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CHEMICAL EOR – THE PAST, DOES IT HAVE A FUTURE?

Sara Thomas
PERL Canada Ltd
STSAUS@aol.com
THE PAST: Limited Commercial Success

FUTURE: Very Bright
- Past experience
- High oil prices
- Scaled models
OBJECTIVES

- Why chemical EOR methods have not been successful?
- Process limitations
- Current status of chemical floods
- Recent changes that make such methods attractive
CHEMICAL EOR HOLDS A BRIGHT FUTURE

- Conventional oil RF <33%, worldwide
  - “Unrecoverable” oil = $2 \times 10^{12}$ bbls
  - Much of it is recoverable by chemical methods

- Chemical methods are attractive:
  - Burgeoning energy demand and high oil prices, most likely for the long-term
  - Diminishing reserves
  - Advancements in technologies
  - Better understanding of failed projects
CHEMICAL EOR TARGET IN SELECTED COUNTRIES

Assumed:
Primary Rec. 33.3 %OOIP
Chem. Flood Rec. 33.3 %OIP
CHEMICAL METHODS

- Chemical EOR methods utilize:
  - Polymers
  - Surfactants
  - Alkaline agents
  - Combinations of such chemicals
    - ASP (Alkali-Surfactant-Polymer) flooding
    - MP (Micellar-Polymer) flooding
CLASSIFICATION

CHEMICAL METHODS

- Alkali
- Surfactant
- Micellar
- Polymer
- Emulsion
- ASP
CHEMICAL FLOODS PROJECTS AND PRODUCTION IN THE USA

Oil Production, B/D

No. of Projects

Years:
- 1980
- 1982
- 1984
- 1986
- 1988
- 1990
- 1992
- 1994
- 1996
- 1998
- 2000
- 2002
- 2004

Data Points:
- 1980: 0
- 1982: 0
- 1984: 0
- 1986: 0
- 1988: 0
- 1990: 0
- 1992: 0
- 1994: 0
- 1996: 0
- 1998: 0
- 2000: 0
- 2002: 0
- 2004: 0
Chemical Floods - CURRENT STATUS WORLDWIDE

Total Number of Projects: 27
Chemical Floods - PRODUCTION WORLDWIDE

Total oil production: 300,000 B/D
OBJECTIVES OF CHEMICAL FLOODING

- Increase the Capillary Number $N_c$ to mobilize residual oil
- Decrease the Mobility Ratio $M$ for better sweep
- Emulsification of oil to facilitate production
Chemical Flooding -

GENERAL LIMITATIONS

- Cost of chemicals
- Excessive chemical loss: adsorption, reactions with clay and brines, dilution
- Gravity segregation
- Lack of control in large well spacing
- Geology is unforgiving!
- Great variation in the process mechanism, both areal and cross-sectional
POLYMER FLOODING

- Loss to rock by adsorption, entrapment, salt reactions
- Loss of injectivity
- Lack of control of in situ advance
- High velocity shear (near wellbore), ageing, cross-linking, formation plugging
- Often applied late in waterflood, making it largely ineffective
Polymer Flood - FIELD PERFORMANCE
Sanand Field, India

