<td>0.75</td>
<td>0.1</td>
</tr>
<tr>
<td>Adena, CO, 2001</td>
<td>2.45</td>
<td>0.75</td>
<td>0.2</td>
</tr>
<tr>
<td>Mellott Ranch, WY, 2001</td>
<td>2.51</td>
<td>1.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>
### Tanner Field

#### ASP Flood - 40% Oil Cut of Waterflood

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation</td>
<td>Minnelusa B</td>
</tr>
<tr>
<td>Depth</td>
<td>8,750 ft</td>
</tr>
<tr>
<td>Temperature</td>
<td>175 °F</td>
</tr>
<tr>
<td>Pore Volume</td>
<td>2,528 Mbbl</td>
</tr>
<tr>
<td>Thickness</td>
<td>25 ft</td>
</tr>
<tr>
<td>Average Porosity</td>
<td>20%</td>
</tr>
<tr>
<td>Average Permeability</td>
<td>200 md</td>
</tr>
<tr>
<td>Oil API Gravity</td>
<td>21°</td>
</tr>
<tr>
<td>Oil Viscosity</td>
<td>11 cp</td>
</tr>
<tr>
<td>Water Viscosity</td>
<td>0.45 cp</td>
</tr>
<tr>
<td>Mobility Ratio</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Tanner Alkaline-Surfactant-Polymerflood
Net Pay Isopach
Tanner, Wyoming
Alkaline-Surfactant-Polymer Flood
## Tanner Alkaline-Surfactant-Polymer Flood
Recovery Summary through July 2005

<table>
<thead>
<tr>
<th>Description</th>
<th>Recovery % OOIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Oil Recovery</td>
<td>65.0</td>
</tr>
<tr>
<td>Primary and Waterflood to 3% Oil Cut</td>
<td>48.0</td>
</tr>
<tr>
<td>ASP Increment Recovery</td>
<td>17.0</td>
</tr>
<tr>
<td>Primary and Waterflood to 7/2003 - 26% Oil Cut</td>
<td>36.5</td>
</tr>
<tr>
<td><strong>Cost per Incremental Barrel</strong></td>
<td><strong>$4.49 (estimated)</strong></td>
</tr>
<tr>
<td>(Includes Chemical and Facilities)</td>
<td></td>
</tr>
</tbody>
</table>

\[(Includes Chemical and Facilities)\] $4.49 (estimated)
Alkaline-Surfactant Flood Field Tests

• White Castle, Q sand
• West Kiehl, Minnelusa Lower “B” sand
• Cambridge Minnelusa
• Gudong
• Daqing, West Central Saertu
• Daqing, XF
• Karamay
Incremental Oil Recovery

W. Castle  Cambridge  Gudong  Daqing, WCS  Daqing, XF  Karamay

Incremental Oil Recovery

% OOIP  % ROIP
ASP Chemical Costs

1.5% Na₂CO₃; 0.2% sulfonate; 1000 ppm polymer; 0.3 PV slug; 0.2 PV drive; 0.5 bbl inc. oil/bbl slug

- Na₂CO₃: @ $0.0425/lb = $0.45/bbl oil
- Sulfonate: @ $0.68/lb = $0.95/bbl oil
- Polymer: @ $1.50/lb = $1.75/bbl oil
- Total chemicals: = $3.15/bbl oil
Selected Highlights from 1960s

• Petroleum sulfonates used in lab and field tests
• Critical role of mobility control demonstrated
• Hydrolyzed polyacrylamide polymers used in both polymer floods and surfactant floods
• First commercial polymer floods started
• Alternative approaches to chemical flooding developed by different companies
  – Marathon used microemulsions and did extensive testing in the Robinson field
  – Shell and Exxon used aqueous surfactant-polymer slugs and did tests at Benton and Loudon
  – Alkaline and Alkaline-polymer flooding
• Insufficient knowledge of geology and reservoir characteristics often most significant problem
Selected Highlights from 1970s

• Major advances in scientific understanding made by both industry and universities
  – Microemulsion phase behavior
  – Polymer rheology
  – Surfactant adsorption
  – Interfacial tension
  – Pure surfactants synthesized and tested in lab
  – Xanthan gum and other new polymers tested
  – Concepts such as salinity gradient developed and tested
  – Better understanding of alkali and soap reactions
• Development of models and simulators
• More and larger pilots conducted
  – Most significant variable turned out to be amount of polymer injected
  – Low temperature, low viscosity oil, sandstones
Selected Highlights from 1980s

• EO and EO/PO surfactants developed and tested
  – High salinity and calcium tolerance
  – Low adsorption
  – Good performance in lab tests
• Exxon did series of pilots at Loudon with disappointing results from the larger well spacing pilots
• First 3D mechanistic simulators developed and applied to interpret pilots
• Co-surfactant enhanced alkaline flooding developed and tested
• Field tests of surfactant-polymer flooding stopped after crude oil prices fell below $20/Bbl
• Some commercial polymer floods conducted despite low prices
  – Very successful polymer flood done at Chateaurenard
Selected Highlights from 1990s

- Surfactant Enhanced Aquifer Remediation (SEAR) Developed
  - Development and testing of PO sulfates
  - Numerous small SEAR field demonstrations. 99% of TCE removed from aquifer at HAFB in 1996 using UT design
  - Hirasaki and associates at Rice working with Intera and UT performed successful test of SEAR with foam at HAFB
  - UTCHEM continued to be developed, applied and validated with both laboratory and field data as well extended a wider variety of processes

- Low cost ASP pilots started in U.S. and China
  - UT designed several ASP pilots in China and trained Chinese engineers
  - SURTEC reports $5/Bbl of oil in small commercial projects

- Large polymer flood started in the Daqing field in China
  - Chinese make very high molecular weight HPAM polymers
Selected Highlights from 2000s

• New pilots started in U.S., Canada, and China due to high oil price and pilots in other parts of the world now in planning stages
• Research at the University of Texas shows new propoxy sulfates are highly effective in dolomite cores
• Research at Rice shows surfactant adsorption on limestone can be reduced to almost zero by using sodium carbonate
• Research at Rice, UH and UT show that anionic surfactants and alkali can be used to change wettability and recover oil from fractured carbonates
• New polymers under development by SNF
• New surfactants under development by Sasol, Shell Chemical, Stepan, and other detergent companies
• Use of horizontal wells for chemical floods
• Better understanding and acceptance of polymer injection above parting pressure
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 surfactant performance in dolomite reservoir rock just as high as in sandstones using the same low cost anionic surfactants as we use for sandstones
Summary and Conclusions

- Many ASP floods made money even at $20/Bbl oil but were under designed for current oil prices so oil companies can both increase oil recovery and make more profit by using
  - larger amounts of surfactant and polymer
  - 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
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 is a very complex technology requiring a high level of expertise and experience to successfully implement in the field

• At current oil prices, oil companies can make a high rate of return using chemical EOR methods