COST-EFFECTIVE SURFACTANT FORMULATIONS FOR IMPROVED OIL RECOVERY IN CARBONATE RESERVOIRS

California Institute of Technology
Power, Environmental, and Energy Research (PEER) Center

SUMMARY

New project funded by DOE for 3 years -- 2004 -2007

Objective: More cost-effective chemical formulations for EOR in carbonate reservoirs. Target U.S. mature waterfloods in fractured carbonates.

Approach:

- Emphasize chemicals to alter oil-wet to water-wet conditions
- Primarily experimental study
- Some focused theoretical (molecular simulation) work

RATIONALE

Opportunity:

Waterflood efficiency low in fractured carbonate reservoirs….
Hence, a **LARGE EOR RESIDUAL OIL TARGET** remains.

Carbonate reservoirs a significant fraction resource (> one-third)

Many such reservoirs are onshore and relatively shallow….

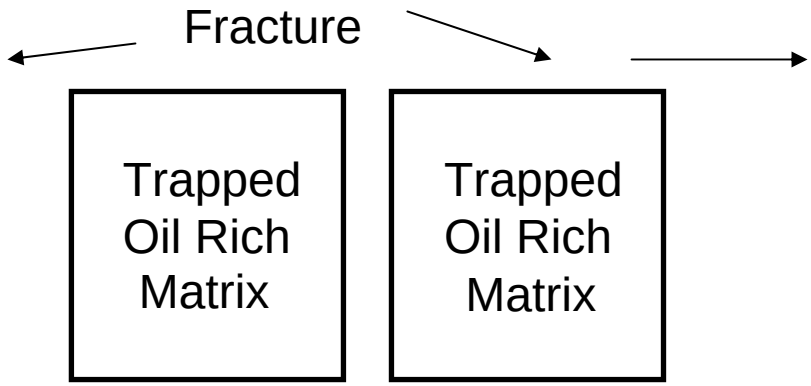
Economic Advantages of Target Reservoirs

Cheap to drill
Established infrastructure
Lower temperature

MECHANISMS

Common Problem:

Fast sweep in fractures – early water breakthrough
Poor penetration (imbibition) of water into matrix because is **oil-wetting.**
Oil trapped by capillary forces.



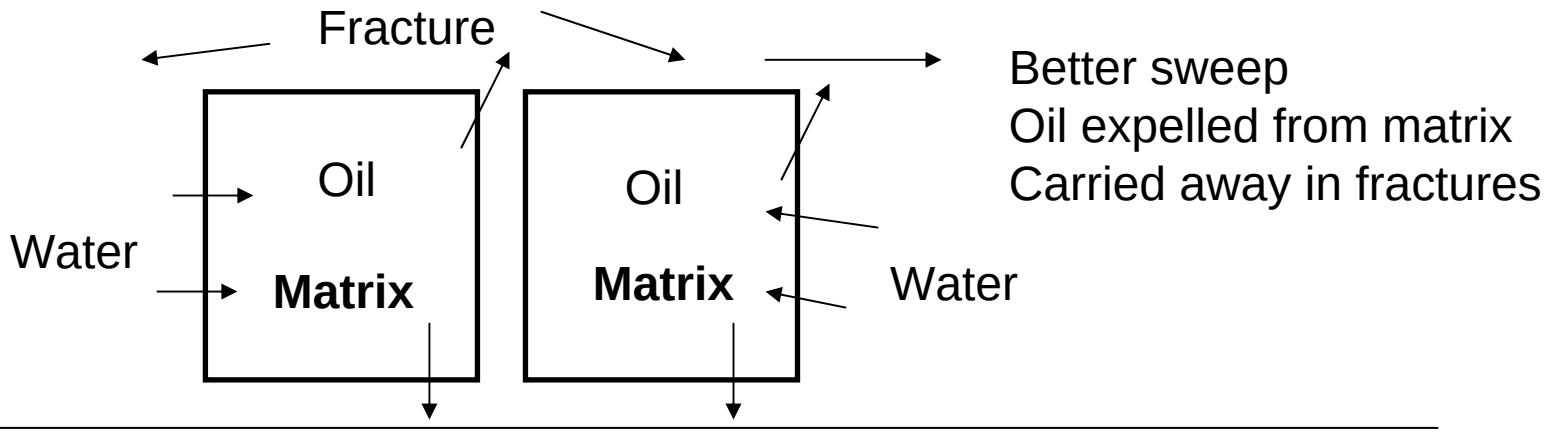
Poor sweep
Oil in fractures produced
Little oil from matrix

