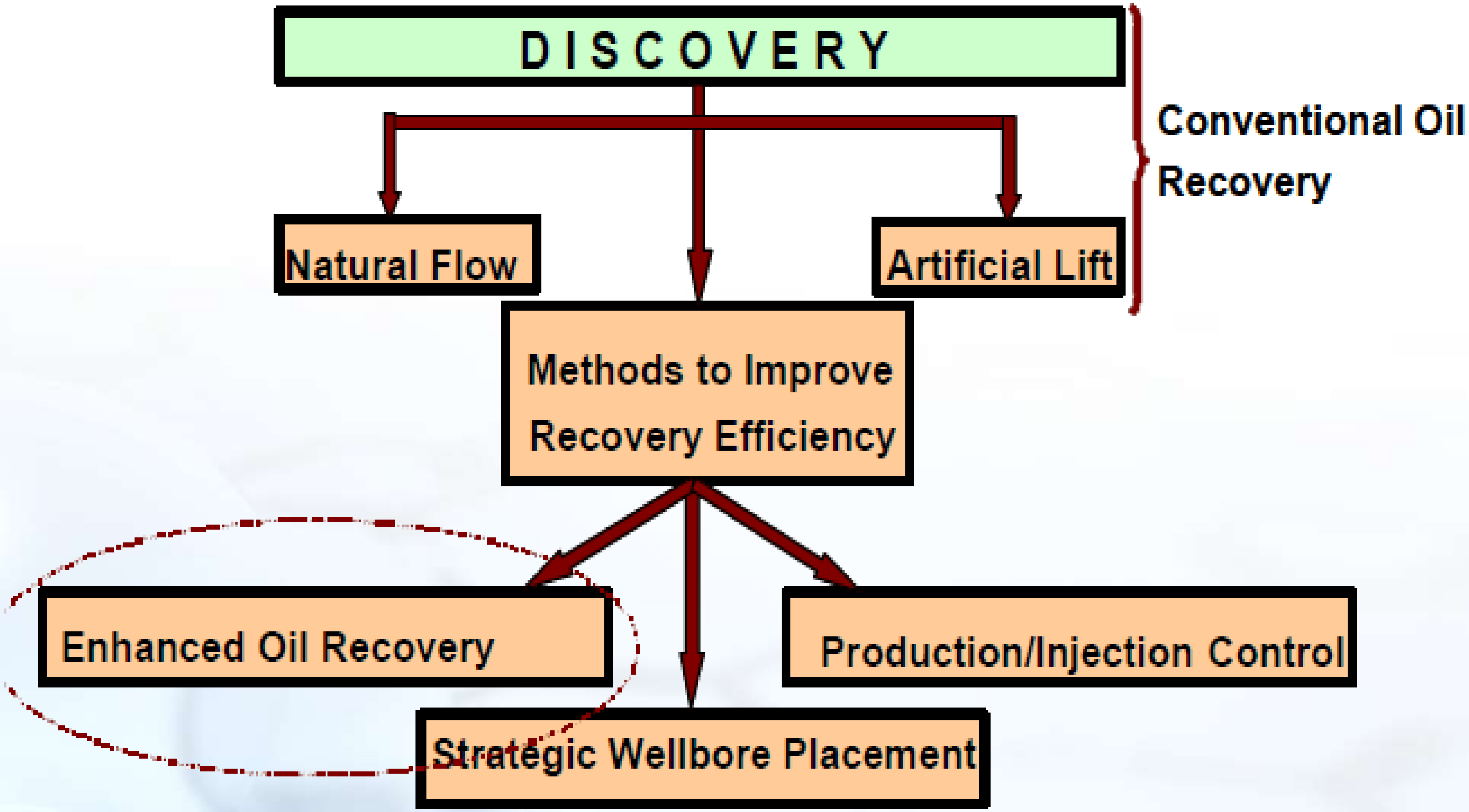
Overview of Enhanced Oil Recovery

ULTIMATE EOR

The Ultimate Source for Enhanced Oil Recovery

Improved Recovery Methods



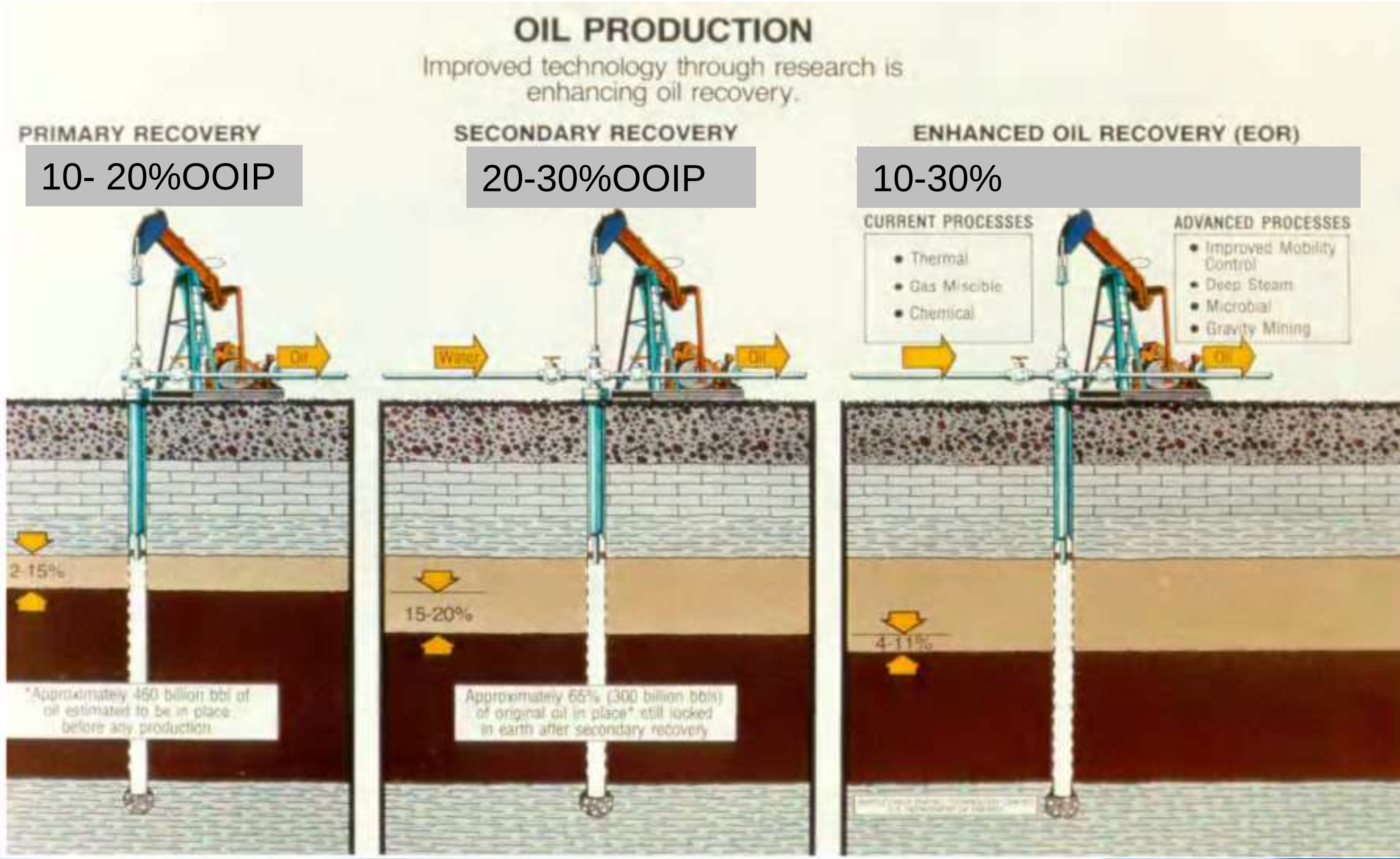
Oil Recovery Techniques

- 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
  - CO_2

Oil Recovery Techniques

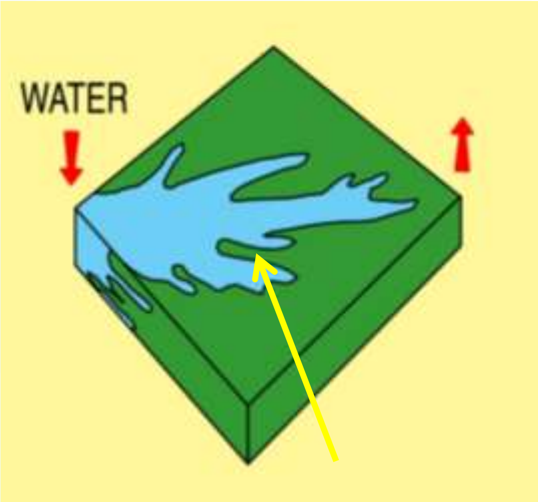
- Solvent Flooding
  - CO_2
  - Hydrocarbon Gas
- Chemical Flooding
  - Polymer Flooding
  - Surfactant / Polymer Flooding (SP)
  - Alkaline / Surfactant / Polymer Flooding (ASP)
  - Conformance Improvement Methods
- Thermal Techniques for Heavy Oil
  - Steam drive, steam stimulation, SAGD
  - Solvent, insitu combustion
- Carbonate Reservoirs and Wettability Alteration

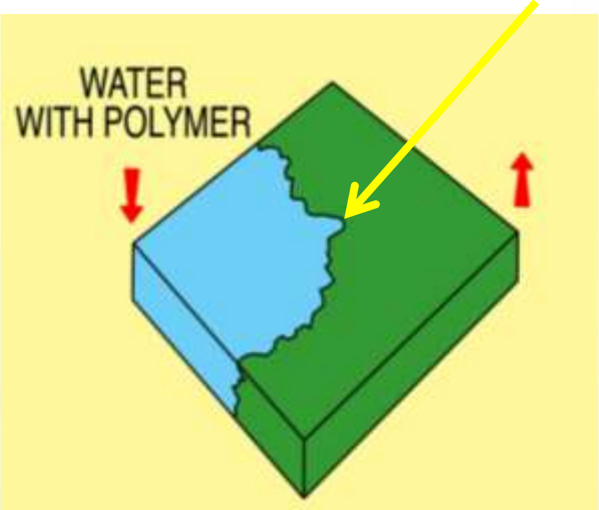
Oil Production Processes



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

<u>Light Oil</u>

Primary Recovery: 10–20% Original-Oil-In-Place

Secondary Recovery 20–30% OOIP

Waterflooding, Gas cycling

Enhanced Recovery

- Polymer flooding 5 – 15% OOIP
- Gas flooding 5 – 15% OOIP
- Surfactant flooding 15 – 30% OOIP

<u>Heavy Oil</u>

Primary Recovery 0–10% OOIP

Thermal EOR > 50% OOIP

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

- CO_2 injection
- Air injection
- HC injection
- Nitrogen injection
- Flue gas injection
- WAG (water alternating gas)
- FAWAG (foam assisted WAG)

Water-Based EOR

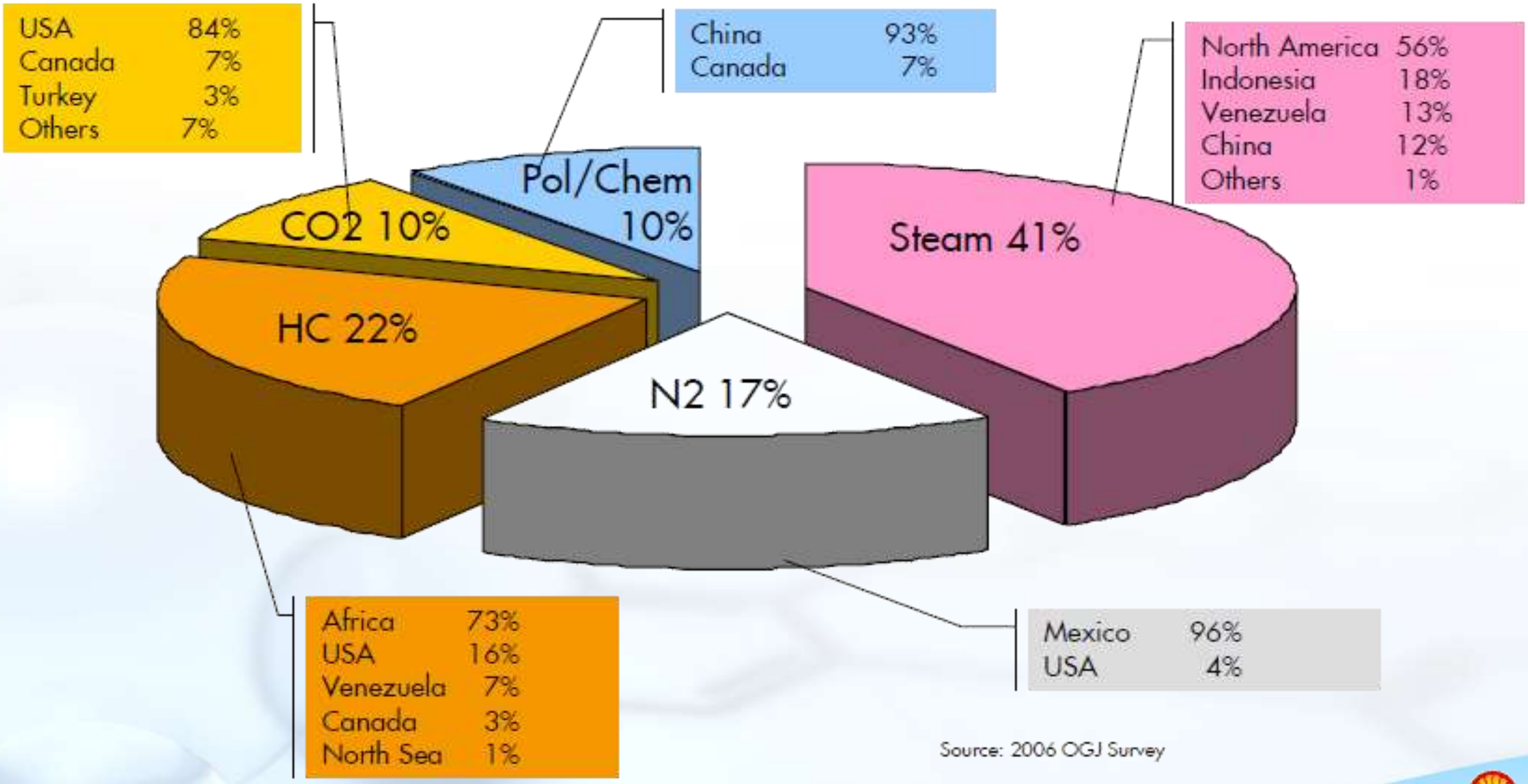
- Surfactants
- Polymer
- Alkaline
- Polymer gels
- MEOR (microbial EOR)
- Low salinity waterflood

