Overview of Enhanced Oil Recovery
Improved Recovery Methods

Discovery

- Natural Flow
- Artificial Lift

Methods to Improve Recovery Efficiency

- Enhanced Oil Recovery
- Production/Injection Control
- Strategic Wellbore Placement

Conventional Oil Recovery
Oil Recovery Techniques

• Primary Depletion
• Water Flooding
  • Water Drive/Pattern Injection
  • Low Salinity Waterflood (BP)
  • Smart Waterflood (Armaco)
  • Ion Management Waterflood (Exxon)
  • Low Tension/Low Salinity Waterflood (The U. of Bergen, Norway)
  • Microbial EOR
• Immiscible Gas Injection
  • Nitrogen
  • Flue gas
  • Air injection
  • CO₂
Oil Recovery Techniques

- Solvent Flooding
  - CO$_2$
  - Hydrocarbon Gas
- Chemical Flooding
  - Polymer Flooding
  - Surfactant / Polymer Flooding (SP)
  - Alkaline / Surfactant / Polymer Flooding (ASP)
- Conformance Improvement Methods
- Thermal Techniques for Heavy Oil
  - Steam drive, steam stimulation, SAGD
  - Solvent, insitu combustion
- Carbonate Reservoirs and Wettability Alteration
Oil Production Processes

10-20% OOIP

20-30% OOIP

10-30%

Approximately 450 billion bbl of oil estimated to be in place before any production.

Approximately 66% (300 billion bbls) of original oil in place still locked in earth after secondary recovery.

Improved technology through research is enhancing oil recovery.

CURRENT PROCESSES:
- Thermal
- Gas Miscible
- Chemical

ADVANCED PROCESSES:
- Improved Mobility Control
- Deep Steam
- Microbial
- Gravity Mining
Enhanced Oil Recovery (EOR)

- Process **recovers oil not produced** by primary or secondary recovery
- Improves **sweep efficiency** in the reservoir by the injection of materials not normally present
- Can **reduce** remaining **oil saturation**
  - Produce oil **trapped** by capillary forces (residual oil)
  - Produce oil in **areas not flooded** by earlier injections (bypassed)
# Life of an Oil Field

## Light Oil

<table>
<thead>
<tr>
<th>Recovery Type</th>
<th>Recovery Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Recovery</td>
<td>10–20% OOIP</td>
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<tr>
<td>Secondary Recovery</td>
<td>20–30% OOIP</td>
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<tr>
<td>Enhanced Recovery</td>
<td></td>
</tr>
<tr>
<td>• Polymer flooding</td>
<td>5 – 15% OOIP</td>
</tr>
<tr>
<td>• Gas flooding</td>
<td>5 – 15% OOIP</td>
</tr>
<tr>
<td>• Surfactant flooding</td>
<td>15 – 30% OOIP</td>
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## Heavy Oil

<table>
<thead>
<tr>
<th>Recovery Type</th>
<th>Recovery Percentage</th>
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<tbody>
<tr>
<td>Primary Recovery</td>
<td>0–10% OOIP</td>
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<tr>
<td>Thermal EOR</td>
<td>&gt; 50% OOIP</td>
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</tbody>
</table>
EOR Application Summary....

• First deliberate application in the 1950s
• Approximately **10% of U.S. production** from EOR
• U.S. accounts for 2/3 of worldwide production
• Chemical projects....
  • Very active in the 1980s; **significant new interest now**
  • Rebirth of activities worldwide
  • **Mostly polymer** because of low cost and simplicity
• Thermal projects
  • Accounts for 60-70% of EOR oil
  • Around 60 projects, but declining
• Solvent projects....
  • Substantial growth in last 10 years to 130 projects
  • Active CO$_2$ projects where CO$_2$ is available
  • Synergy opportunity with CO$_2$ sequestration
EOR Methods

Gas-Based EOR
- CO₂ injection
- Air injection
- HC injection
- Nitrogen injection
- Flue gas injection
- WAG (water alternating gas)
- FAWAG (foam assisted WAG)

Water-Based EOR
- Surfactants
- Polymer
- Alkaline
- Polymer gels
- MEOR (microbial EOR)
- Low salinity waterflood