OIL RECOVERY OF ORDINARY WATERFLOOD IN FRACTURED CARBONATE RESERVOIR IS TYPICALLY POOR

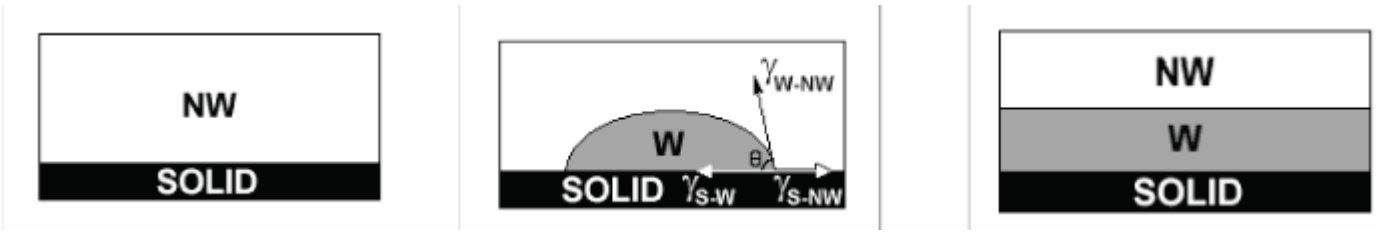
MECHANISMS

<u>One approach -- change to water – wet condition via surfactant:</u>

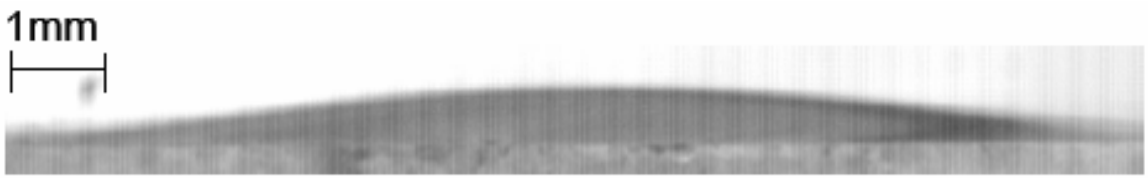
Spontaneous imbibition of aqueous phase
Oil expelled
Fractures are a conduit for oil released



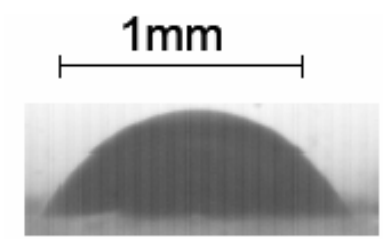
CHANGING TO A WATER WET CONDITION



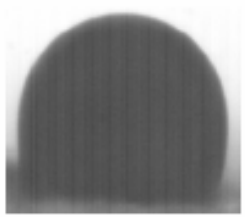
NW - non-wetting phase displaced by water at surface