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

PLANNED PROJECTS | **TABLE A**

Type and operator	Field	Location	Pay zone	Size, acres	Depth, ft	Gravity, °API	Start date
CO_2 immiscible							
Anadarko	Salt Creek	Natrona County, Wyo.	Lakota formation	2,400	2,400	34	6/13
Anadarko	Salt Creek	Natrona County, Wyo.	Sundance formation	1,534	2,900	33	6/13
Anadarko	Sussex	Natrona County, Wyo.	Tensleep	1,598	9,000	29.5	6/14
Core Energy	Niagaran "B"	Otsego, Mich.	Brown Niagaran	140	5,700	43	2012
Occidental	Slaughter (S.A. Slaughter 'B')	Hockley County, Tex.	San Andres	279	4,900	32	6/12
Occidental	West Seminole San Andres Unit	Gaines County, Tex.	San Andres	360 (Phase 1 only)	5,000	33	7/12
Steam							
Imperial Oil	Nabiye	Alberta					2014
Occidental	Kern Front	Kern County, Calif.	Etchegoin/Chanac	450	1,800-2,100	12-15	2013
Wintershall	Emlichheim Block 4	Lower Saxony/ Graftschaft Bentheim/ Emlichheim, Germany	Valanginian	320	2,500-2,700	25	2012
Wintershall	Bockstedt	Lower Saxony, Kreis Diepholz, Bockstedt, Germany	Valanginian	11	3,600-4,300	29	2012
Polymer							
Zargon Oil & Gas Ltd.	Little Bow Upper Manville I	Alberta					2013
Combustion							
Petrobras	Rio Preto Oeste	Brazil onshore	Mucuri	1,045	3,380	17	2012

Oil and Gas Journal, 2012

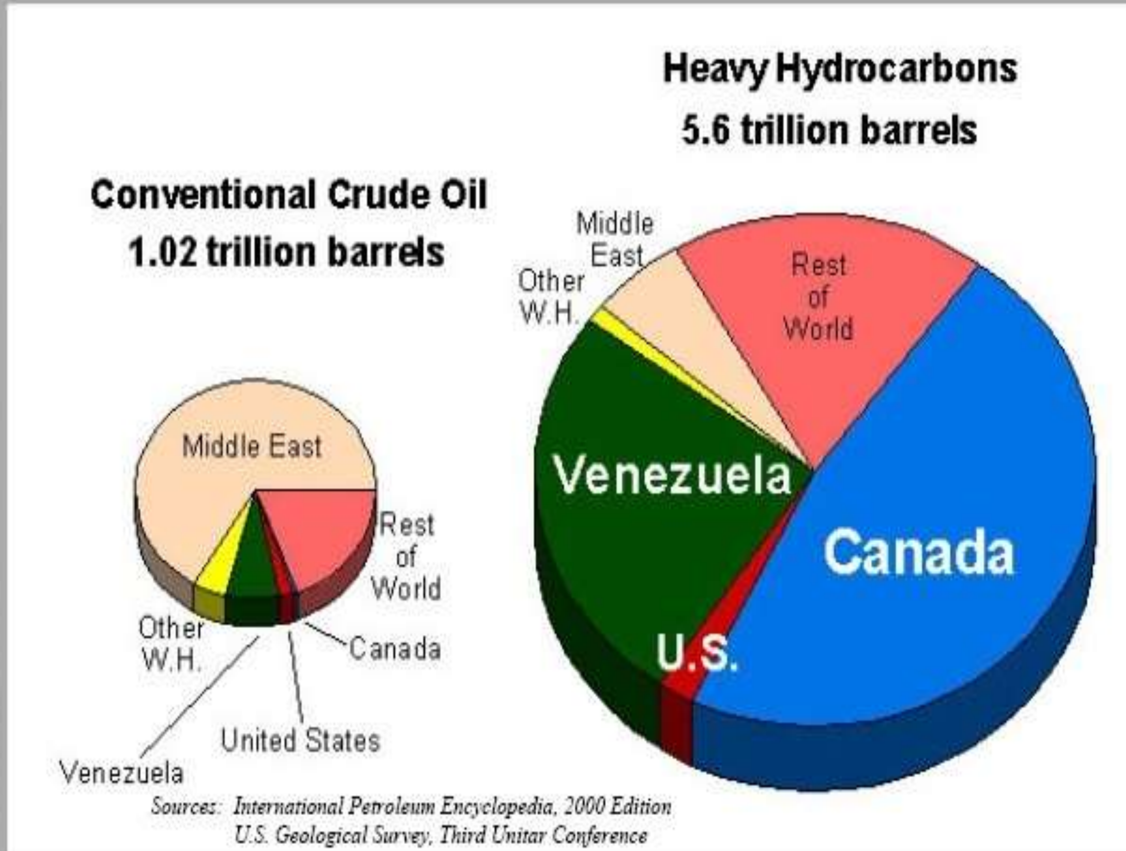
Screening EOR

Dickson et al., SPE 129768, 2010

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

Conventional Oil Reserves

Heavy Hydrocarbon Resources



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 *16 Hours* *5 Days*

- 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

P.J. Shuler, 2010

45,000 cp

Almost no flow occurs at room temperature

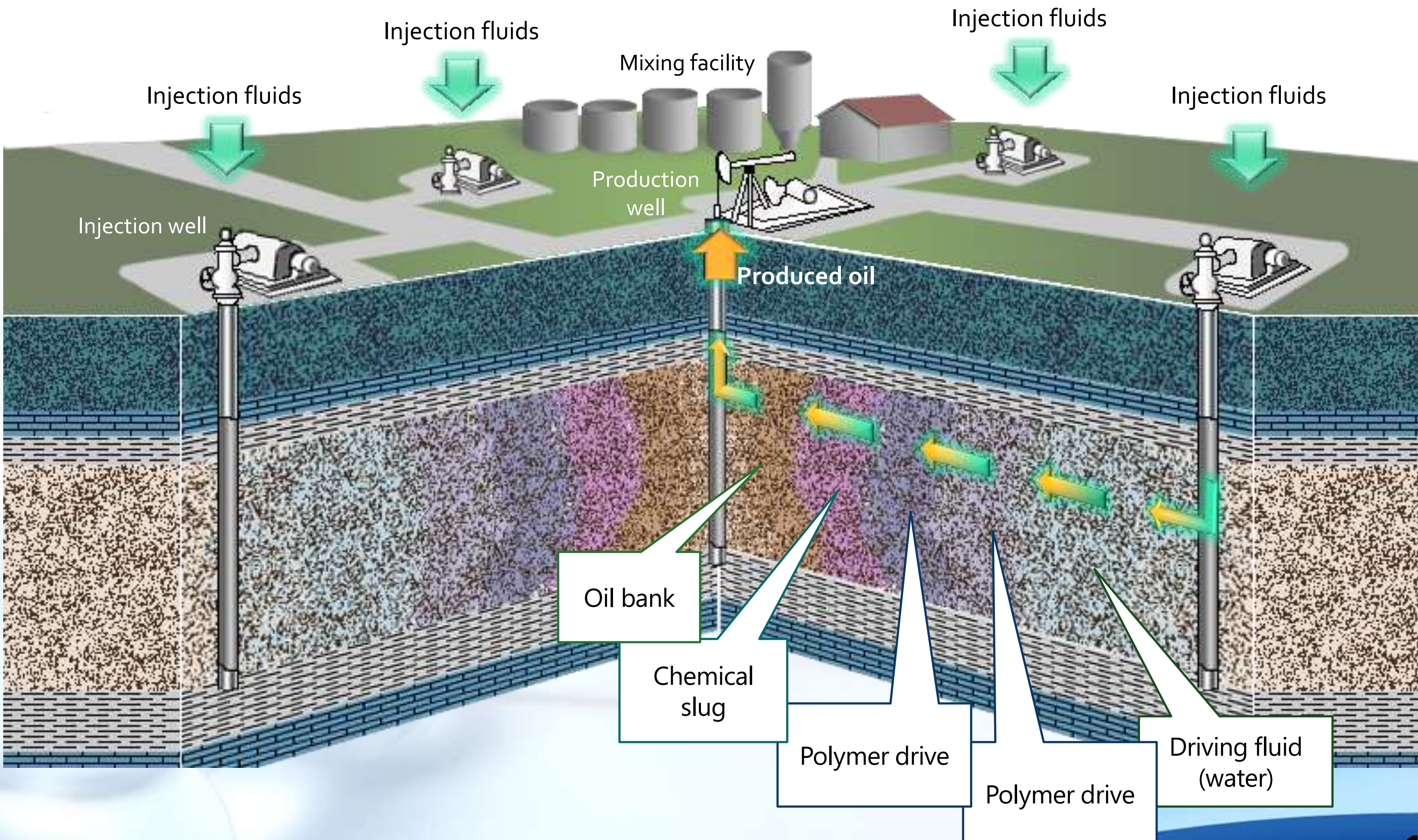
Less than 100 cp after slow stirring

Chemical added as 400 ppm in oil (Chemical added in a water solution)