Oil Rate, m³/D

Cumulative Oil Prod., Mm³

1989 1991 1993 1995
### Polymer Flood – FIELD PROJECTS

<table>
<thead>
<tr>
<th>Project</th>
<th>Flood Type</th>
<th>Formation</th>
<th>Polymer</th>
<th>Rec., %OIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Taber Manville South</td>
<td>Secondary</td>
<td>Sandstone</td>
<td>PAA</td>
<td>2</td>
</tr>
<tr>
<td>2 Pembina</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
</tr>
<tr>
<td>3 Wilmington</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
</tr>
<tr>
<td>4 East Colinga</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Biopolymer</td>
<td>0</td>
</tr>
<tr>
<td>5 Skull Creek South</td>
<td>&quot;</td>
<td>&quot;</td>
<td>PAA</td>
<td>8</td>
</tr>
<tr>
<td>6 Skull Creek Newcastle</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>10</td>
</tr>
<tr>
<td>7 Oerrel</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>23</td>
</tr>
<tr>
<td>8 Hankensbuettel</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>13</td>
</tr>
<tr>
<td>9 Owasco</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>7</td>
</tr>
<tr>
<td>10 Vernon</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>30</td>
</tr>
<tr>
<td>11 Northeast Hallsville</td>
<td>&quot;</td>
<td>Carbonate</td>
<td>&quot;</td>
<td>13</td>
</tr>
<tr>
<td>12 Hamm</td>
<td>&quot;</td>
<td>Sandstone</td>
<td>&quot;</td>
<td>9</td>
</tr>
<tr>
<td>13 Sage Spring Cr. Unit A</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1.2</td>
</tr>
<tr>
<td>14 West Semlek</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>5</td>
</tr>
<tr>
<td>15 Stewart Ranch</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>8</td>
</tr>
<tr>
<td>16 Kummerfeld</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>6</td>
</tr>
<tr>
<td>17 Huntington Beach</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>4</td>
</tr>
<tr>
<td>18 North Stanley</td>
<td>Tertiary</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1.1</td>
</tr>
<tr>
<td>19 Eliasville Caddo</td>
<td>Tertiary</td>
<td>Carbonate</td>
<td>&quot;</td>
<td>1.8</td>
</tr>
<tr>
<td>20 North Burbank</td>
<td>Tertiary</td>
<td>Carbonate</td>
<td>&quot;</td>
<td>2.5</td>
</tr>
</tbody>
</table>
SURFACTANT FLOODING

- Variations
  - Surfactant-Polymer Flood (SP)
  - Low Tension Polymer Flood (LTPF)
- Adsorption on rock surface
- Slug dissipation due to dispersion
- Slug dilution by water
- Formation of emulsions
  - Treatment and disposal problems
## Surfactant flood - FIELD PROJECTS

<table>
<thead>
<tr>
<th>Project</th>
<th>Size</th>
<th>Type</th>
<th>PV</th>
<th>T. Rec. % OIP</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Benton ILL</td>
<td>1 acre, 5 - spot</td>
<td>preflush, surf. formulation</td>
<td>1.4</td>
<td>10</td>
<td>Injection problems, Emulsion production, Poor sweep efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polymer buffer</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Salem Unit ILL</td>
<td>5 acre, 5 - spot</td>
<td>preflush, surf. formulation</td>
<td>0.3</td>
<td>14</td>
<td>Surf. Precipitation, High surfactant loss, Schedule change due to delay in surf. Supply.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polymer buffer</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Big Muddy WY</td>
<td>10 - acre, 5 - spot x 9</td>
<td>preflush, surf. formulation</td>
<td>0.1</td>
<td>10</td>
<td>Faults and fractures, Poor fluid confinement, Pressure parting, Poor sweep efficiency Emulsion production, Corrosion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polymer buffer</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Glenn Pool OK</td>
<td>92 acres</td>
<td>preflush, surf. formulation</td>
<td>0.1</td>
<td>32</td>
<td>Lack of mobility control, Low oil prices made expansion uneconomic.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polymer buffer</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Surfactant flood - FIELD PERFORMANCE

Glenn Pool Field, OK

Oil Rate, B/D or WOR

1984 85 86 87 88 89 90 91 92

1,000

100

10

100

WOR

OIL
ALKALINE FLOODING

- Process depends on mixing of alkali and oil
  - Oil must have acid components
- Emulsification of oil, drop entrainment and entrapment occur
  - Effect on displacement and sweep efficiencies?
- Polymer slugs used in some cases
  - Polymer alkali reactions must be accounted for
- Complex process to design
## Alkaline flooding - FIELD PERFORMANCE

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% PV</td>
<td>wt%</td>
<td>% PV</td>
<td>mg/g rock</td>
<td>%OIP</td>
</tr>
<tr>
<td>1 Whittier</td>
<td>8</td>
<td>0.2</td>
<td>51</td>
<td>2.4-11.2</td>
<td>4</td>
</tr>
<tr>
<td>2 Singleton</td>
<td>8</td>
<td>2.0</td>
<td>40</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>3 N. Ward Estes</td>
<td>15</td>
<td>4.9</td>
<td>64</td>
<td>17.2</td>
<td>8</td>
</tr>
<tr>
<td>4 L. A. Basin</td>
<td>5</td>
<td>0.4</td>
<td>30</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>5 Orcutt Hill</td>
<td>2</td>
<td>0.42</td>
<td>50</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>6 Van</td>
<td>12</td>
<td>0.14</td>
<td>25-35</td>
<td>0.6-1.2</td>
<td>3</td>
</tr>
<tr>
<td>7 Kern River</td>
<td>48</td>
<td>0.15</td>
<td>52</td>
<td>1.3</td>
<td>none</td>
</tr>
<tr>
<td>8 Harrisburg</td>
<td>9</td>
<td>2.0</td>
<td>30-40</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>9 Brea-Olinda</td>
<td>1.2</td>
<td>0.12</td>
<td>50-60</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>
ASP: ALKALI-SURFACTANT-POLYMER FLOODING

