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SMART SCAL (SPECIALIZED CORE ANALYSIS) FOR SMART IOR SOLUTIONS

Presented at the National IOR Conference

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Agenda

- **Joining Forces to Recover More – Why?**
- **Comparison of Chemical EOR Methods**
  - **Nanoparticle, Surfactant, Smart Water**
- **Smart SCAL**

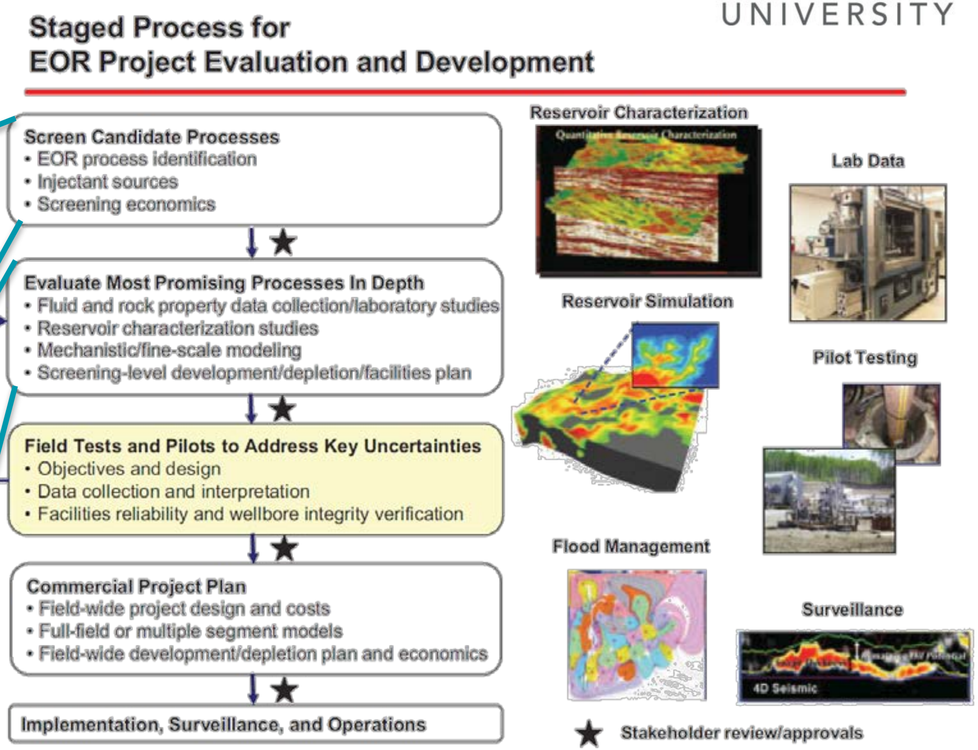
EOR Screening

- **EOR incremental oil recovery is 5-15% at the field scale**

Screen Candidate Processes
- EOR Process Identification
- Injectant sources
- Screening economics

Evaluate Promising EOR Methods
- Fluid & rock property data collection/laboratory studies
- **Reservoir Characterization**
- Mechanistic/fine-scale modeling

- Must consider **sweep efficiency** & **pore scale recovery mechanisms**



Staged Process for EOR Project Evaluation and Development

Screen Candidate Processes
- EOR process identification
- Injectant sources
- Screening economics

Evaluate Most Promising Processes In Depth
- Fluid and rock property data collection/laboratory studies
- Reservoir characterization studies
- Mechanistic/fine-scale modeling
- Screening-level development/depletion/facilities plan

Field Tests and Pilots to Address Key Uncertainties
- Objectives and design
- Data collection and interpretation
- Facilities reliability and wellbore integrity verification

Commercial Project Plan
- Field-wide project design and costs
- Full-field or multiple segment models
- Field-wide development/depletion plan and economics

Implementation, Surveillance, and Operations

★ Stakeholder review/approvals

G. F. Teletzke, R. C. Wattenbarger and J. R. Wilkinson, "Enhanced Oil Recovery Pilot Testing Best Practices," in *SPE International Petroleum Exhibition and Conference*, Aby Dhabi, 2010.