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

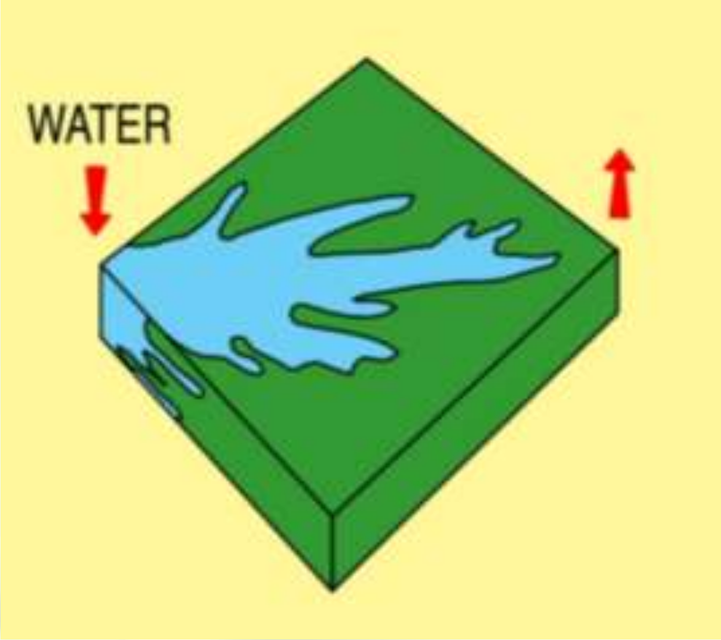


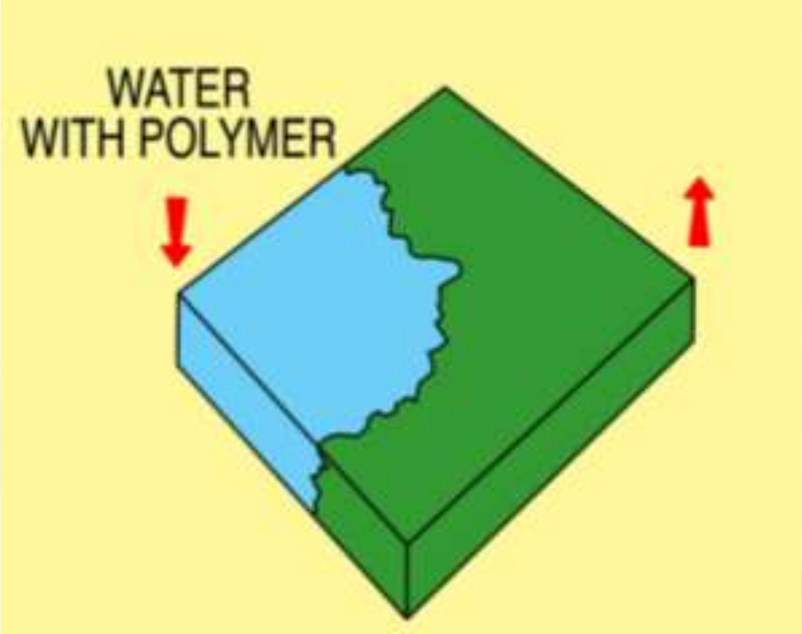
Technical Basis for Polymer Flooding

Polymer flooding recovers mobile oil that has been bypassed

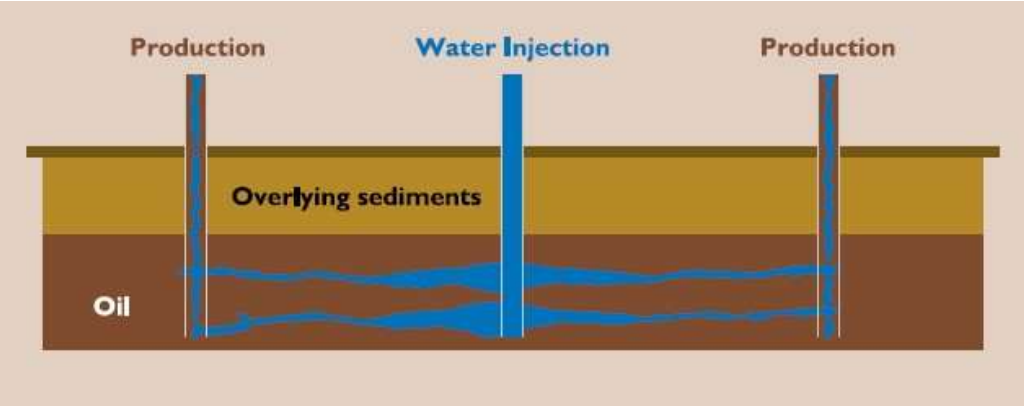
- during earlier waterflooding or aquifer intrusion
- due to reservoir heterogeneity.

It does not recover the residual oil that is trapped in rock pores after extensive waterflooding.





Polymer to Improve Mobility Control



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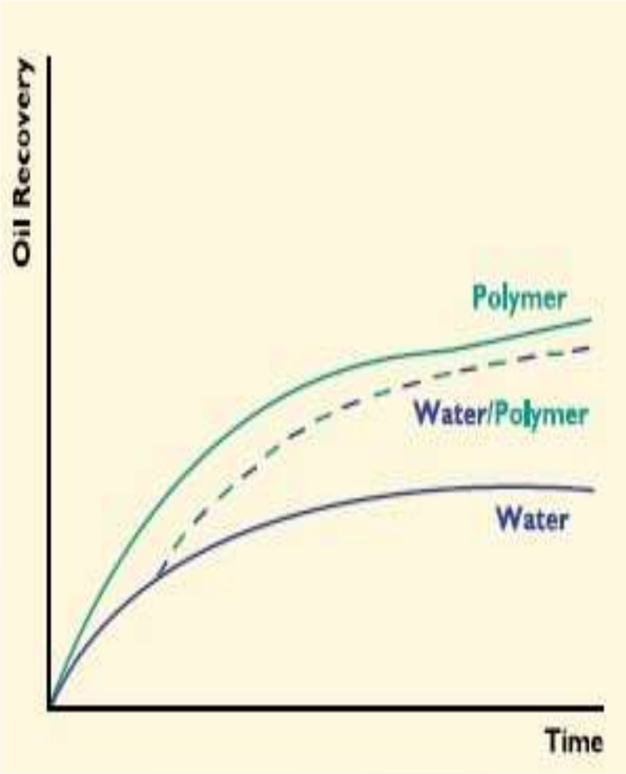
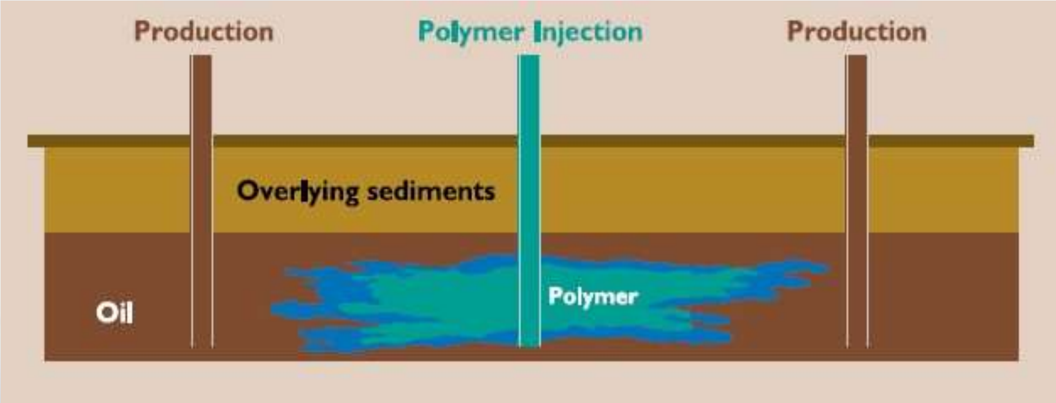




Polymer Flooding

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

Limitations

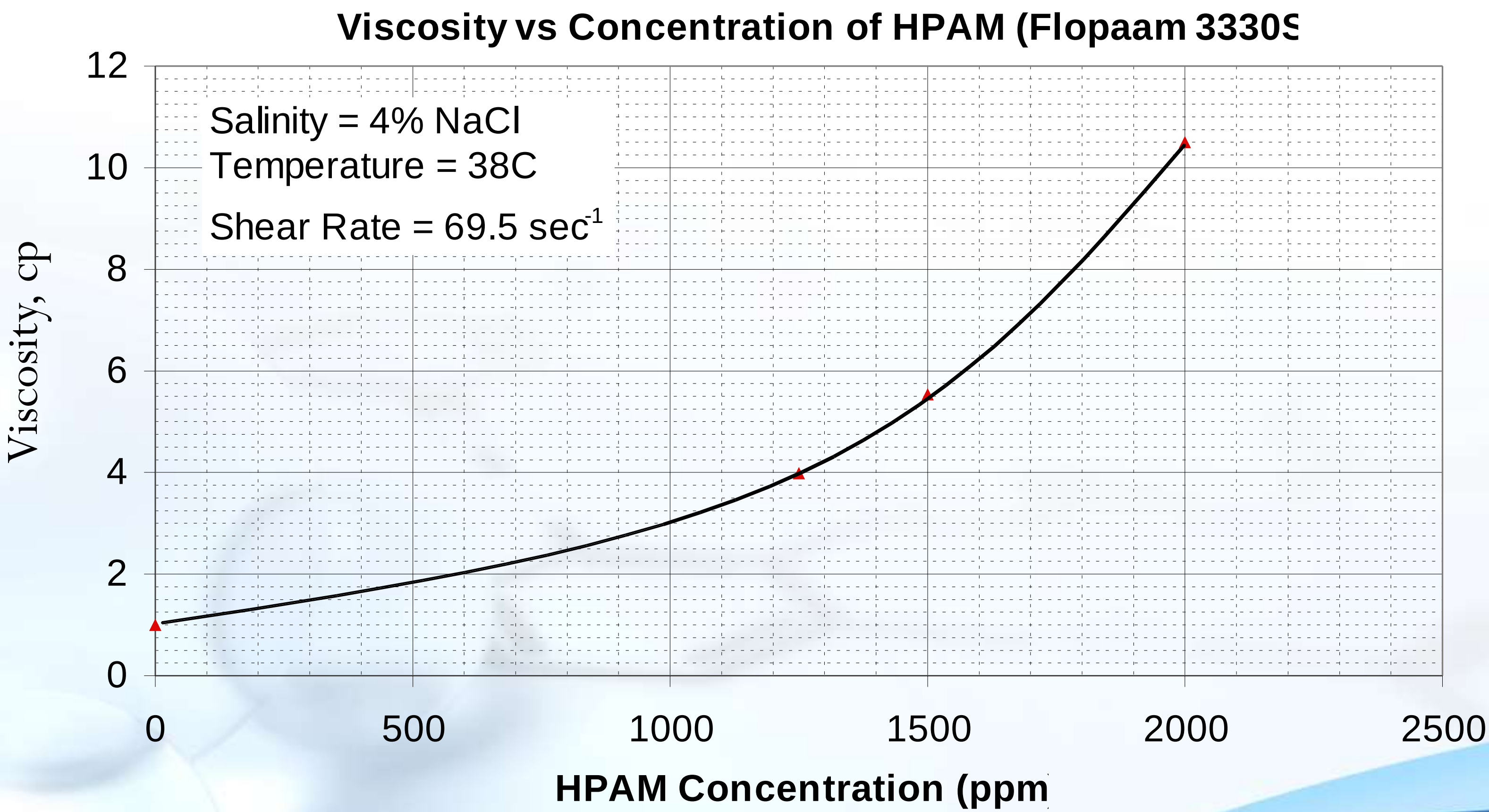
- **Mechanical, thermal, chemical degradation**
- **Injectivity concerns**
- **Loss of viscosity at high T, Salinity, and hardness**

Initial Phase of Lab Program

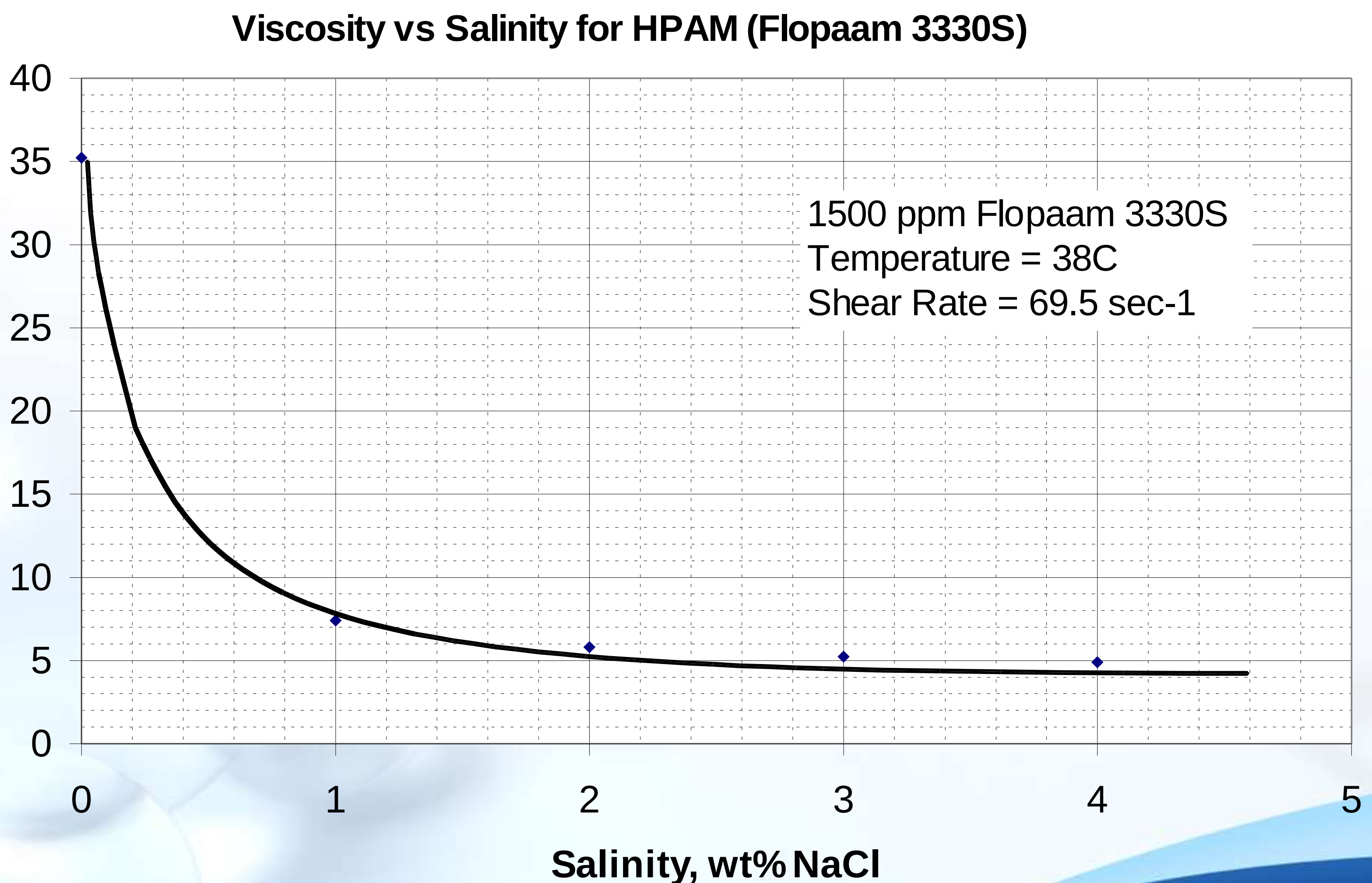
- Polymer Selection
- Polymer Screening
  - Viscosity and cost for feasible salinity options
  - Filtration and quality control
  - Thermal stability
  - Chemical stability
- Core flooding
  - Reservoir conditions and fluids
  - Pressure taps on core
  - Wide range of variables