- Several variations:
  - ASP
  - SAP
  - PAS
  - Sloppy Slug

  *Injected as premixed slugs or in sequence*

- Field tests have been encouraging
- Successful in banking and producing residual oil
- Mechanisms not fully understood
ASP PILOT – Daqing, China

Oil Rate

Oil Cut

Water

Polymer

ASP


Oil Rate, m³/D; Oil Cut, %
Utilizes microemulsion and polymer buffer slugs
Miscible-type displacement
Successful in banking and producing residual oil
Process Limitations:
- Chemical slugs are costly
- Small well spacing required
- High salinity, temperature and clay
- Considerable delay in response
- Emulsion production
ASP vs. MICELLAR FLOOD -
Lab Results – Mitsue Oil Core Floods

Earlier oil breakthrough and quicker recovery in micellar flood

Micellar Flood
- Slug 5% Buffer 50%
- Oil Cut
- Soi 32%
- 92% OIP

ASP Flood
- Alkali 5%, Surfactant 10%, Polymer 60%
- Oil Cut
- Soi 38%
- 80% OIP

Oil Cut, %; Cum. Recovery, % OIP

Pore Volumes Injected

Pore Volumes Injected
Micellar flood –
TYPICAL PERFORMANCE
Bradford Special Project No. 8

![Graph showing Oil Rate and Oil Cut over time from Dec. 81 to Dec. 85. The graph indicates a rise in Oil Cut and Oil Rate post-micellar injection.](Image)

- **Oil Rate** in yellow, starts to rise significantly post Nov. 82 (Dec. 82).
- **Oil Cut** in red, shows a rise post Nov. 82 (Dec. 82), reaching a peak in Dec. 83, and then stabilizing post Dec. 84.

**Note:** The graph illustrates the typical performance of micellar flood with significant changes in Oil Rate and Oil Cut post-micellar injection.
Micellar flood – PROCESS EFFICIENCY

Cumulative Oil Recovery, %OIP vs. Micellar Slug Size, %PV

Solid lines - Lab
Dots - Field

Henry S
Bedrock
Wilkins
Henry W
119-R

ST200601
## ASP AND MP FIELD PROJECTS

<table>
<thead>
<tr>
<th>ASP Floods</th>
<th>Started</th>
<th>Appln.</th>
<th>Acre</th>
<th>Rec., % OOIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>David, Alberta</td>
<td>1986</td>
<td>Tertiary</td>
<td>252</td>
<td>21</td>
</tr>
<tr>
<td>West Kiehl, Wyoming</td>
<td>1987</td>
<td>&quot;</td>
<td>106</td>
<td>34.4</td>
</tr>
<tr>
<td>Gudong, China</td>
<td>1992</td>
<td>&quot;</td>
<td>766</td>
<td>29.4</td>
</tr>
<tr>
<td>Cambridge, Wyoming</td>
<td>1993</td>
<td>&quot;</td>
<td>72</td>
<td>26.8</td>
</tr>
<tr>
<td>Daqing, China</td>
<td>1994</td>
<td>&quot;</td>
<td>8.4</td>
<td>23.9</td>
</tr>
<tr>
<td>Karamay, China</td>
<td>1996</td>
<td>&quot;</td>
<td>766</td>
<td>24</td>
</tr>
<tr>
<td>Viraj, India</td>
<td>2002</td>
<td>&quot;</td>
<td>68</td>
<td>24</td>
</tr>
</tbody>
</table>