Oil wetting on calcite

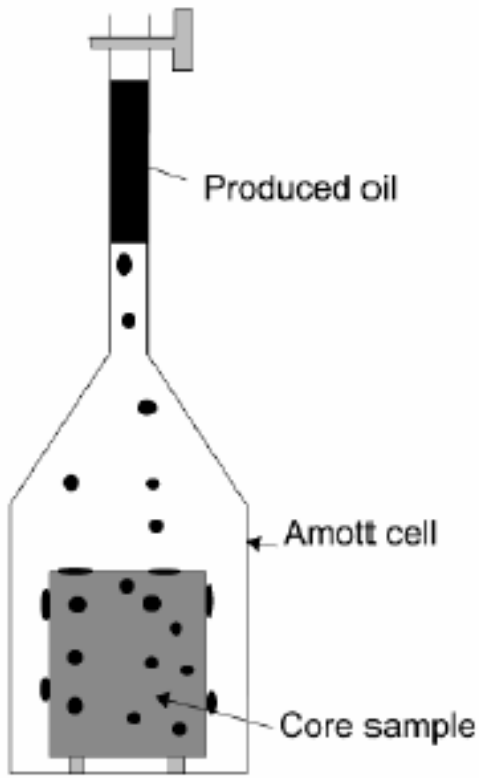


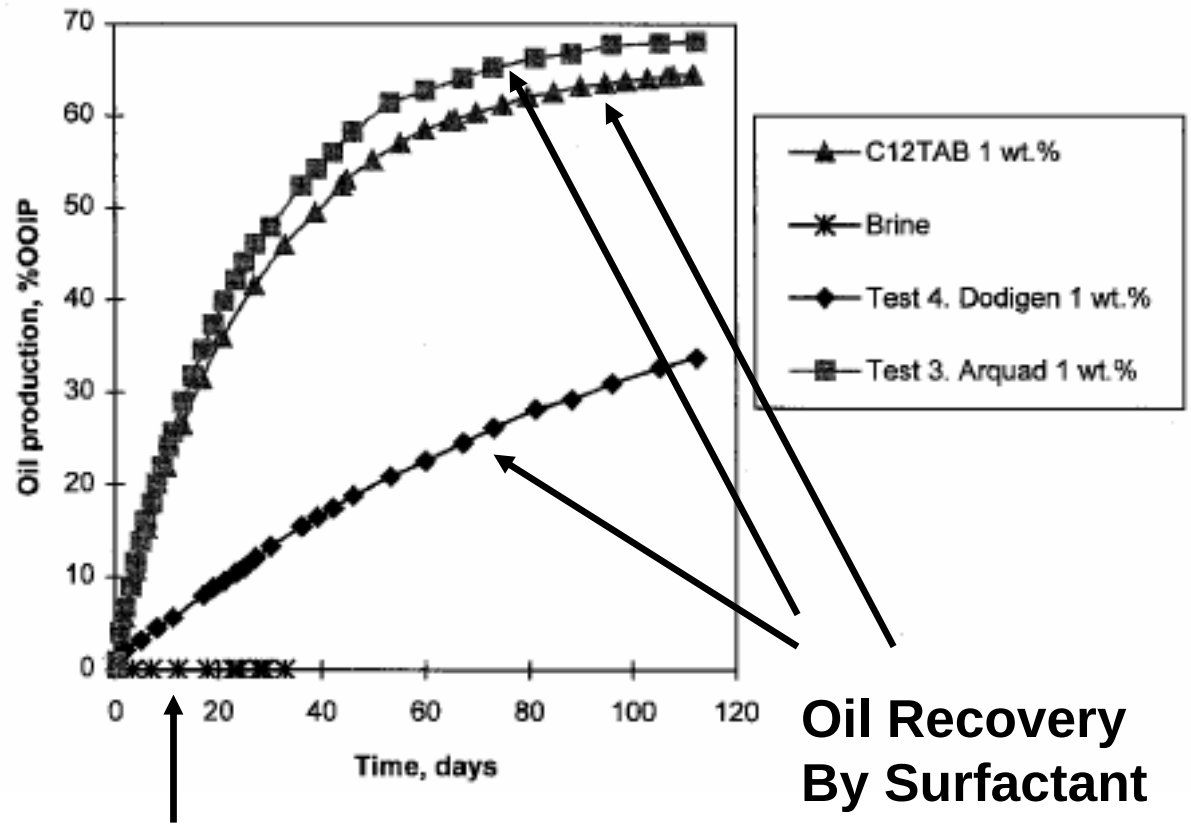
Oil less wetting –
Treated with aqueous solution A



Oil even less wetting –
Treated with aqueous solution B
Solution B may be attractive