Thermal Methods
- Steam
- SAGD (Steam Assisted Gravity Drainage)
- CSS (Cyclic Steam Stimulation)
- High pressure air (Combustion)
World EOR Production in 2006

3 MM B/D

Source: W. Shulte, 2010
# Planned EOR Projects

## Table A

<table>
<thead>
<tr>
<th>Type and operator</th>
<th>Field</th>
<th>Location</th>
<th>Pay zone</th>
<th>Size, acres</th>
<th>Depth, ft</th>
<th>Gravity, °API</th>
<th>Start date</th>
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<tbody>
<tr>
<td><strong>CO₂, immiscible</strong></td>
<td></td>
<td></td>
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<tr>
<td>Anadarko</td>
<td>Salt Creek</td>
<td>Natrona County, Wyo.</td>
<td>Lakota formation</td>
<td>2,400</td>
<td>2,400</td>
<td>34</td>
<td>6/13</td>
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<tr>
<td>Anadarko</td>
<td>Salt Creek</td>
<td>Natrona County, Wyo.</td>
<td>Sundance formation</td>
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<td>2,900</td>
<td>33</td>
<td>6/13</td>
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<td>Anadarko</td>
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<td>Natrona County, Wyo.</td>
<td>Tensleep</td>
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<td>29.5</td>
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<td>Occidental</td>
<td>Slaughter (S.A. Slaughter ‘B’)</td>
<td>Hockley County, Tex.</td>
<td>San Andres</td>
<td>279</td>
<td>4,900</td>
<td>32</td>
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<td>Occidental</td>
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<td>Gaines County, Tex.</td>
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<td><strong>Steam</strong></td>
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<td></td>
<td></td>
<td></td>
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<td>Imperial Oil</td>
<td>Nabiye</td>
<td>Alberta</td>
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<tr>
<td>Occidental</td>
<td>Kern Front</td>
<td>Kern County, Calif.</td>
<td>Etchegoin/Chanac</td>
<td>450</td>
<td>1,800-2,100</td>
<td>12-15</td>
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<tr>
<td>Wintershall</td>
<td>Emlichheim Block 4</td>
<td>Lower Saxony/Grafschaft Bentheim/Emlichheim, Germany</td>
<td>Valanginian</td>
<td>320</td>
<td>2,500-2,700</td>
<td>25</td>
<td>2012</td>
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<td>11</td>
<td>3,600-4,300</td>
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<td><strong>Polymer</strong></td>
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<tr>
<td>Zargon Oil &amp; Gas Ltd.</td>
<td>Little Bow Upper Manville 1</td>
<td>Alberta</td>
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<td></td>
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<td><strong>Combustion</strong></td>
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<tr>
<td>Petrobras</td>
<td>Rio Preto Oeste</td>
<td>Brazil onshore</td>
<td>Mucuri</td>
<td>1,045</td>
<td>3,380</td>
<td>17</td>
<td>2012</td>
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*Oil and Gas Journal, 2012*
### Screening EOR