### Micellar Floods

<table>
<thead>
<tr>
<th>Micellar Floods</th>
<th>Started</th>
<th>Appln.</th>
<th>Acre</th>
<th>Rec., % OOIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dedrick (IL)</td>
<td>1962</td>
<td>Secondary</td>
<td>2.5</td>
<td>49.7</td>
</tr>
<tr>
<td>Robinson, 119-R (IL)</td>
<td>1968</td>
<td>Tertiary</td>
<td>40</td>
<td>39</td>
</tr>
<tr>
<td>Benton (IL) Shell</td>
<td>1972</td>
<td>&quot;</td>
<td>160</td>
<td>29</td>
</tr>
<tr>
<td>Robinson, 219-R (IL)</td>
<td>1974</td>
<td>&quot;</td>
<td>113</td>
<td>27</td>
</tr>
<tr>
<td>North Burbank (OK)</td>
<td>1976</td>
<td>&quot;</td>
<td>90</td>
<td>11</td>
</tr>
<tr>
<td>Robinson, M1 (IL)</td>
<td>1977</td>
<td>&quot;</td>
<td>407</td>
<td>50</td>
</tr>
<tr>
<td>Bradford (PA)</td>
<td>1980</td>
<td>&quot;</td>
<td>47</td>
<td>50</td>
</tr>
<tr>
<td>Salem Unit (IL)</td>
<td>1981</td>
<td>&quot;</td>
<td>200</td>
<td>47</td>
</tr>
<tr>
<td>Louden (IL)</td>
<td>1977</td>
<td>&quot;</td>
<td>40</td>
<td>27</td>
</tr>
<tr>
<td>Louden (IL)</td>
<td>1980</td>
<td>&quot;</td>
<td>80</td>
<td>33</td>
</tr>
<tr>
<td>Chateaurenard, (France)</td>
<td>1983</td>
<td>&quot;</td>
<td>2.5</td>
<td>67</td>
</tr>
</tbody>
</table>

* % OOIP
OTHER METHODS

- Emulsion flooding
- Micellar-Alkaline-Polymer flood (MAP)
- ASP-Foam process
- Surfactant huff n’puff
- Surfactant with thermal processes
REASONS FOR FAILURE

- Low oil prices in the past
- Insufficient description of reservoir geology
  - Permeability heterogeneities
  - Excessive clay content
  - High water saturation
  - Bottom water or gas cap
  - Fractures
- Inadequate understanding of process mechanisms
- Unavailability of chemicals in large quantities
- Heavy reliance on unscaled lab experiments
SCALE-UP METHODS

- Require:
  - Knowledge of process variables or complete mathematical description
  - Derivation of scaling groups
  - Model experiments
  - Scale-up of model results to field

- Greater confidence to extend lab results to field
SCALING GROUPS

- **Micellar Flood:**

\[
\begin{bmatrix}
\frac{L}{d} \\
\frac{\Delta p}{\rho_o g h} \\
\frac{P_{CL_{EM}}}{P_{CE_{MM}}} \\
\frac{k_{RW_{MAX}}}{k_{RO_{MAX}}} \\
\frac{k_{L_{MAX}}}{k_{RO_{MAX}}} \\
\frac{q_{A}^*}{q_{L}^*} \\
\frac{q_{E}^*}{q_{L}^*}
\end{bmatrix}
\begin{bmatrix}
\frac{\phi S_{oi_{0}} \mu_{0} L^2}{kk_{RO_{MAX}} \Delta p} \\
\frac{q_{L}^* \mu_{0} L^2}{kk_{RO_{MAX}} \Delta p} \\
\phi S_{oi} K_{L} \mu_{0} \\
K_{L} \\
K_{T} \\
\frac{C_{S}}{S_{oi} \rho_{o} C_{L_s}} \\
\frac{C_{S}}{C_{p}}
\end{bmatrix}
\]

- **Additional Groups:**
  - Slug Size, Flood Rate, Mixing Coefficient, Oil Recovery

\[
(PV)_{SP} = \left( \frac{S_{oi_{p}}}{S_{oi_{M}}} \right) (PV)_{SM} \quad \nu_{p} = \left( \frac{k_{p}}{k_{m}} \right) \nu_{M} \quad \alpha_{p} = \left( \frac{S_{oi_{M}}}{S_{oi_{p}}} \right) \alpha_{M} \quad r_{p} = \frac{S_{oi_{M}} \left( 1 - r_{M} \right)}{S_{oi_{p}}}
\]
RESULTS: PREDICTION vs. ACTUAL