SPONTANEOUS IMBIBITION OF AQUEOUS PHASE INTO AN OIL SATURATED CARBONATE CORE



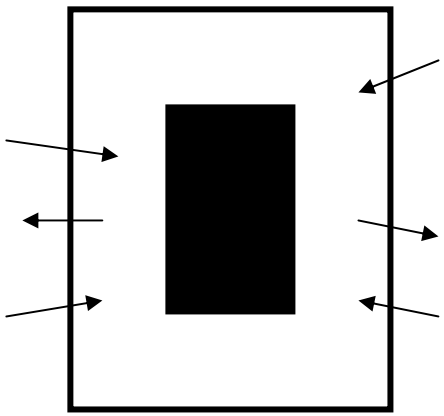


Oil Recovery By Surfactant Solutions

NO Oil Produced By Brine

MECHANISMS -- AQUEOUS PHASE IMBIBES INTO OIL SATURATED CORE

Capillary Forces



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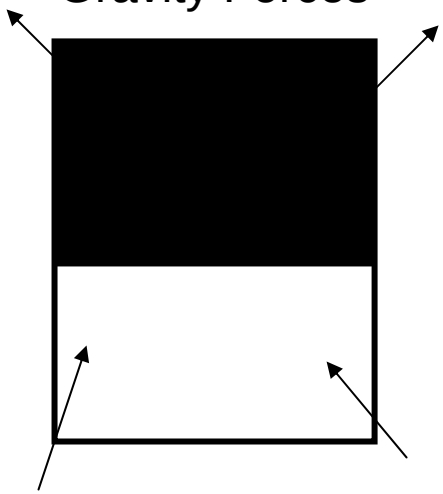
Gravity Forces