Dickson et al., SPE 129768, 2010

<table>
<thead>
<tr>
<th>Property</th>
<th>HC gas</th>
<th>CO2</th>
<th>N2/Flue</th>
<th>CSS</th>
<th>Steam</th>
<th>SAGD</th>
<th>Hot water</th>
<th>Polymer</th>
<th>ASP</th>
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<tr>
<td>Oil API</td>
<td>&gt;30-40</td>
<td>&gt;22</td>
<td>&gt;40</td>
<td>8-35</td>
<td>8-20</td>
<td>7-12</td>
<td>10-35</td>
<td>&gt;15</td>
<td>&gt;20</td>
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<td>Oil viscosity, cp</td>
<td>&lt;3</td>
<td>&lt;10</td>
<td>&lt;0.4</td>
<td>$10^3 - 10^6$</td>
<td>$10^3 - 10^4$</td>
<td>4000 - $10^6$</td>
<td>$10^3 - 10^4$</td>
<td>10-1000</td>
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<td>Reservoir Depth, ft</td>
<td>4000-16000</td>
<td>&gt;2500</td>
<td>&gt;10,000</td>
<td>400-3000</td>
<td>400-4500</td>
<td>250-3000</td>
<td>&lt;3000</td>
<td>800-9000</td>
<td>500-9000</td>
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<td>Permeability, md</td>
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<td>--</td>
<td>--</td>
<td>&gt;250</td>
<td>&gt;250</td>
<td>&gt;5000</td>
<td>&gt;35</td>
<td>&gt;100</td>
<td>&gt;100</td>
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<tr>
<td>Pressure, psia</td>
<td>&gt;MMP</td>
<td>&gt;MMP</td>
<td>&lt;MMP</td>
<td>400-1500</td>
<td>&lt;1500</td>
<td>High</td>
<td>&gt;2000</td>
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<td>Oil saturation, %</td>
<td>&gt;30</td>
<td>&gt;20</td>
<td>&gt;40</td>
<td>&gt;50</td>
<td>&gt;40</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;30</td>
<td>&gt;45</td>
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<tr>
<td>Thickness, ft</td>
<td>Thin</td>
<td>Thin</td>
<td>Thin</td>
<td>&gt;20-150</td>
<td>15-150</td>
<td>50-100</td>
<td>&gt;20</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Salinity, ppm</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>&lt;3000</td>
<td>&lt; 200000</td>
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<tr>
<td>Temperature, F</td>
<td>Affect MMP</td>
<td>Affect MMP</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>&lt; 170</td>
<td>&lt;200</td>
</tr>
</tbody>
</table>
Conventional Oil Reserves

Heavy Hydrocarbon Resources

Conventional Crude Oil
1.02 trillion barrels

Heavy Hydrocarbons
5.6 trillion barrels

Canada
Canada
Venezuela
U.S.
Rest of World
Middle East
Other W.H.

U.S. Geological Survey, Third Unitar Conference

Heavy oil and natural bitumen resources are five times greater than remaining reserves of conventional crude oil, and 80 percent of these resources are in the Western Hemisphere.
EOR Processes

**Heavy Oil Recovery**
- Cyclic Steam Stimulation
- Steam-Assisted Gravity Drainage
- VAPEX (Solvent-Assisted Gravity Drainage)
- Gas-Added CSS (LASER; FAST)
- Gas-Added SAGD
- Steam Flood
- Cold Heavy Oil Production with Sand (CHOPS)
- In-Situ Combustion
- Polymer flood
- Alkaline flood

**Light Oil Recovery**
- Cyclic Steam Stimulation
- Gas Flood ($CO_2$; Hydrocarbon; Nitrogen)
- Gas Huff-n-Puff
- Polymer Flood (HPAM; Biopolymer)
- Surfactant Flood
- Foams (Gas; Steam)
- ASP
- Wettability Alteration
Heavy Oil Recovery Processes

- Cyclic Solvent Process
  - Promising process but field test results uncertain
- VAPEX (vapor extraction)
  - Initiation difficult (use Solvent Assisted VAPEX, SAVEX)
  - Difficult to overcome heterogeneity and to transport across layers of less-soluble/insoluble components
- Polymer Flood
  - Proven technology
  - Careful application could be economical
- ASP flood
  - Under study
Cold Production using Chemicals

Lifting Heavy Oil from Sand

- Observe oil removal versus exposure time by surfactant solution
- Clean sand and heavy oil (Alberta, 25,000 cp at 25°C) mixed to make an oily paste
- Oily paste and surfactant solution in bottle - aged at 30°C (reservoir temperature)

Initial time - sand color very dark blue from the oil
- At 16 hours surfactant solution removes most of the heavy oil
- On far right, 5 days, some oil solubilized into the surfactant solution will break out as a separate oil phase.

IMPROVED TRANSPORTATION OF HEAVY OIL

Heavy Crude Oil from California

45,000 cp
Almost no flow occurs at room temperature

Less than 100 cp after slow stirring
Chemical added as 400 ppm in oil (Chemical added in a water solution)

P.J. Shuler, 2010
Role of Chemicals in Chemical EOR

- **Surfactants**
  - Lower the interfacial tension between the oil and water
  - Change the wettability of the rock
  - Generate foams or emulsions

- **Water soluble polymers** increase water viscosity

- **Polymer gels** for blocking or diverting flow

- **Alkaline** chemicals such as sodium carbonate
  - Increase pH
  - React with crude oil to generate soap (in-situ surfactant)
  - Reduce surfactant adsorption on rock surface
Chemical Enhanced Oil Recovery Processes …..Leverages Existing Infrastructure

- Injection well
- Injection fluids
- Mixing facility
- Production well
- Produced oil
- Oil bank
- Chemical slug
- Polymer drive
- Driving fluid (water)
Technical Basis for Polymer Flooding

Polymer flooding recovers mobile oil that has been bypassed
• during earlier waterflooding or aquifer intrusion
• due to reservoir heterogeneity.