Hydrolyzed Polyacrylamide (HPAM)

Flopaam 3330S from SNF



HPAM Polymer… Salinity

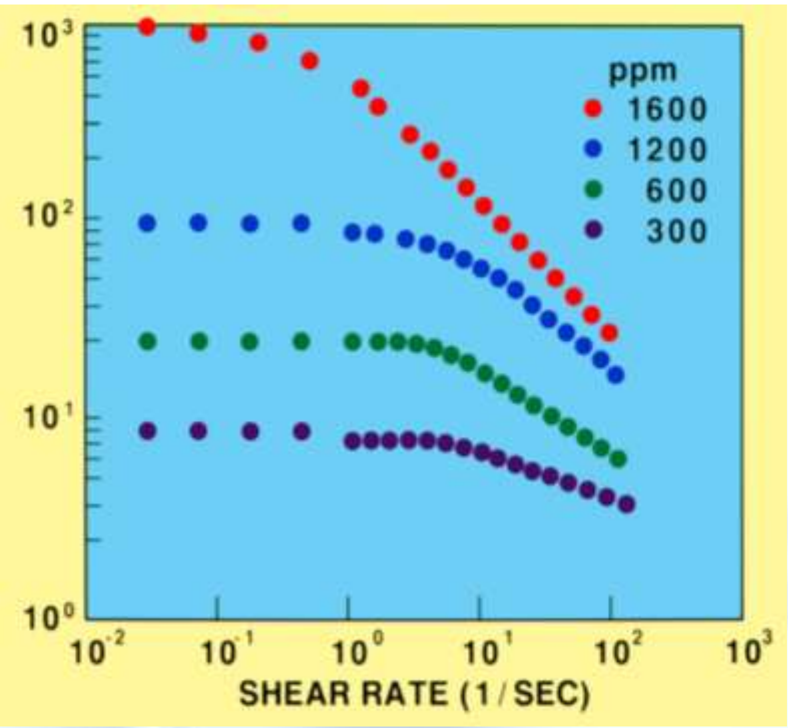


In-situ Viscosity in Rock

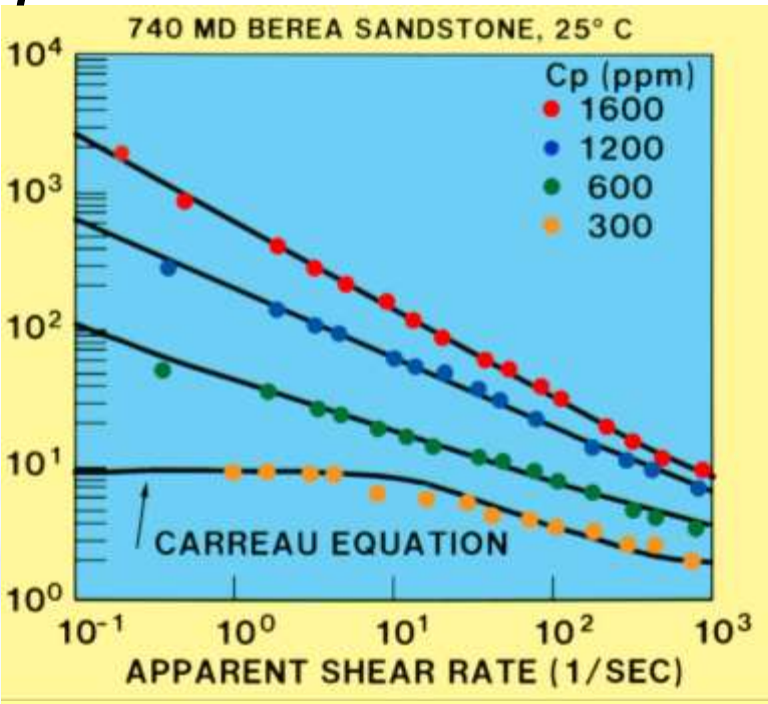
Bulk Viscosity *vs*. Shear Rate and Concentration

Apparent Viscosity in Rock *vs*. Flow Velocity and Concentration

cp

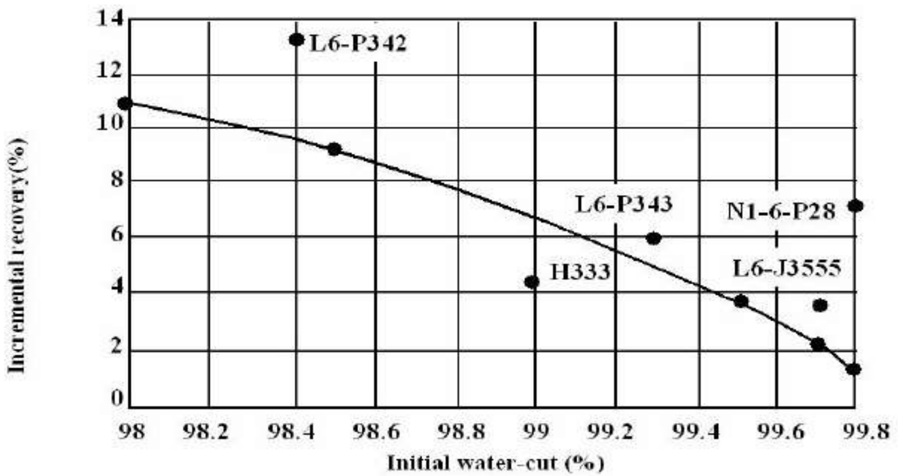


cp



From C. Huh

Daqing Polymer Injection



g. 7 Relationship of incremental recovery by polymer flood versus initial water-cut

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:

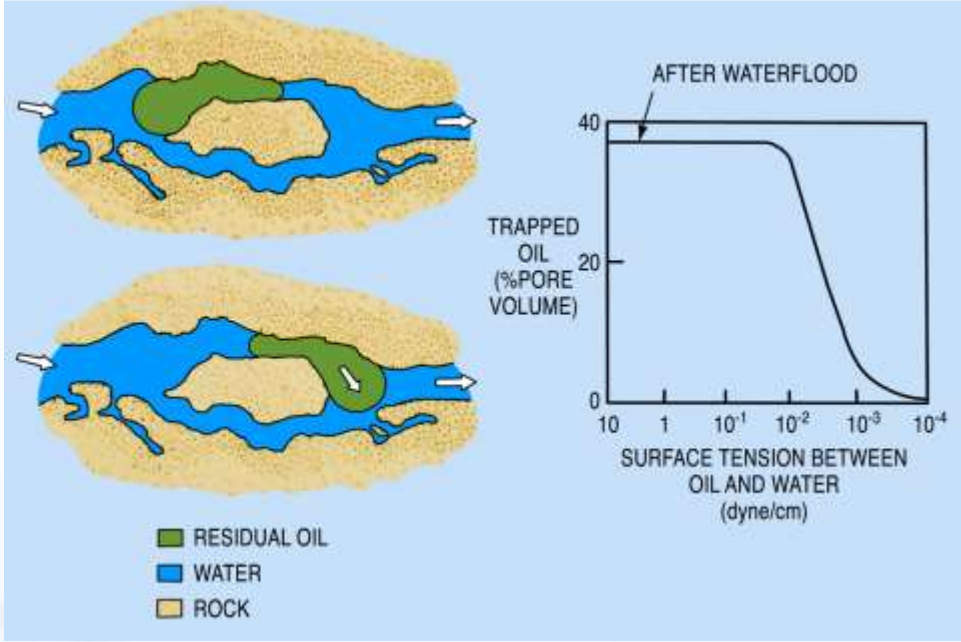
- larger increase in sweep efficiency
- shorter response time to polymer flooding
- strongest influence on recovery is connectivity of pay zones

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_2CO_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

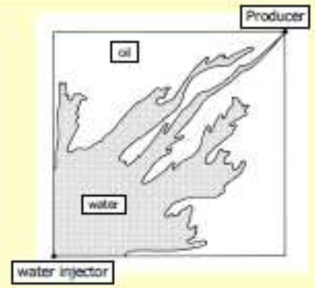
Alkaline/Surfactant/Polymer (ASP)

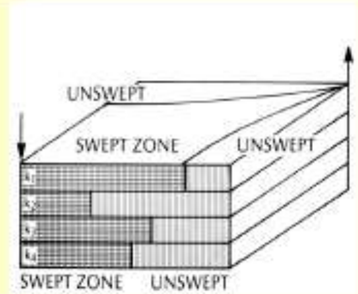
- Alkaline solutions, e.g, NaOH, Na_2CO_3, convert organic acids in crude oils to soaps, “natural surfactants”, much more cheaply than injecting surfactants (an old idea)
- The soap formed is almost always not at “optimum” conditions to produce ultralow tensions for existing temperature, oil & brine 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

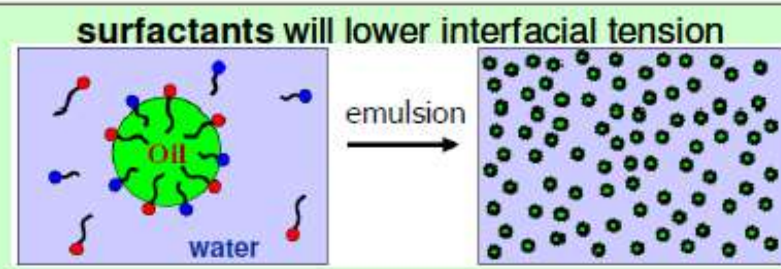
- increase viscosity
- improve mobility control and sweep.





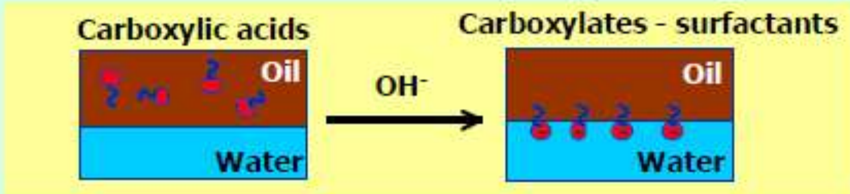
Surfactant

- lower interfacial tension
- mobilize <u>residual</u> oil.
- required: IFT = 10^{-3} mN/m



Alkali

- high pH of 11
- natural surfactants (soaps)
- minimize surf. adsorption



K. Raney, 2011

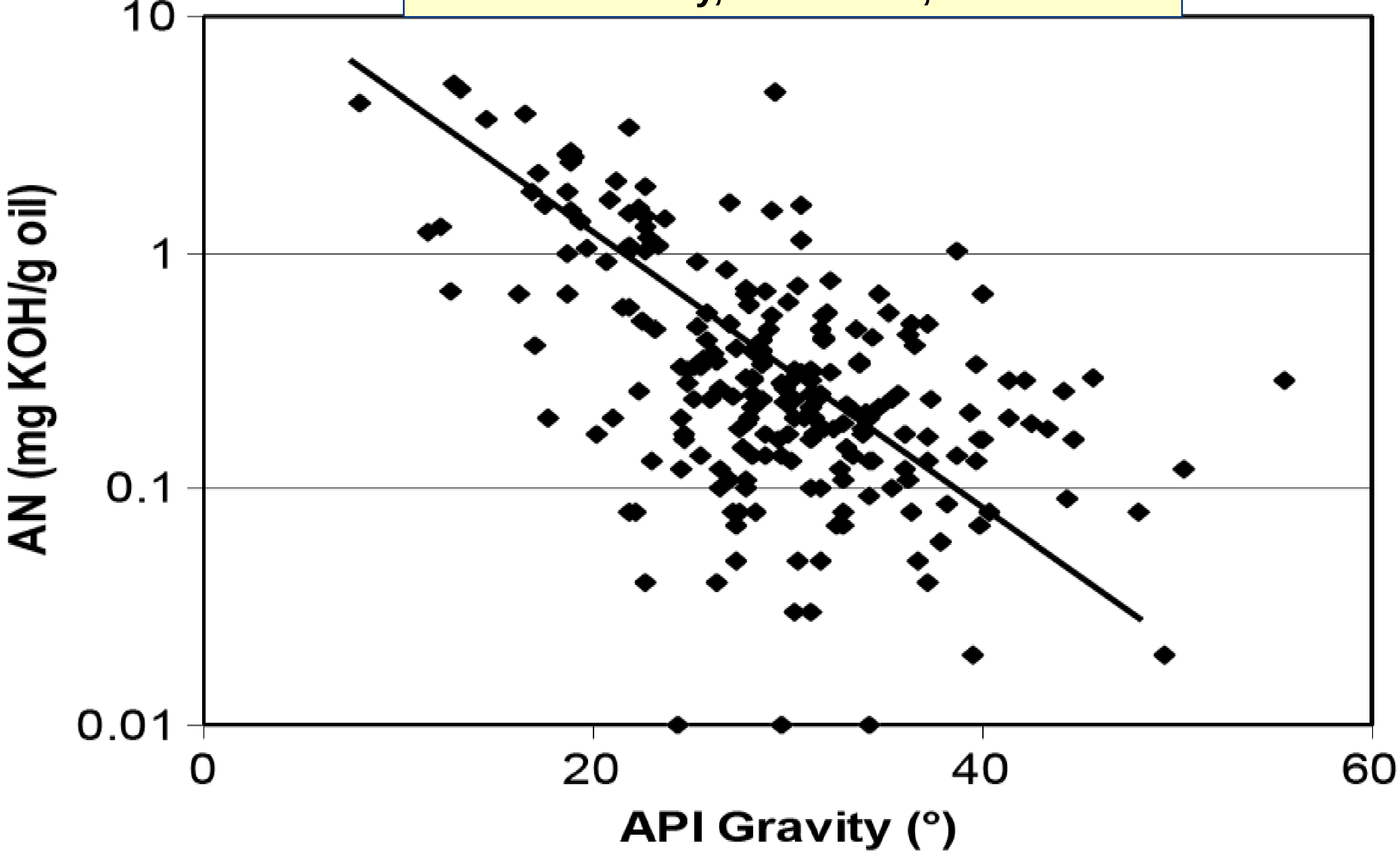
ASP for Viscous Oils

- 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

Two Surfactants

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_2CO_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