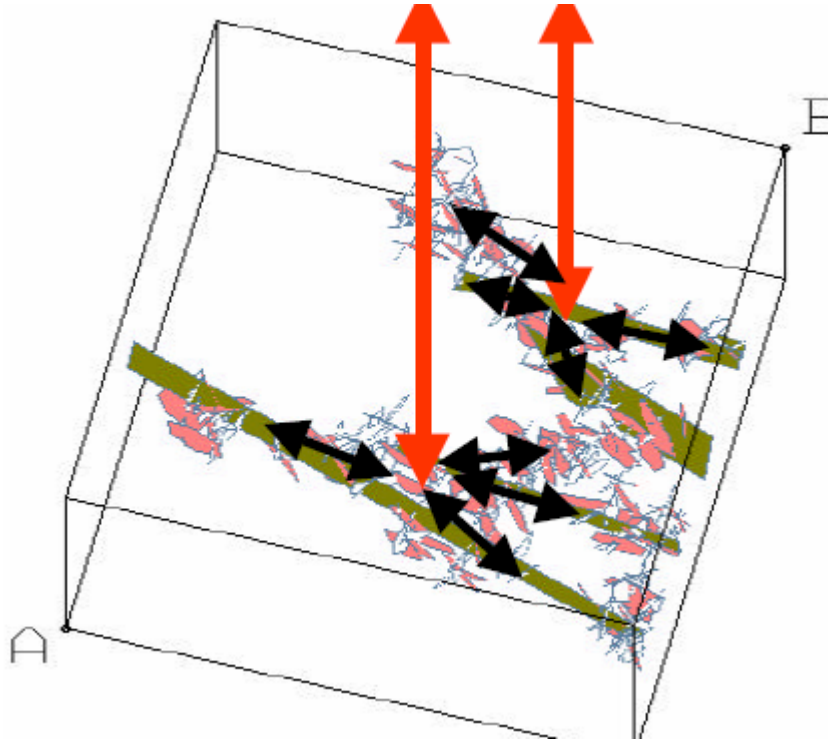


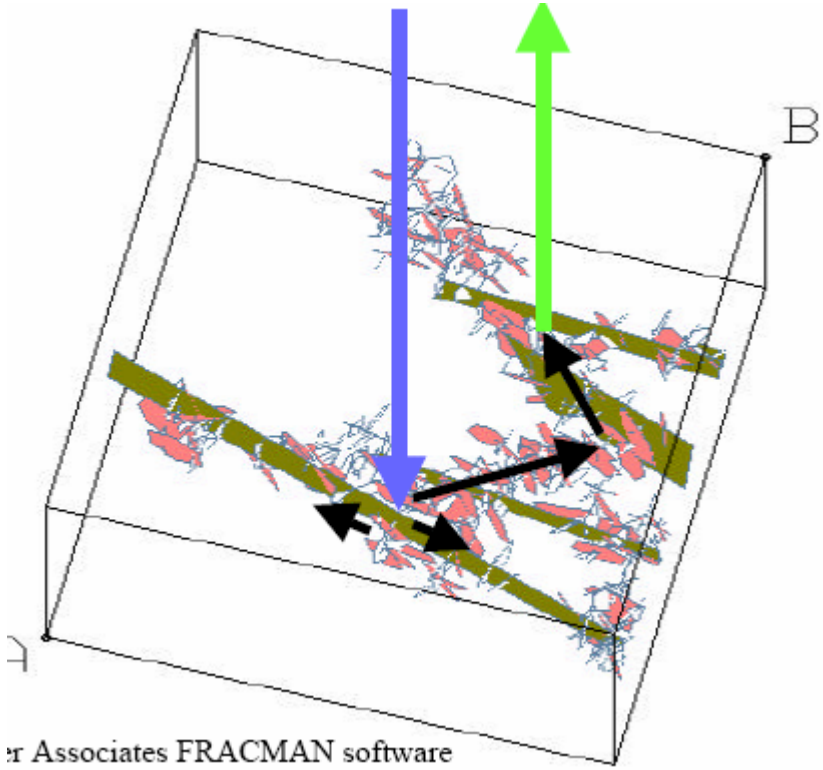
0.2 <

<u>INVERSE BOND NUMBER ---</u>

$$N_B^{-1} = C\frac{\sigma \cos\theta \sqrt{\frac{\phi}{k}}}{\Delta\rho g H}$$

SURFACTANT APPLICATION IN A FRACTURED RESERVOIR





“Huff-Puff” Operation – Treat Individual Production Wells

Surfactant Injection to a Production Well

Previous studies:

Cationic surfactants –

Form ion-pair with absorbed oil polar components
(e.g. naphthenic acids -- carboxylates) --- remove from surface.
Aqueous phase then can imbibe spontaneously.

Anionic and nonionic surfactants --

Form a bilayer on surface to make it water-wetting
High adsorption may occur

Recent work with **caustic plus anionic surfactants** --

Change carbonate surface charge to negative – reduce surfactant adsorption losses at pH about 10
Can create very low IFT

New studies -- Opportunites:

Many classes of surfactants NOT yet tried
Little work yet on surfactant **formulations**

DOE STUDY APPROACH -- MAIN TASKS

1) Develop fast screening tools --
   test many surfactants for ability to alter wettability

2) Follow-up wettability studies on promising candidates –
   measure contact angles on carbonate minerals

3) Theoretical study
   -- molecular model of surface/solution energies

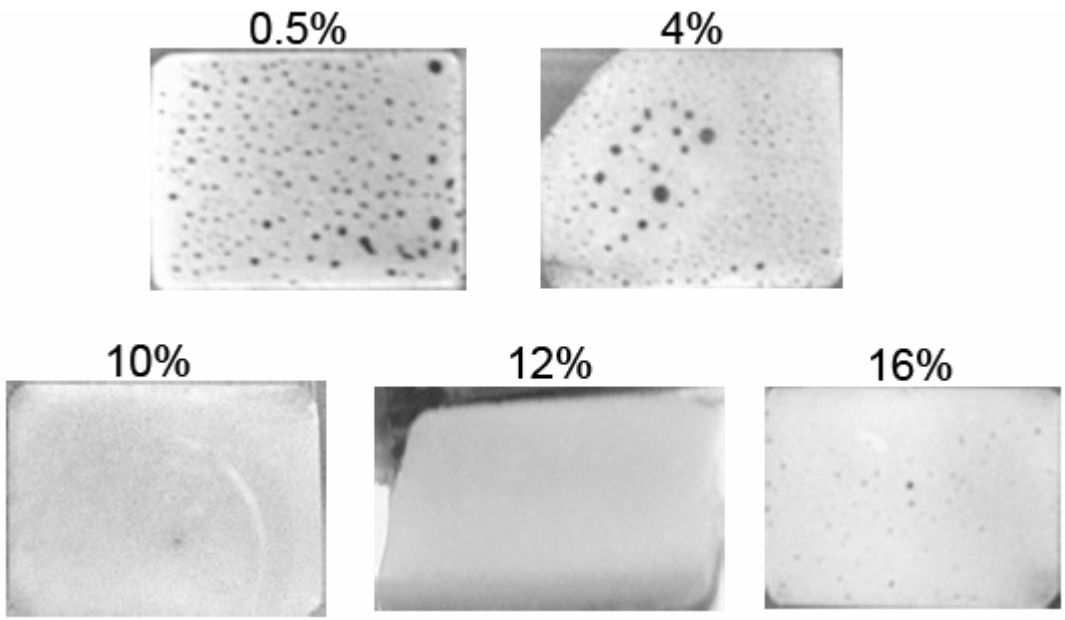
4) Phase Behavior/IFT -- focus on better wettability agents

5) Oil displacement tests from carbonate porous media

SCREENING TESTS FOR SURFACTANT EOR -- CARBONATE RESERVOIRS

EXAMPLE …. Ability to remove crude oil adhered to carbonate surface.