It does not recover the residual oil that is trapped in rock pores after extensive waterflooding.
Polymer flooding recovers the mobile oil that has been bypassed
  • by earlier waterflooding or aquifer intrusion
  • due to reservoir heterogeneity.
Polymer Flooding

- HPAM is the only commonly used polymer in the field
- Molecular weights up to 30 million now available
- Quality has improved

Limitations

- Mechanical, thermal, chemical degradation
- Injectivity concerns
- Loss of viscosity at high T, Salinity, and hardness
Initial Phase of Lab Program

- Polymer Selection
- Polymer Screening
  - Viscosity and cost for feasible salinity options
  - Filtration and quality control
  - Thermal stability
  - Chemical stability
- Core flooding
  - Reservoir conditions and fluids
  - Pressure taps on core
  - Wide range of variables
Hydrolyzed Polyacrylamide (HPAM)

Flopaam 3330S from SNF

Viscosity vs Concentration of HPAM (Flopaam 3330S)

- Salinity = 4% NaCl
- Temperature = 38°C
- Shear Rate = 69.5 sec⁻¹
Viscosity vs Salinity for HPAM (Flopaam 3330S)

1500 ppm Flopaam 3330S
Temperature = 38°C
Shear Rate = 69.5 sec⁻¹

Salinity, wt% NaCl
Viscosity (cp)
In-situ Viscosity in Rock

Bulk Viscosity vs. Shear Rate and Concentration

Apparent Viscosity in Rock vs. Flow Velocity and Concentration

From C. Huh
Daqing Polymer Injection

Project Description
- Over 2000 wells 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): 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 molar weight
Theoretical Basis for Surfactant/Polymer Flooding

- The main target of surfactant/polymer flood is the residual oil ganglia trapped at pore throats even after extensive waterfloods.
- Mobilization of the residual oil is governed by the capillary number correlation.
Surfactants

**Anionic** surfactants preferred

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

What:
- Injecting a high pH agent (NaOH, Na$_2$CO$_3$, etc.) dissolved in water

How:
- Agent reacts with component(s) in acidic (active) crude oil to form surfactant.
- More effective in crude oils with higher acidity (usually below 20° API) and in sandstone reservoirs below 200°F
- Alteration of wettability
- Reduction of injected surfactant concentration
- Wider range of low IFT

Problems:
- Cation exchange
- Reaction with solid
- Precipitation of hydroxides
- Few acidic crudes
Alkaline/Surfactant/Polymer (ASP)

- Alkaline solutions, e.g., NaOH, Na$_2$CO$_3$, convert organic acids in crude oils to soaps, “natural surfactants”, much more cheaply than injecting surfactants (an old idea)

- The soap formed is almost always not at “optimum” conditions to produce ultralow tensions for existing temperature, oil & brine compositions

- In 1984 Dick Nelson and others (Shell) suggested that injecting a little of another surfactant could give optimum conditions and low tensions

- Ethoxylated or propoxylated surfactants desirable to provide hardness tolerance
ASP Flooding

Polymer
- increase viscosity
- improve mobility control and sweep.

Surfactant
- lower interfacial tension
- mobilize residual oil.
- required: IFT = 10^{-3} \text{ mN/m}

Alkali
- high pH of 11
- natural surfactants (soaps)
- minimize surf. adsorption
ASP for Viscous Oils

- Typically **viscous oils** contain sufficient organic acids to **generate soap** when reacted with alkali
- **High** residual **oil saturation** after water flood
- Often found in reservoirs with **high porosity and permeability**
- When sufficient mobility control is applied, the **oil cut** in the tertiary oil bank is **greater** than the oil cut for light oils

**Viscosity Range**: 100 cp to 5000
Acid Number vs. API Gravity of Oil

Fan and Buckley, SPE 99884, 2006
ASP: Two Surfactants from Different Sources

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

Synthetic surfactant
- A hydrophilic surfactant
- Injected as the surfactant slug
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 by several folds
- 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
Alkaline Flooding

Possible interactions between fluids and rock during the alkaline flooding that can be present in the reservoir.