Raise pH

Alkaline

Formation and injection water compatibility

Generate natural surfactant (Soap)

Water

Oil

Mineral precipitation
Mineral dissolution

Wettability Alteration

Rock

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

SPE 166478, 2013

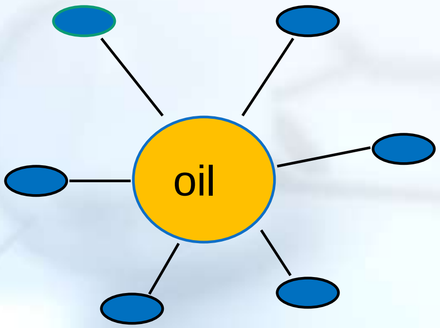
Microemulsion phase behavior

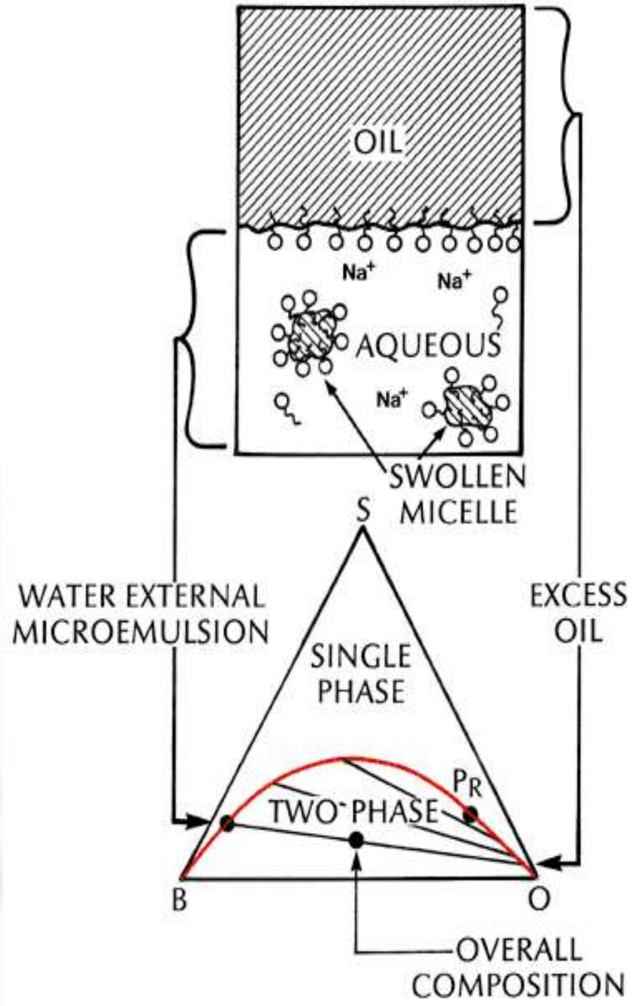
Salinity screening (0.2 – 1.25 %)