Smart SCAL

- **Determine how our complex, multi-component, multi-phase systems impact reservoir properties:**
  - Understand pore scale mechanisms
  - Design specific EOR processes
  - Reduce cost
  - Improve recovery

- **Systematic, smart, intelligent approach to understanding of fluid-fluid and fluid-rock interactions:**
  - Simple systems
  - Complex systems
  - Consider temperature and pressure

Smart Solutions for IOR

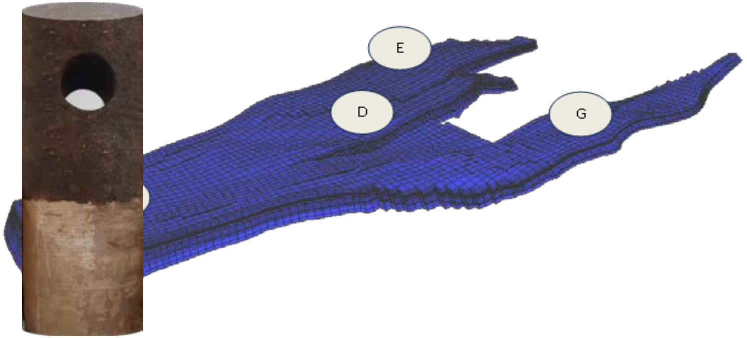
- ☐ **Smart Water**
  - ✓ Low salinity water injection
  - ✓ Selected ion water content injection

- ☐ **Chemical Additives**
  - ✓ Nanoparticles
  - ✓ Surfactants

SCAL in Scale

Core/Field Scale Modelling:

- Resolution in cubic meters
- Permeability
- Relative permeability
- Interfacial tension
- Hysteresis
- Capillary pressure
- Depositional models



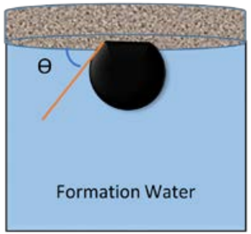
Properties

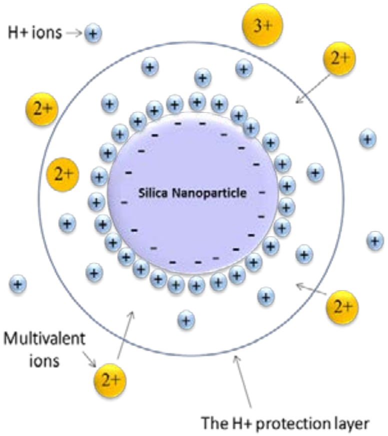
1. Fluid-Fluid Interaction

- ✓ **IFT reduction**
- ✓ Emulsion formation
- ✓ Capillary Pressure

2. Fluid-Rock Interaction

- ✓ **Wettability Alteration**
- ✓ Relative Permeability
- ✓ Adsorption/desorption/ dissolution





Joining & Opposing Molecular Forces:

- ✓ Electrostatic
- ✓ Van der Waals
- ✓ Hydrophobic forces
- ✓ Steric effect
- ✓ Bridging
- ✓ Hydration force

Joining & Opposing Molecular Forces

- Electrostatic
- Van der Waals
- Hydrophobic forces
- Steric effect
- Bridging
- Hydration force

Electrical Double Layer

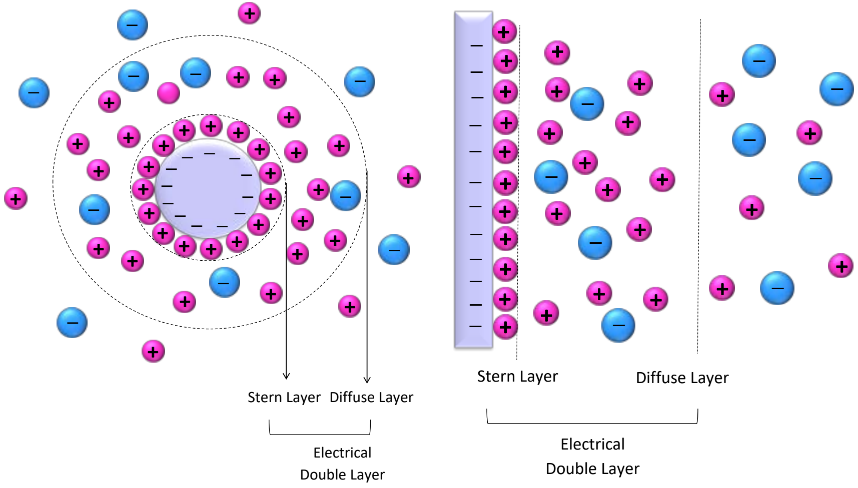


Figure 1a: Ion distribution around charged surface [after 1]