Formation and injection water compatibility

Water

Mineral precipitation
Mineral dissolution

Oil

Rock

Wettability Alteration

Alkaline

Raise pH

Generate natural surfactant (Soap)
AP Floods with Co-Solvent (ACP)

- Addition of co-solvent to AP flood leads to ACP
  - Ultra-low IFT & mobility control without synthetic surfactant
  - Custom phase behavior
  - Breaks viscous, unstable emulsions
  - Effective only with oils that form soaps (active oil)

- Co-Solvents are small, non-ionic molecules
  - Often alcohols, like IBA-xEO
  - Don’t lower IFT

- Very robust
  - Co-solvents insensitive to geochemistry, temperature
  - Low adsorption
  - Lower emulsion viscosity compared to ASP

- Can be less expensive than ASP
Microemulsion phase behavior

Salinity screening (0.2 – 1.25 %)
Surfactant Phase Behavior

**Winsor Type I (II-) Behavior**

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

**Winsor Type II (II+) Behavior**

- Water-in-oil microemulsion
- Surfactant lost to the oil and observed as surfactant retention
- Should be avoided in EOR
Type III Microemulsion
Phase Behavior, IFT, and Salinity

**Oil Solubilization Ratio**

- **TYPE I**
  - Optimum Solubilization Ratio

- **TYPE II**
  - ULTRA LOW IFT
  - \( \gamma = \frac{C}{\sigma^2} \)
  - \( IFT = \frac{0.3}{(15)^2} = 0.0013 \frac{mN}{m} \)

- **TYPE III**

**Water Solubilization Ratio**

- Optimum salinity

**Salinity (ppm Na2CO3)**

- 0
- 5
- 10
- 15
- 20
- 25
- 30

**Volume of oil Solubilized**

- 0
- 5
- 10
- 15
- 20
- 25
- 30

**Volume of Surfactant**

- 0
- 5
- 10
- 15
- 20
- 25
- 30
The Width of Low IFT Region is Much Wider When Soap is Generated by Alkali

IFT values are equilibrium IFT

Hirasaki and Miller, 2007
Alkali Reduces Adsorption of NEODOL 25-3S in Berea

Nelson, 1984
Interface Fluidity

Increasing Electrolyte Concentration
Microemulsion Phase 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 (mPaÁs)

Salinity, wt. % NaCl
Interfacial Tension

Optimum salinity: 4.9 wt% NaCl
Solubilization ratio, $\sigma$: 16 cc/cc
Interfacial tension: $0.3 / \sigma^2 \approx 0.0012$ dyne/cm

***After 21 days***
Capillary number is a dimensionless number: ratio of viscous to capillary forces

\[ NC = \frac{\vec{k} \cdot (\nabla \Phi)}{\sigma} \]
Relative Permeability vs. Capillary Number

- **NT = 10^-8**
  - Water flood

- **NT = 10^-4**
  - Surfactant flood

- Water flood
- Surfactant flood
- Normal range waterfloods
- Wetting phase
- Nonwetting phase
- Critical (N_AW)
- Critical (N_W)
- Nonwetting total (N_W)
Need for Mobility Control
Alkali and Surfactant Concentrations

% Concentration

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

[Bar chart showing concentrations for different locations.]

- **Carbonate**
- **Surfactant**
Reservoir Clays

$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

$\text{(K,H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$
Retention and Clay Content

Kaolinite (clay)

Authigenic kaolinite, Carter sandstone, Black Warrior basin, Alabama


Illite (clay)

"Hairy" illite clay found in the Coconino sandstone - 2000X — The fine hair-like structure is actually crystalline mineral and is a diagenetic alteration product of other minerals in the subsurface.

http://www.creationresearch.org/vaerc/sem02.html