Surfactant Phase Behavior

<u>Winsor Type I (II-)Behavior</u>

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

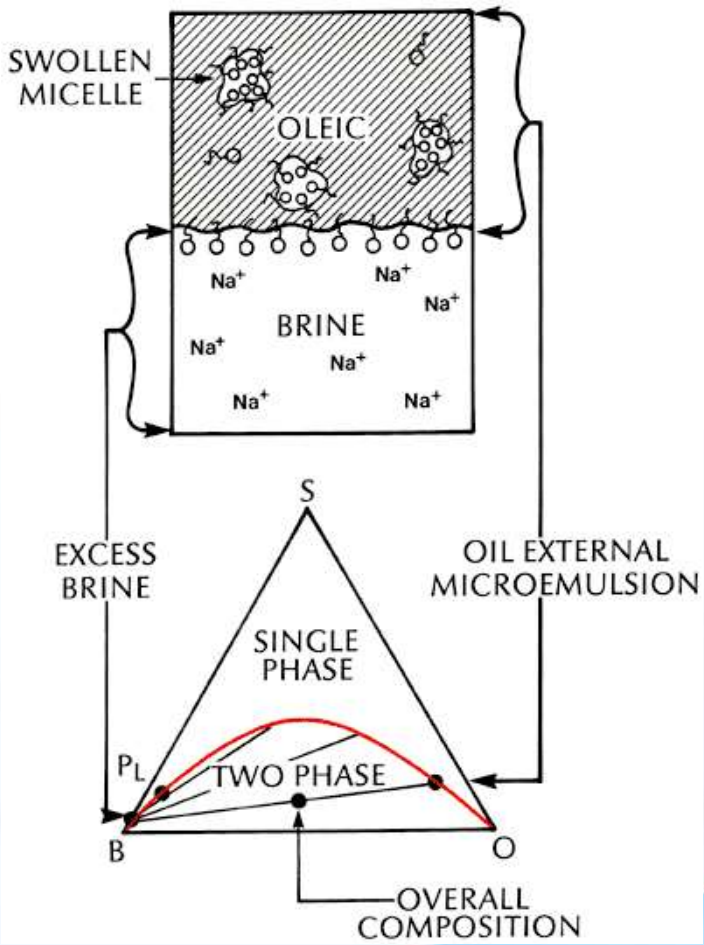


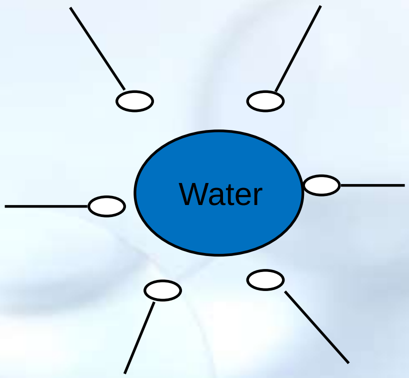


Surfactant Phase Behavior

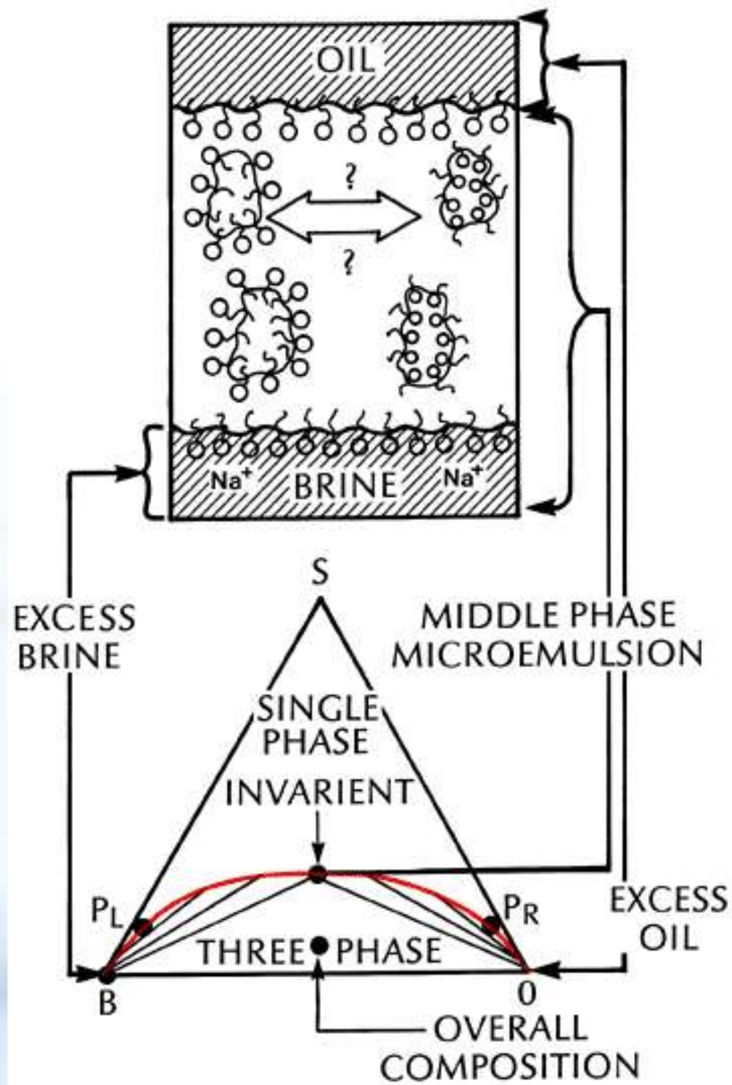
Winsor Type II (II+) Behavior

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

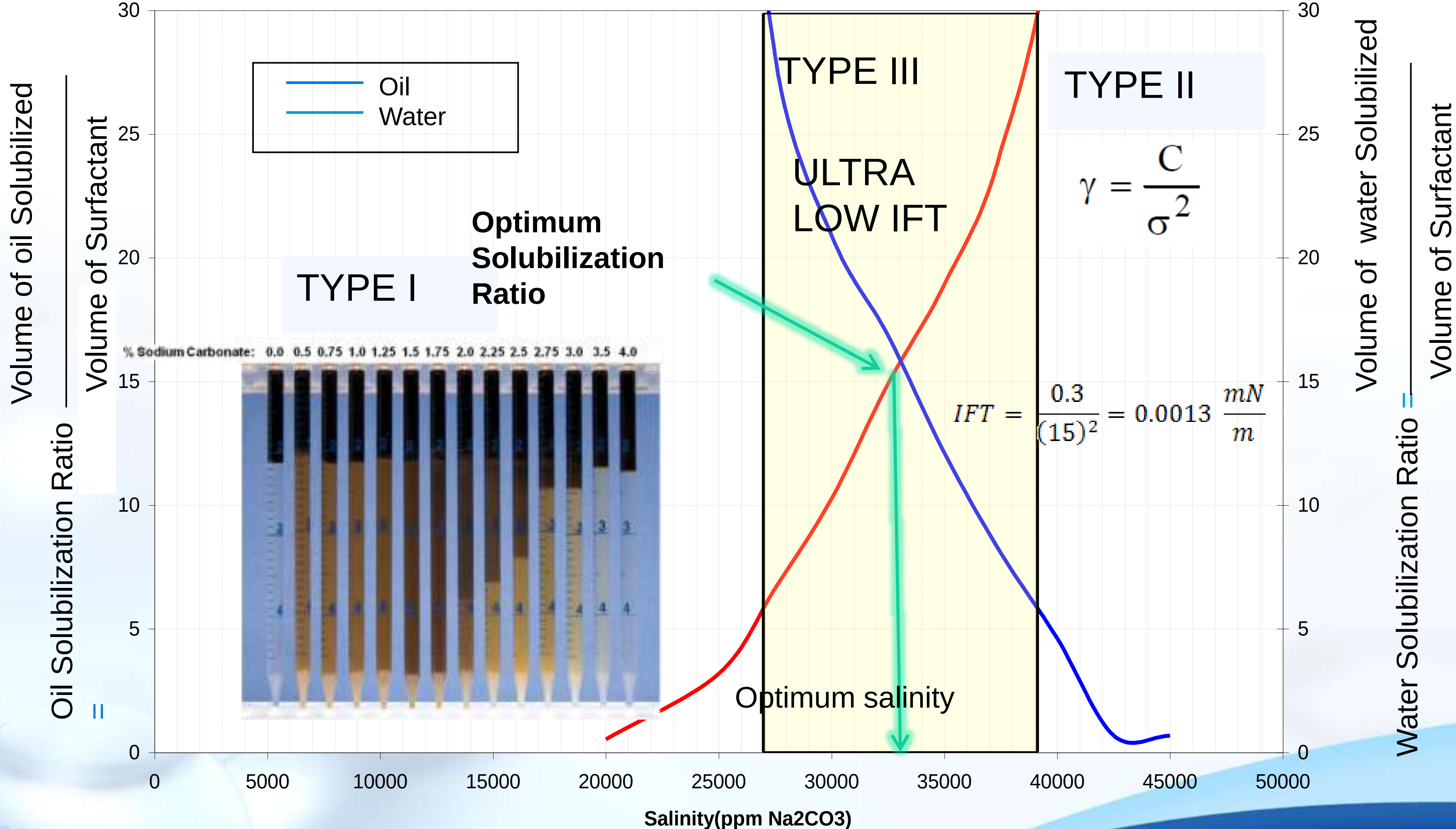




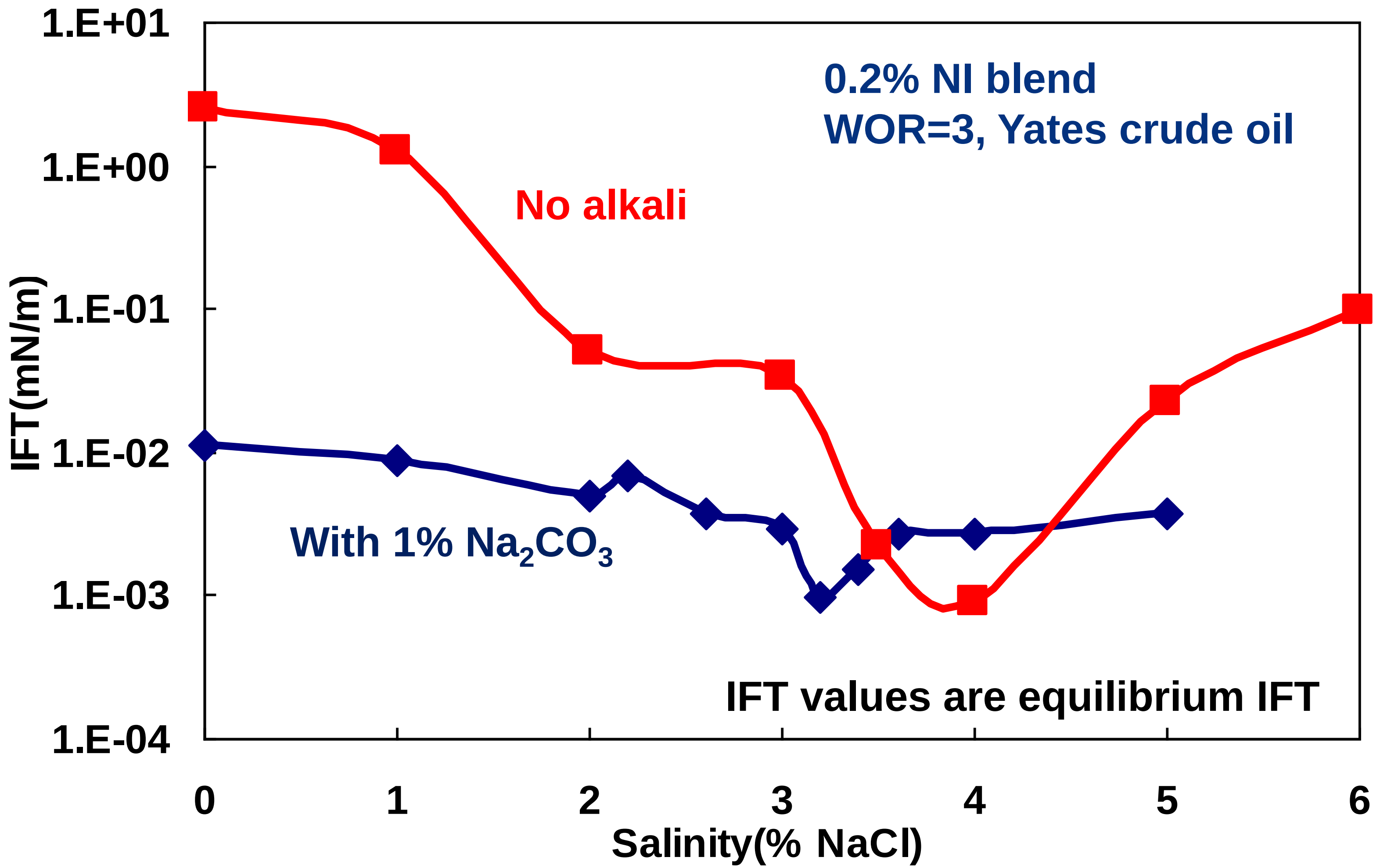
Type III Microemulsion



Phase Behavior, IFT, and Salinity

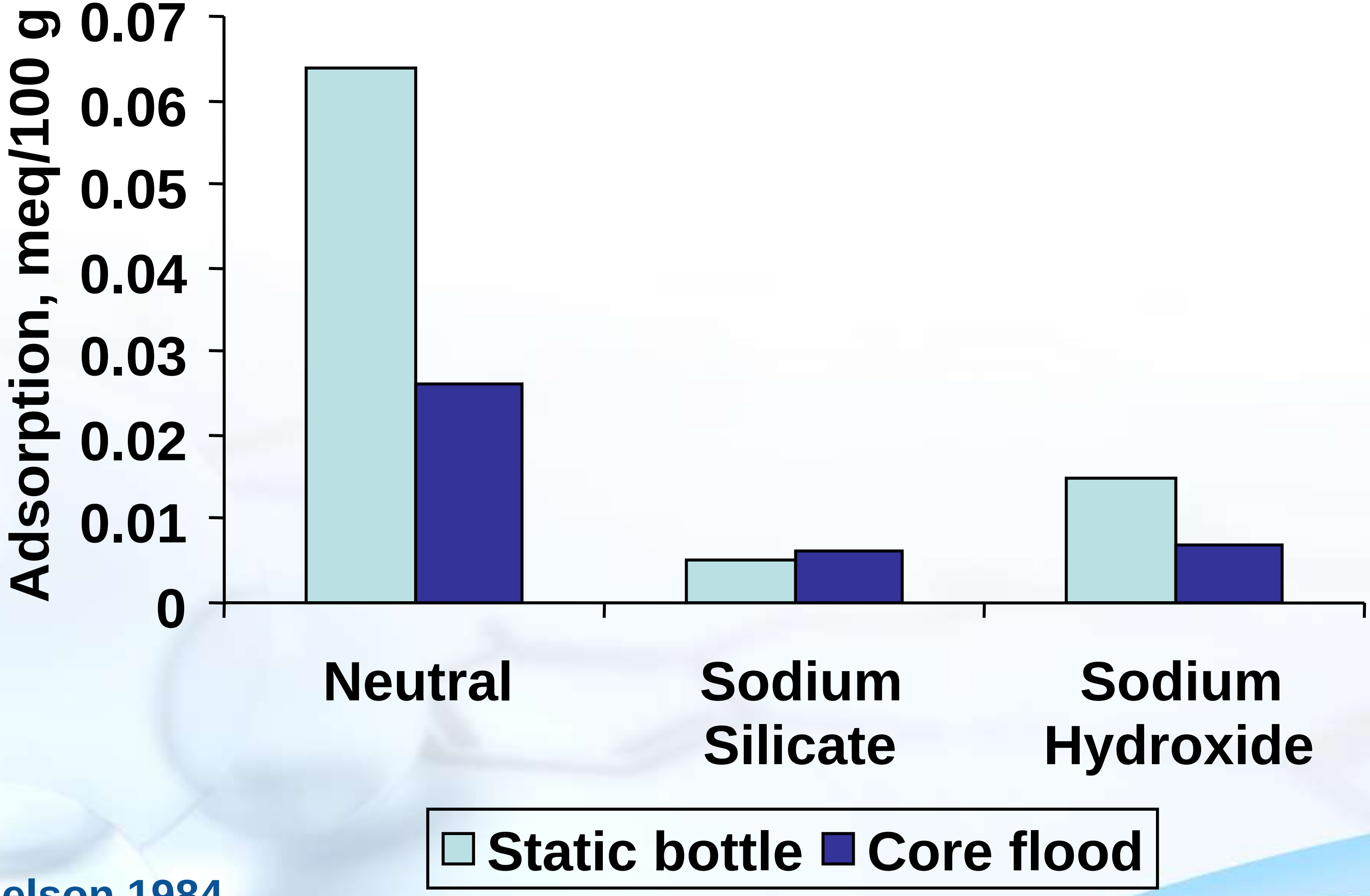


The Width of Low IFT Region is Much Wider When Soap is Generated by Alkali



Hirasaki and Miller, 2007

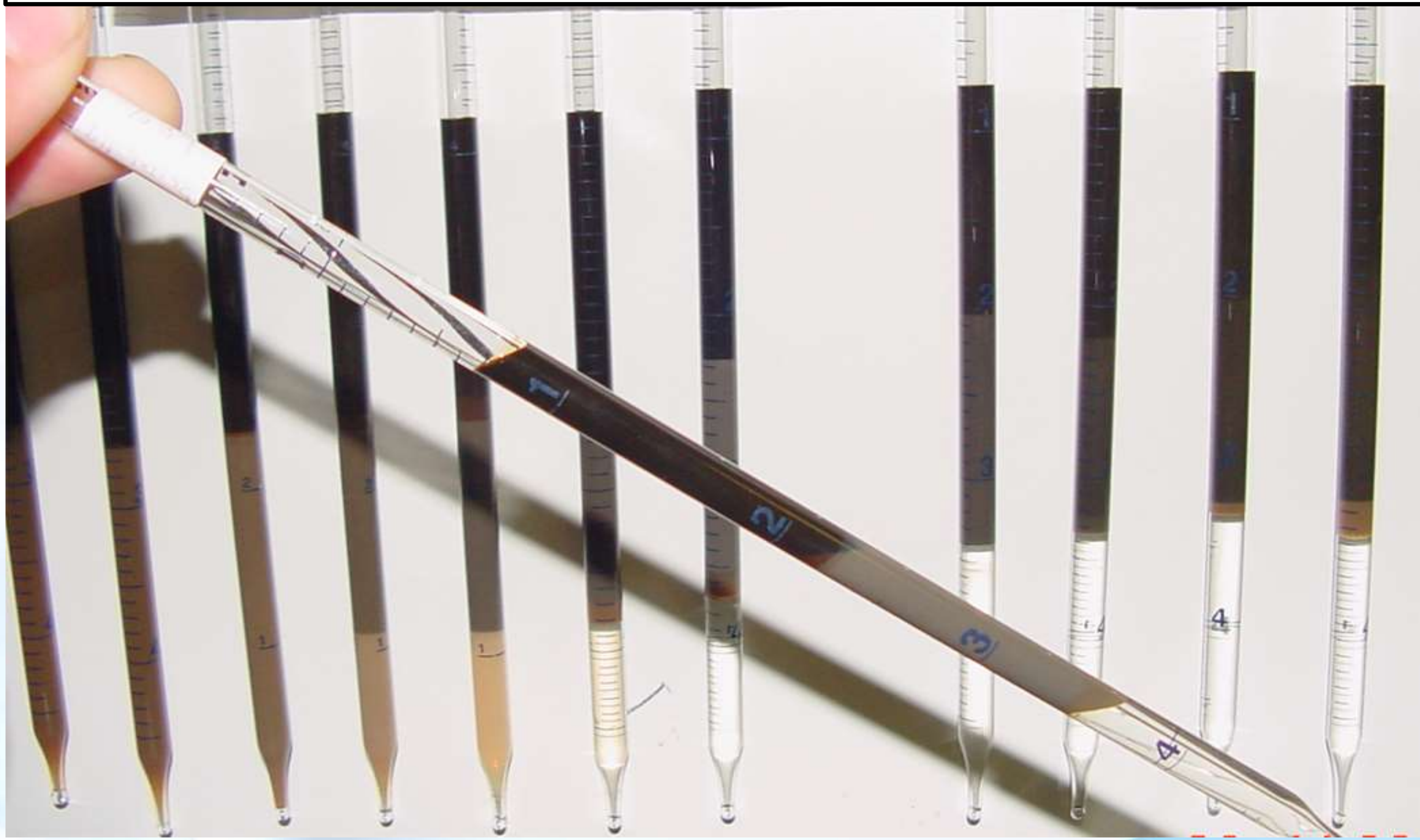
Alkali Reduces Adsorption of NEODOL 25-3S in Berea