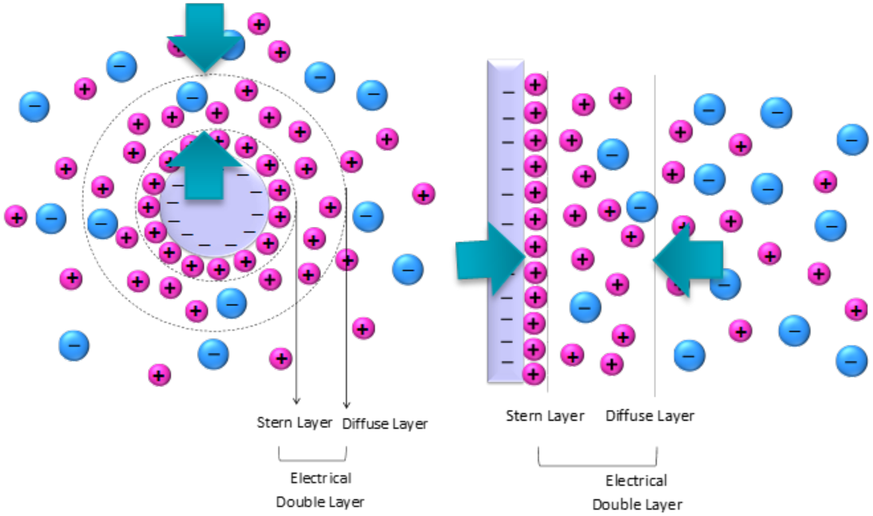
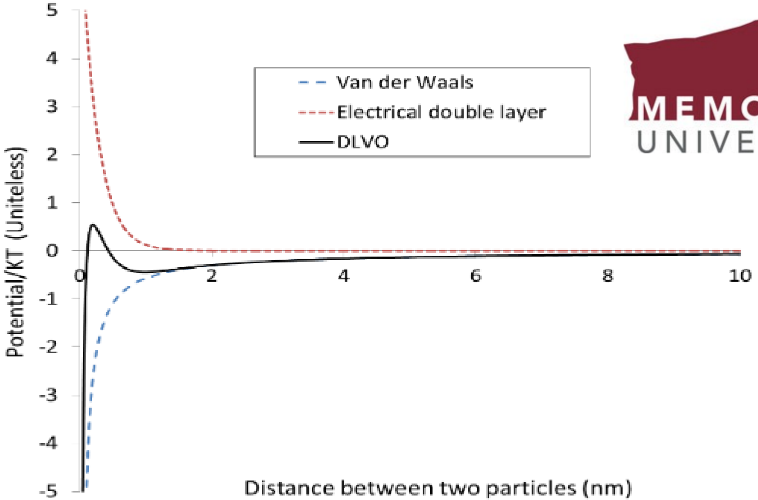


Figure 1b: The effect of increasing salinity of the ion distribution around charged surface [after 1]

Electrostatic and Van der Waals Forces (DLVO Theory)