![Graph showing oil recovery comparison between predicted and actual performance](image)

- **Predicted**
- **Actual**

- **X-axis**: Pore Volumes Produced
- **Y-axis**: Oil Recovery, %OIP

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CHEMICAL EOR & HEAVY OIL

- Problems:
  - Unfavourable mobility ratio
  - Gravity segregation
  - Rock-fluid reactions, chemical loss, dilution
  - Lack of scaling criteria, inadequate simulation
  - Often used where steam is not suitable

- Applicable methods:
  - Surfactant flooding unsuccessful
  - Alkaline flooding unsuccessful
  - CO₂ immiscible; cyclic stimulation Limited success with WAG
CHEMICAL EOR OFFSHORE

**Challenges:**
- Platform space limited
- High salinity
- Large well spacing
- Environmental concerns

**Likely Processes:**
- Micellar flooding
- ASP flooding
- Polymer flooding

* Solutions may be mixed onshore and shipped
* Constant supervision required
IMPROVED CHEMICALS

- Candidate reservoirs often have:
  - High temperature
  - High salinity
  - High water saturations
  - Low permeability
  - Clay content >5%

- Need chemicals suitable for above conditions
  - Polymers stable above 80° C and at high salinity
  - Polymers with high RF
  - Surfactant with low adsorption, tolerant of clay
  - Inexpensive chemicals coupling surfactant and polymer properties
EOR SCREENING CRITERIA

Most important: geology and mineralogy

- Oil viscosity < 35 cp
- Oil API gravity > 30 API
- Permeability ≥ 100 md
- Porosity ≥ 15%
- Temperature < 150 F
- Depth < 9,000 ft
- Pressure not critical
- Oil saturation ≥ 45%
- Oil in place at process start ≥ 600 Bbl/acre-ft

- Formation sdst preferred
- Thickness 20-30 ft
- Stratification desirable
- Clay content < 5%
- Salinity < 20,000 ppm
- Hardness < 500 ppm
- Oil composition Light, intermediates & organic acids desirable
- No bottom water or gas cap
HOW TO PLAN A FLOOD

- Choose a process likely to succeed in a candidate reservoir
- Determine the reasons for success *or* failure of past projects of the process
- Research to “fill in the blanks”
  - Determine process mechanisms
  - Derive necessary scaling criteria
  - Carry out lab studies
- Field based research
- Establish chemical supply
- Financial incentives essential
PROCESS EVALUATION

- Compare field results with lab (numerical) predictions
- Relative permeability changes?
- Oil bank formation? If so, what size?
- Mobility control?
- Fluid injectivity?
- Extent of areal and vertical sweep?
- Oil saturations from post-flood cores?
INTERPRETATION OF RESULTS

- Large number of chemical floods with little technical success
- Field tests implemented for tax advantage misrepresent process performance
- Questionable interpretations distort process potential
COST OF CHEMICALS

- As the oil prices rise, so does the cost of chemicals, but not in the same proportion
- Typical Costs:
  - Polymer - $3/lb
  - Surfactant - $1.20/lb
  - Crude oil - $60/bbl
  - Caustic - $0.60/lb
  - Isopropanol - $20/gallon
  - Micellar slug - $25/bbl
- Process Efficiency: volume of oil recovered per unit volume (or mass) of chemical slug injected
THE CASE FOR CHEMICAL FLOODING –

- Escalating energy demand, declining reserves
- Two trillion bbl oil remaining, mostly in depleted reservoirs or those nearing depletion
- Infill drilling often meets the well spacing required
- Fewer candidate reservoirs for CO₂ and miscible
- Opportunities exist under current economic conditions
- Improved technical knowledge, better risk assessment and implementation techniques
CONCLUSIONS

- Valuable **insight** has been gained through chemical floods in the past – failures as well as successes

- MP and ASP methods hold the greatest **potential** for commercial success; polymer flooding a third option

- Chemical flooding processes must be **re-evaluated** under the current technical and economic conditions
CONCLUSIONS –

- Chemical floods offer the **only chance of commercial success** in many depleted and waterflooded reservoirs

- Chemical flooding is **here to stay** because it holds the key to maximizing the reserves in our known reservoirs