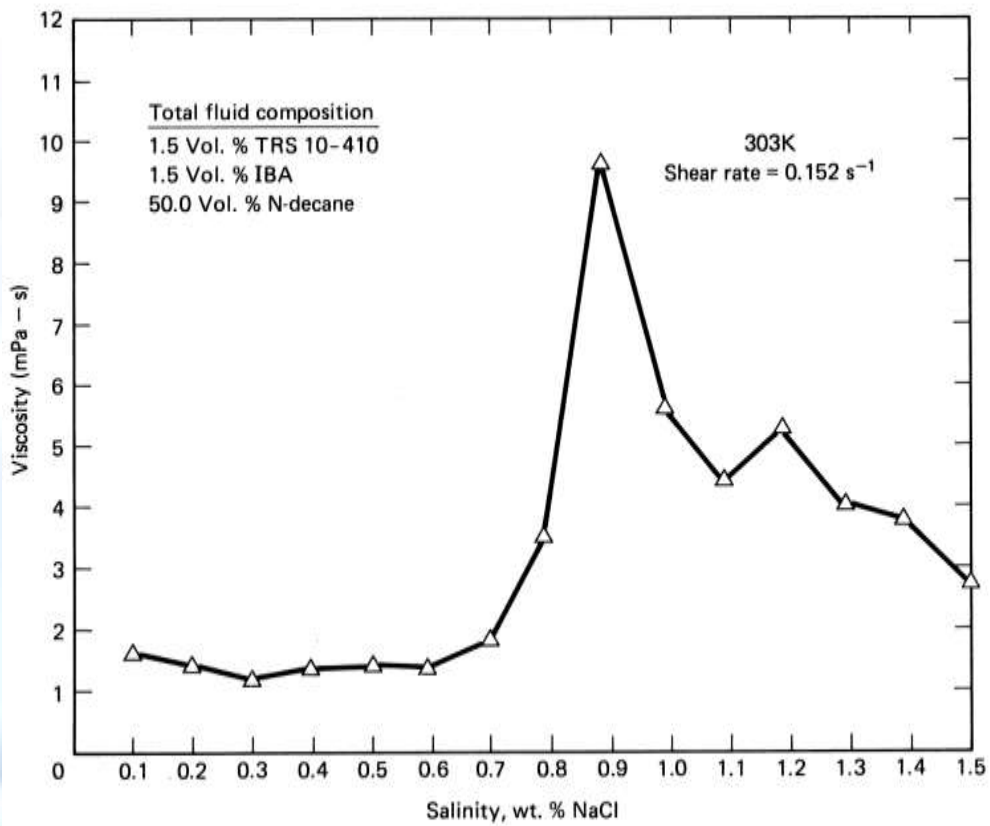
Nelson,1984

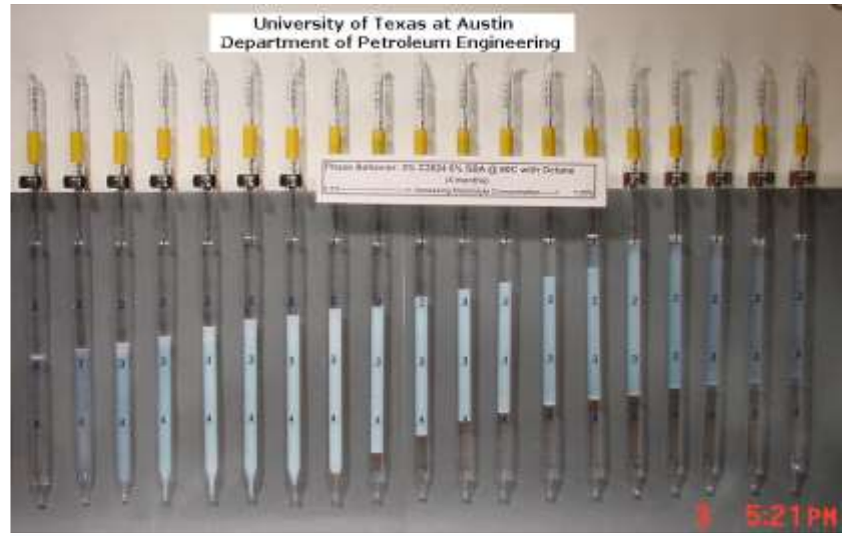
Interface Fluidity

Increasing Electrolyte Concentration →

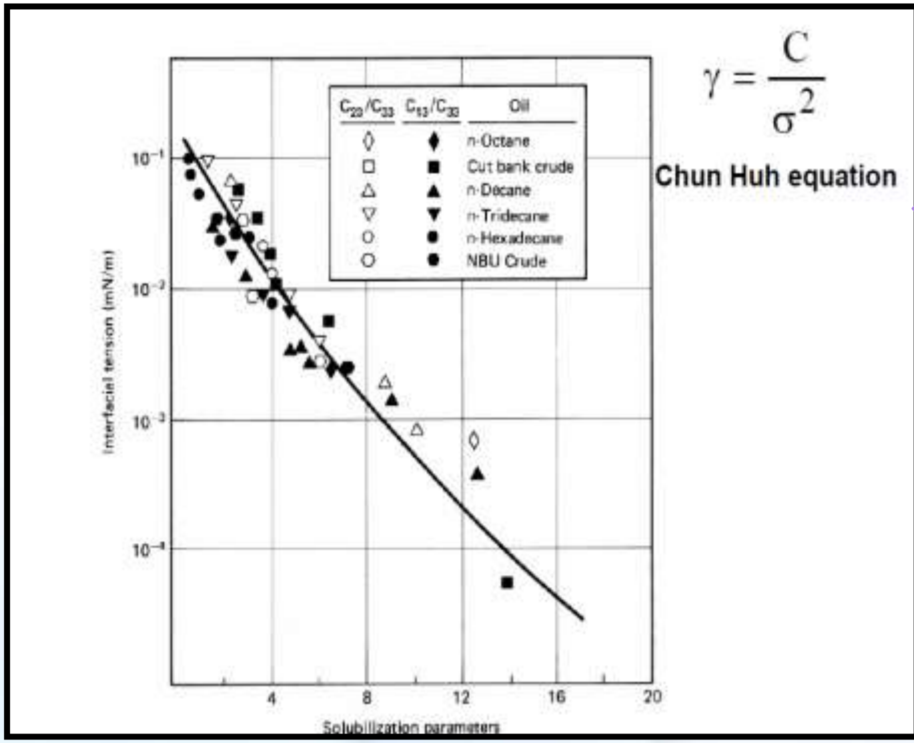


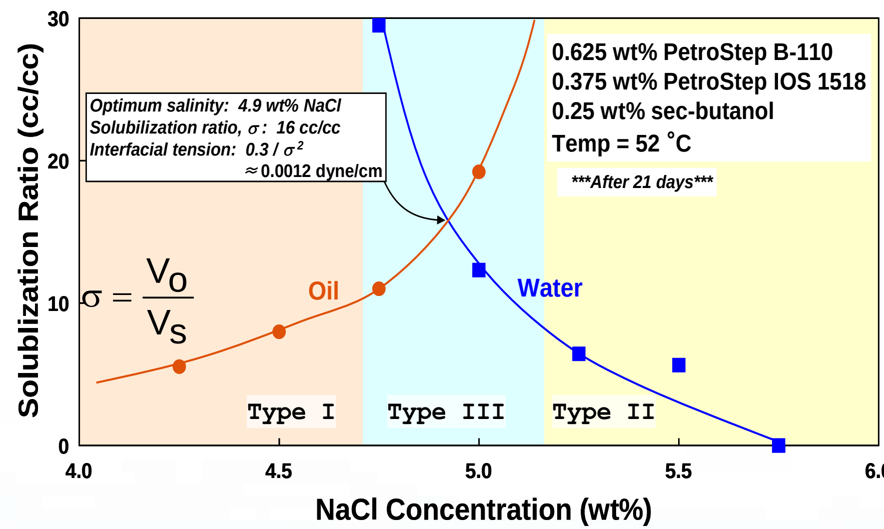
Microemulsion Phase Viscosity

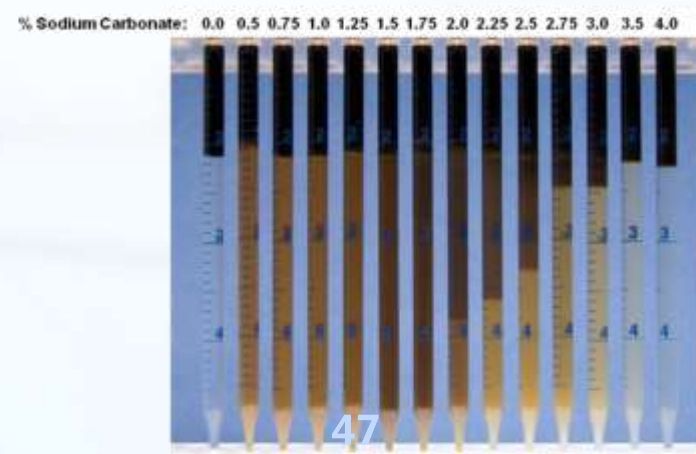




Interfacial Tension







Residual Saturation vs. Capillary Number

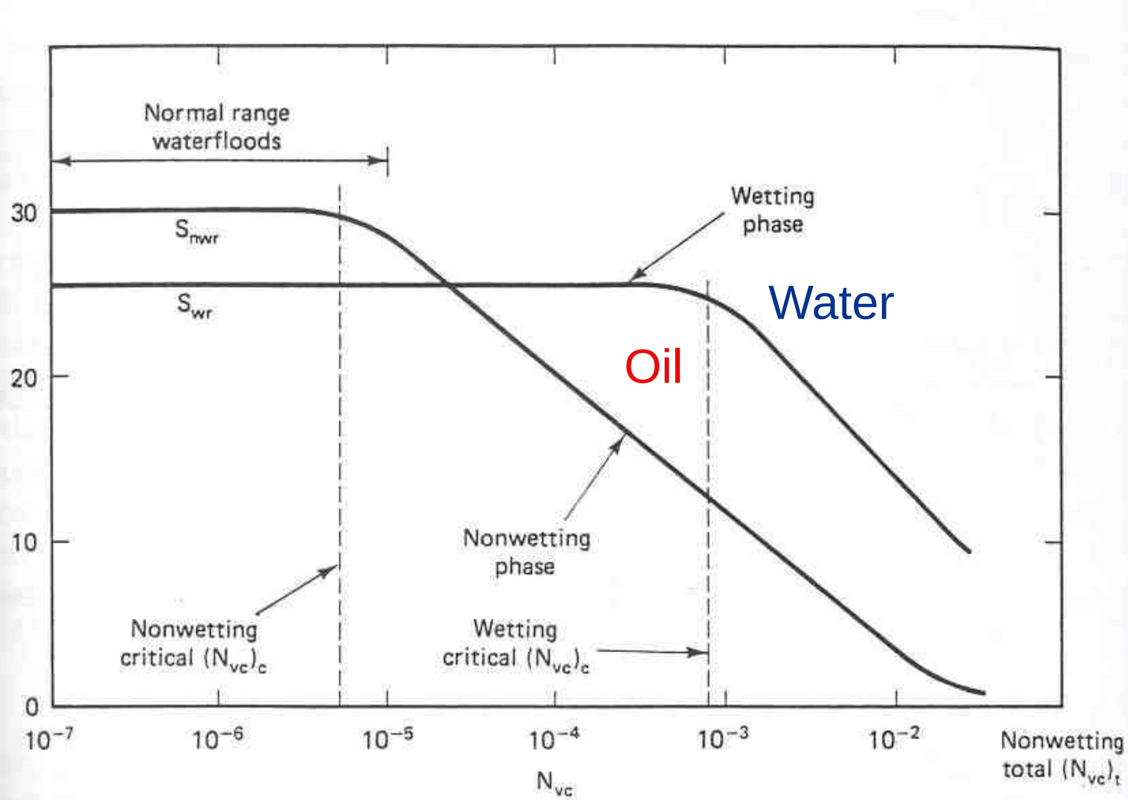
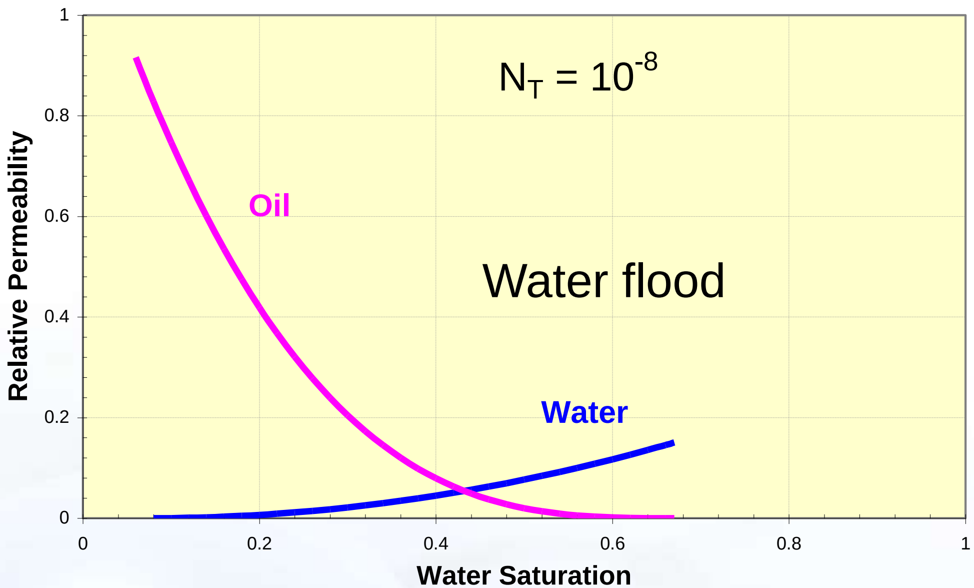