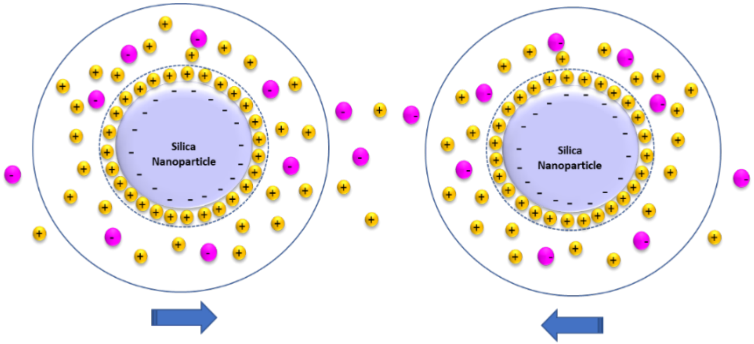
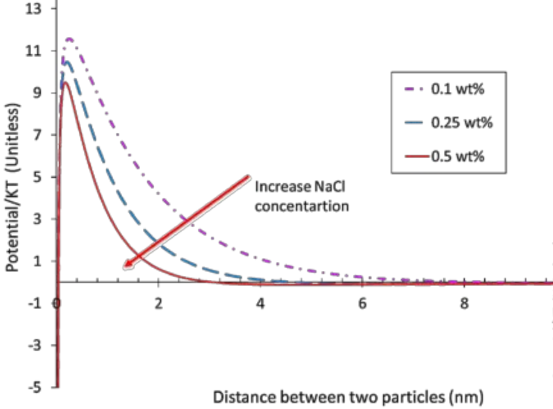
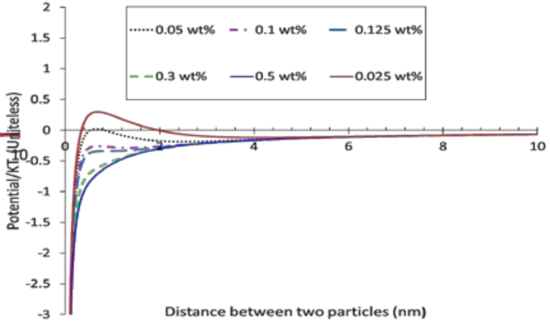


Figure 2: Increasing the ionic strength (salt concentration) & multivalent ions compresses the EDL and reduces electrostatic forces. The impact of multivalent ions are much more than monovalent ions [2]



Increase Monovalent ions

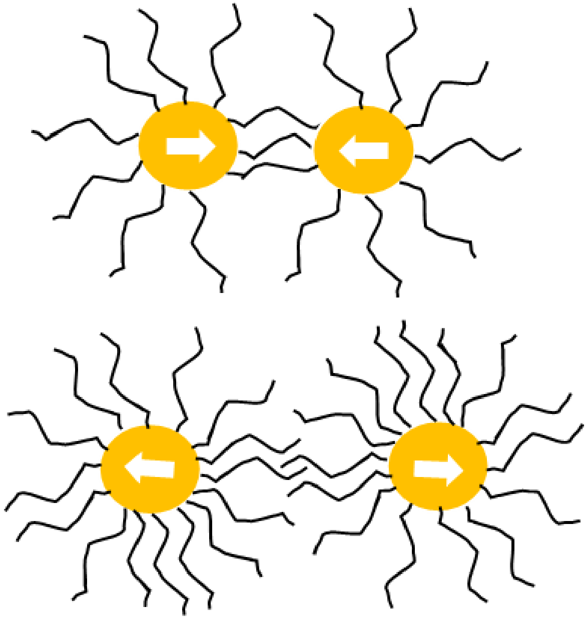


Increase Multivalent ions

Steric And Bridging Effect

- Each atom within a molecule can only occupy a limited space. When atoms become close together, the energy of system is increase due to overlapping electron clouds [3]. Increase in the energy of system when to atoms approach together is known as steric repulsion or steric hindrance.

- Bridging between particles particularly under conditions where particles are not totally coated by the polymeric species. If particles are already fully covered with polymers, bridging can take place only if there is either detachment of some portion of the polymer already on a particle to provide sites for attachment of polymer fractions adsorbed on other particles or polymer–polymer bonding itself [4].



Bridging

Joining forces

Steric effect

Opposing forces

Figure 3: Schematic diagram of bridging and steric effect [after 4]

Other Forces

Hydration force: When charged surfaces are being contacted with water, the surfaces induce some changes in adjoining layers of fluid. The properties of this thin layer (known as hydration layer) differ from the bulk. Overlap of hydration layers in two nanoparticles approaching together causes some interaction which called hydration force [5]. The hydration force is a strong short-range repulsive force that acts between polar surfaces separated by a thin layer of water, which decays quasi-exponentially with decay lengths of about 1 nm [6].

Hydrophobic interaction: Hydrophobic surfaces have a tendency to clump up together when placing in the polar solvent (typically water). This force can exist naturally or be induced by the adsorbed hydrophobic species [7]. Hydrophobic interaction gives an opportunity to hydrophobic surfaces to minimize their contact with water [8].