Formulations that remove stain are better candidates.



EXAMPLE …. Oil residue disappears as Salinity increases > 4% for surfactant C.

OTHER IDEAS FOR SCREENING SURFACTANTS

Spreading of solutions:

Treat surface with crude oil or polar organic species so is oil wet
Smear a film of oil on top
Place a small drop of surfactant solution
Solutions that spread and move the oil are better candidates.

“Mini”-imbibition test:

The normal size imbibition test uses 1”x3” cores; test can takes weeks

Alternative would be a small packed column of limestone or dolomite saturated with oil. Faster inflow of aqueous solution means that surfactant solution is better

COMMENTS ON THEORETICAL MODELING

Comparison of surface energies

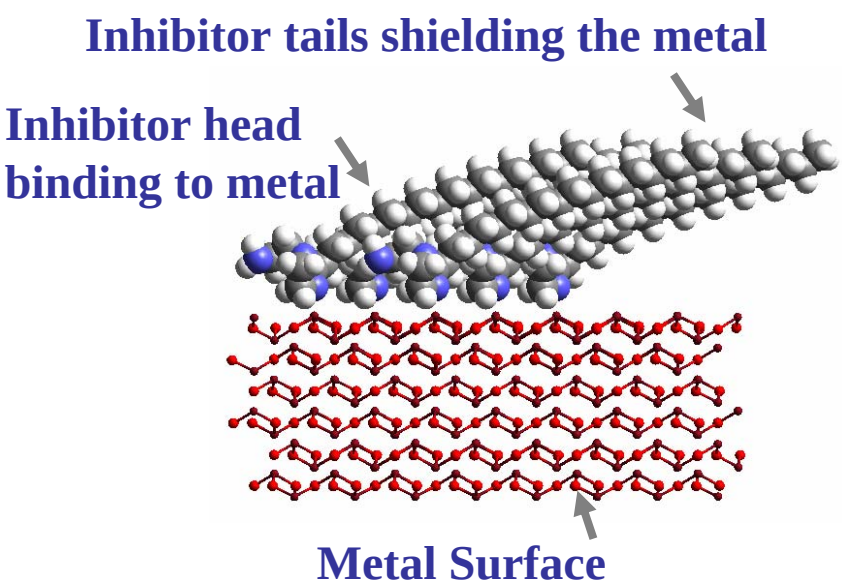
different oil wetting compounds (e.g. naphthenic acids)
different surfactants

Test proposed mechanisms

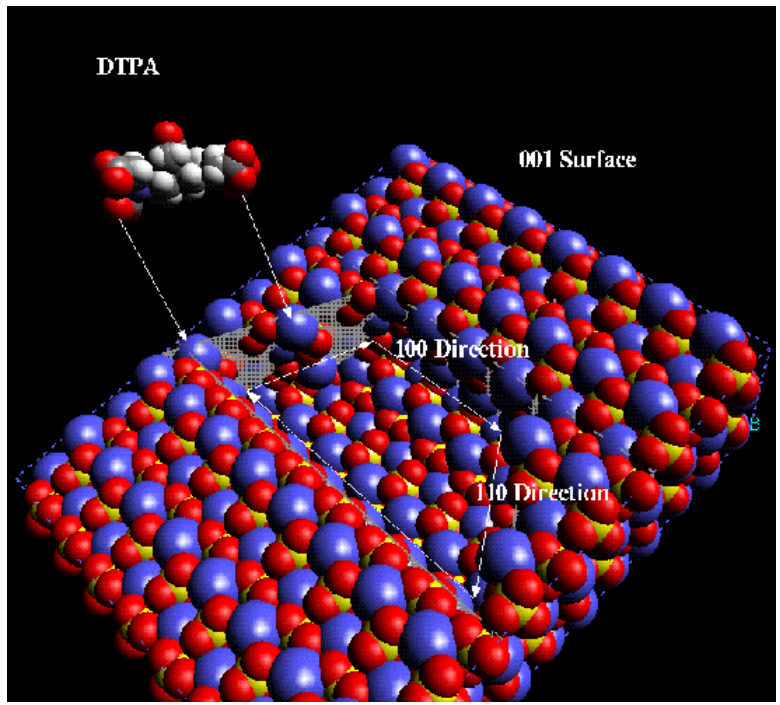
cationic surfactants – complex with naphthenic acids to remove?