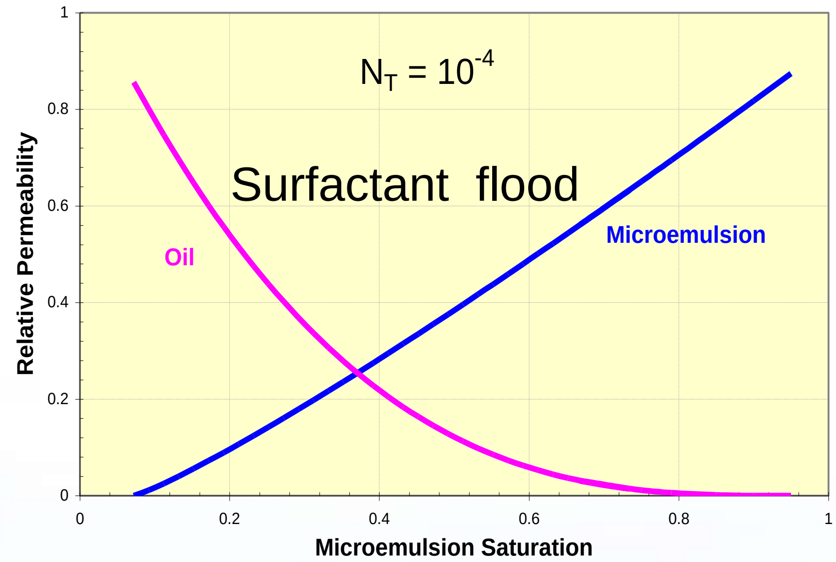
Figure 3-17 Schematic capillary desaturation curve (from Lake, 1984)

Capillary number is a dimensionless number : ratio of viscous to capillary forces

$$N_C = \frac{\left| \vec{\vec{k}} \cdot (\nabla \Phi) \right|}{\sigma}$$

Relative Permeability vs. Capillary Number





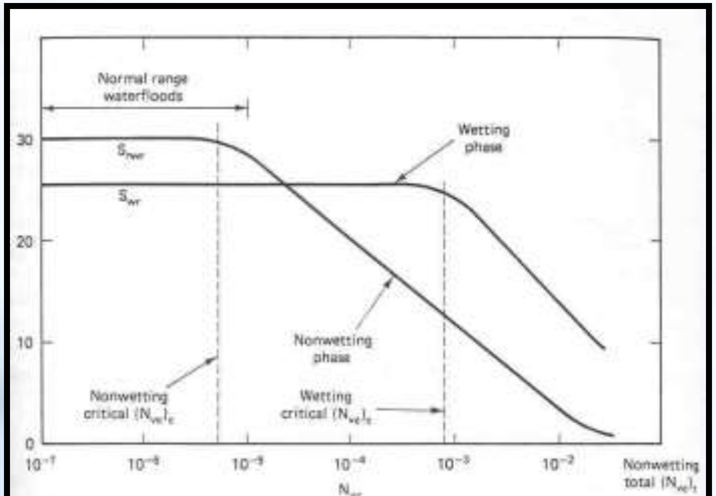
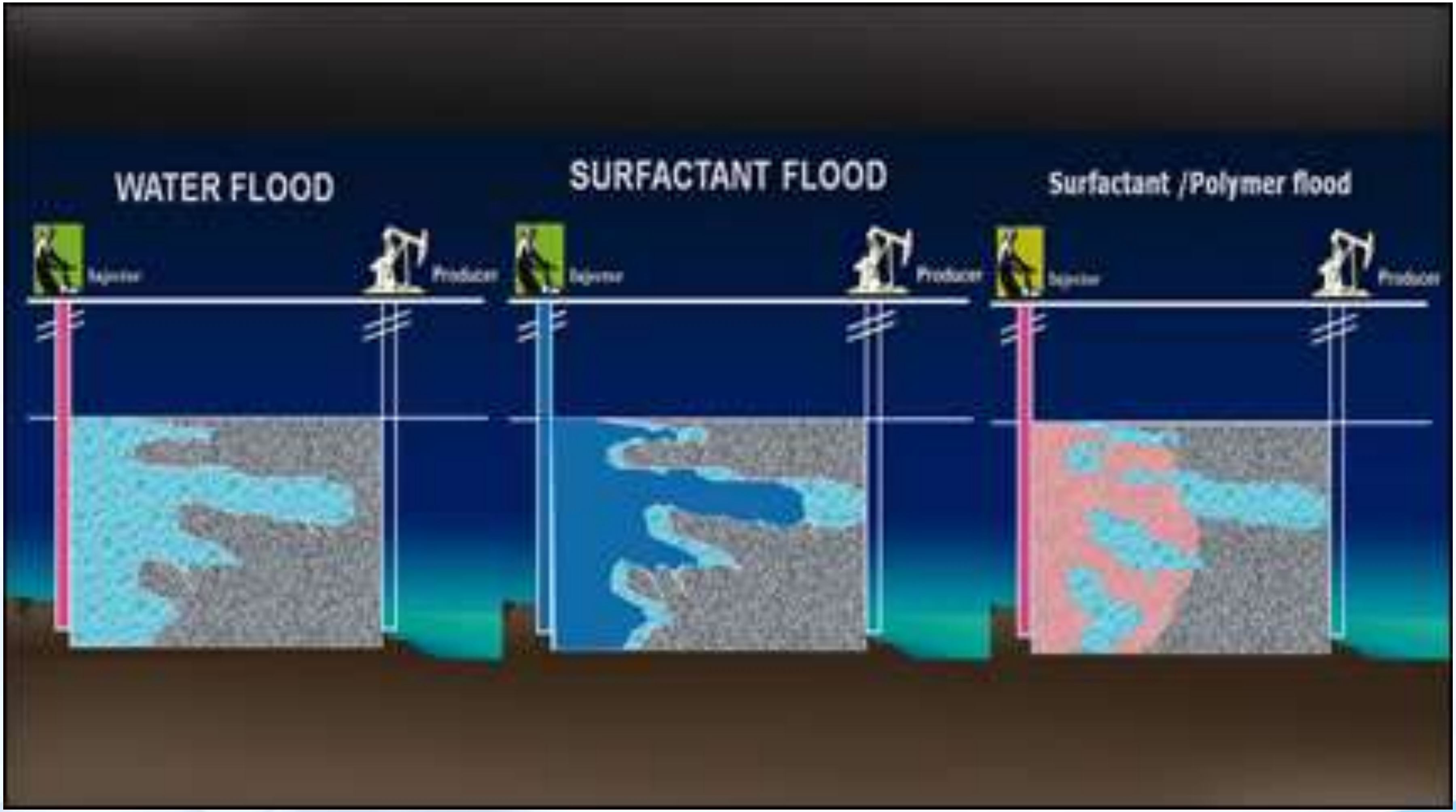
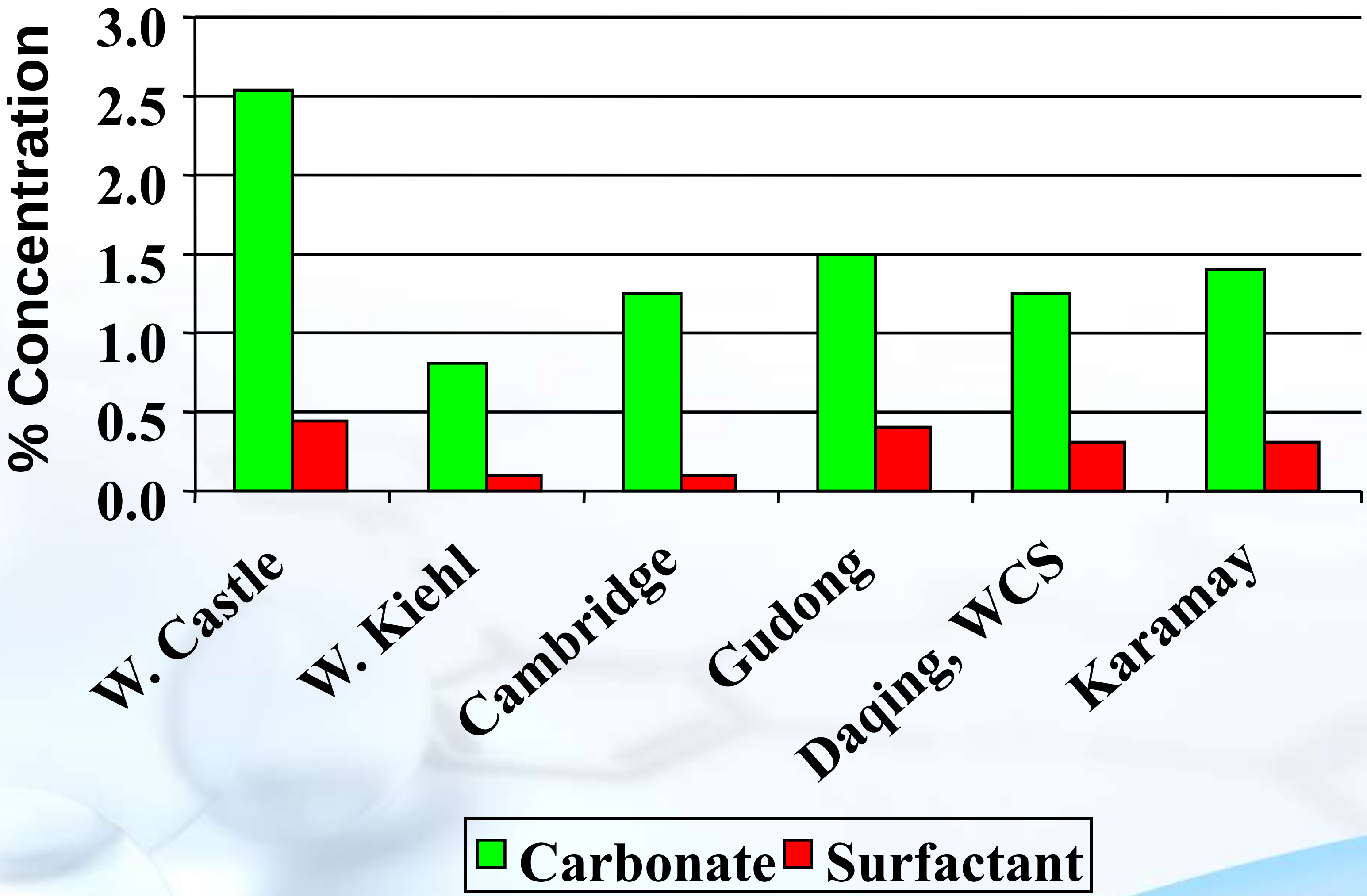


Figure 3-17 Schematic capillary desaturation curve (from Lake, 1984)

Need for Mobility Control

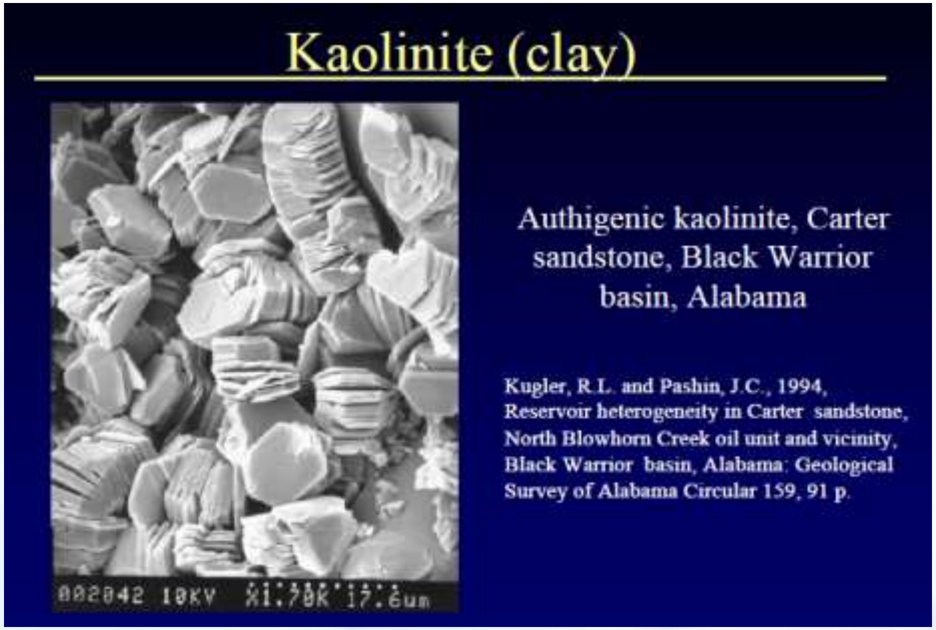


Alkali and Surfactant Concentrations



Reservoir Clays

$Al_2Si_2O_5(OH)_4$



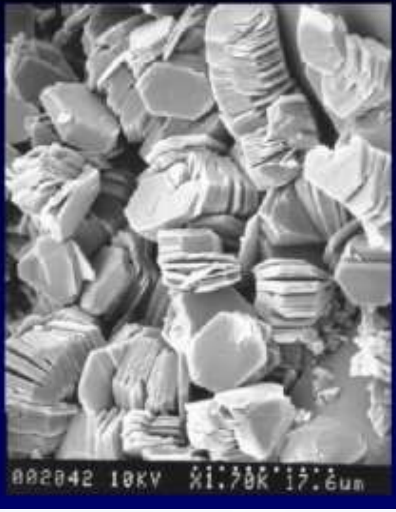
$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$

montmorillonite clay = Smectite

Drilling mud

Retention and Clay Content

Kaolinite (clay)



Authigenic kaolinite, Carter sandstone, Black Warrior basin, Alabama

Kugler, R.L. and Pashin, J.C., 1994, Reservoir heterogeneity in Carter sandstone, North Blowhorn Creek oil unit and vicinity, Black Warrior basin, Alabama: Geological Survey of Alabama Circular 159, 91 p.

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/vacrc/sem02.html