Major Components In Three Phases

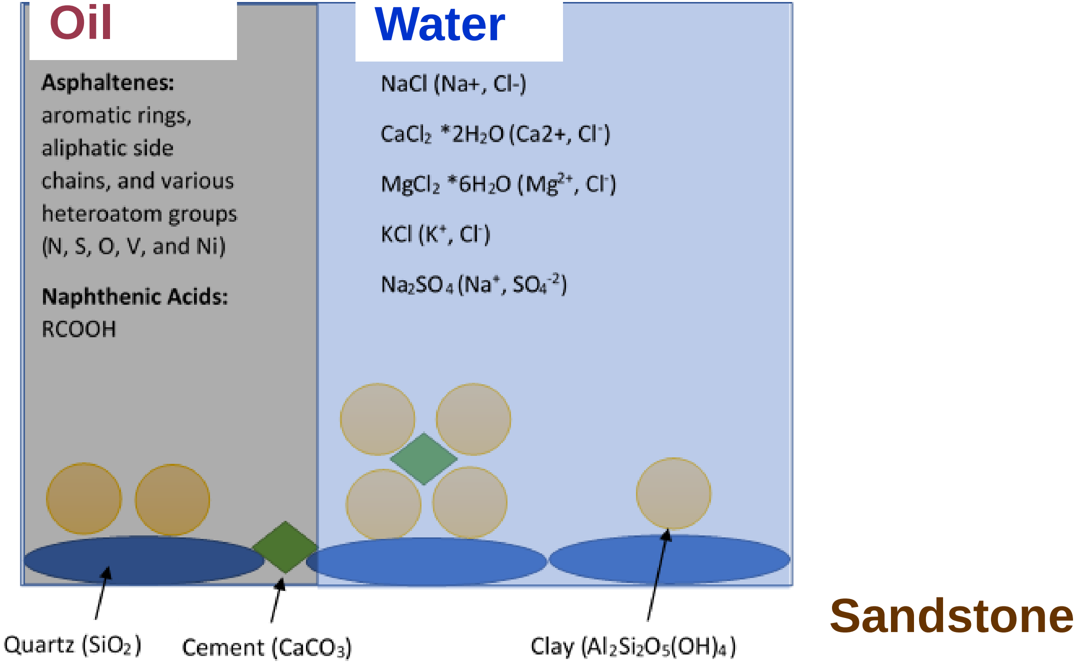


Figure 4: Major components in the three phases (oil-water-rock) [45]

IFT Reduction

- **Smart Water**
- **Surfactants**
- **Nanopraticle Fluids**

IFT Reduction – Field Scale

- IFT reduction is related to the capillary number in the field scale; capillary number is defined as a ratio between viscous forces to capillary forces;
- **Most researchers proposed that critical capillary number can be achieved in ultralow IFT values (0.1 to 0.01 mN/m) [32-33]**

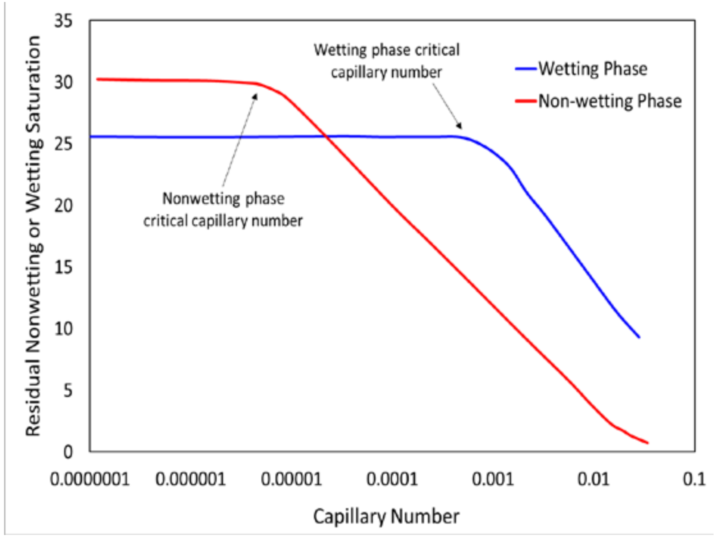


Figure 10: Schematic graph of capillary number effect on oil residual saturation [34]

1. **Smart water:** IFT reduction cannot affect residual oil because the concentration of surface active materials is not sufficient.