Analogous to Previous Caltech Studies -- Oilfield Chemicals

CORROSION INHIBITORS



SCALE DISSOLVERS



Spinning Drop Interfacial Tensiometer

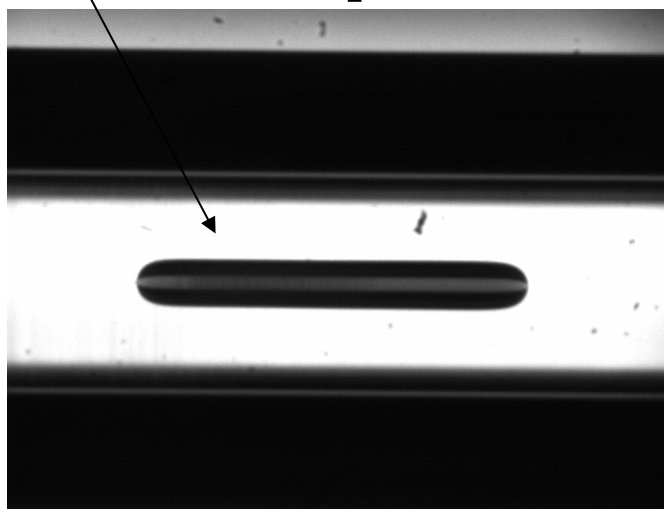
Video Camera

Glass Tube

Control Box
- Rotation speed
- Temperature

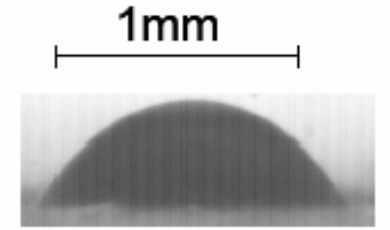
Light Source

Oil drop in tube



Principle of Operation
- Oil drop in aqueous phase is spun at high speed
- Shape of drop can be related to IFT

OTHER SURFACTANT EVALUATION TESTS



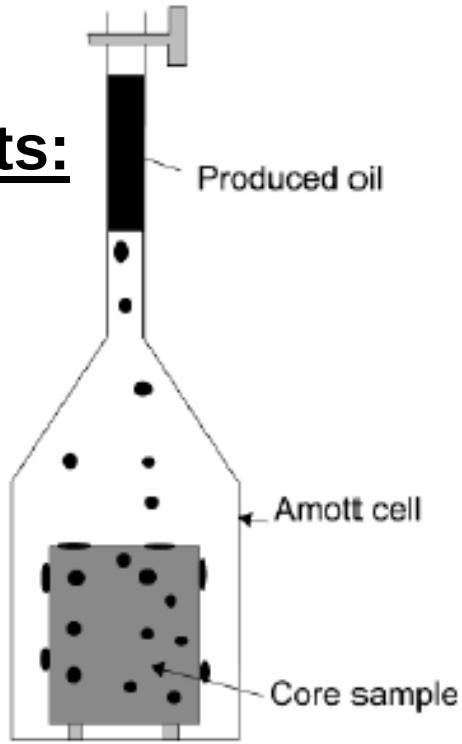
Contact Angle Measurements –

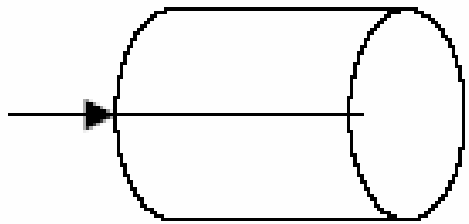
Treated vs. Untreated Surfaces

Crude oils & model compounds

Imbibition Tests:

Different sizes



Coreflood / Oil Displacement:

Fractured cores