2. **Nanoparticles:** Due to the size of nanoparticles, the number of adsorbed materials at oil-water interface is not sufficient to reduce IFT significantly.

3. **Surfactants:** Surfactants can reduce IFT value behind the critical capillary number.

IFT Reduction

Smart Water

Surface Adsorption:

1. Desorbed organic materials from the clay surfaces [8]
2. In situ surfactant produced by reacting the organic acids (saponifiable components) in crude oil [9]
3. Natural surfactants (including asphaltene and resin) [12]

IFT is inversely proportional to natural surfactant concentration

Limiting Parameters:
Salinity, pH and oil composition

Nanoparticles

Surface Adsorption:
Nanoparticles at oil-water interface [10]

IFT is inversely proportional to nanoparticle concentration

Limiting Parameters:
Charge, size, and concentration of the nanoparticles

Surfactants

Surface Adsorption:
Surfactants at oil-water interface [11]

IFT is inversely proportional to surfactant concentration

Limiting Parameters:
Critical Micelle Concentration (CMC) and salinity

IFT Reduction – Smart Water

There is no general trend between IFT and salinity:

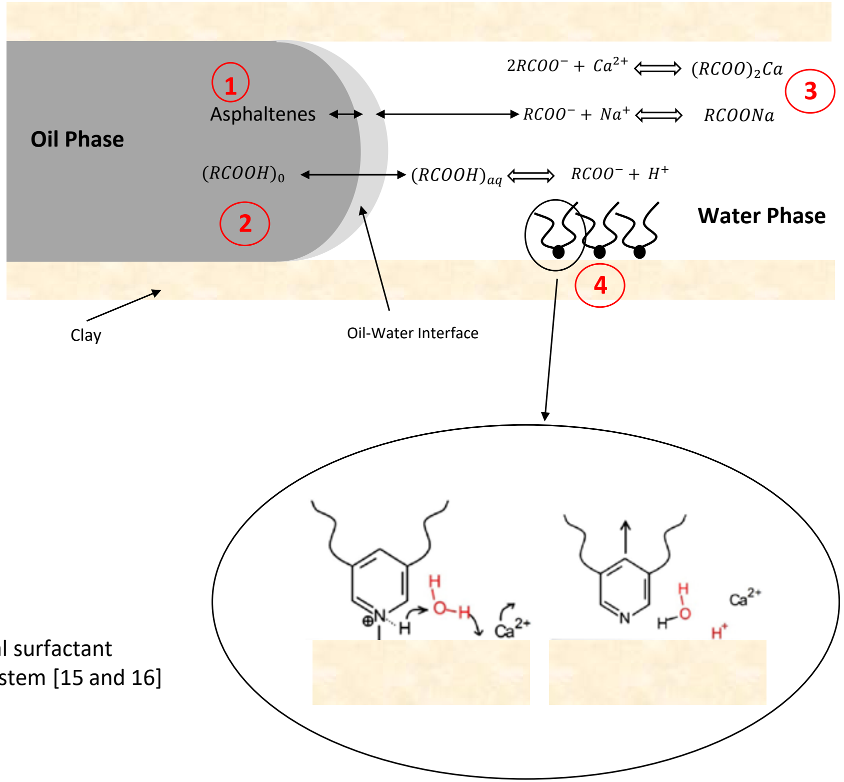
- ✓ IFT decreased with adding the salt concentration. Because, due to the electrostatic forces, the addition of salts into solution alters the distribution of natural surfactants (including asphaltene and resin) at the interface [12].
- ✓ There is an optimum salinity for different salts that minimum IFT can be achieved [13].
- ✓ Salt concentration has no significant effect the IFT because most of the interfacial active substance might be oil-soluble and salt concentrations cannot change their distribution [14].

Effective Parameters:

1. Presence of natural surface active components in the crude oil (Naphthenic acid, asphaltenes)
2. The ability of salts to release surfactants from clay surface (compressed electrical double alyer)
3. Presence of sufficient basic solution (pH greater than 9) to start saponification
4. The ability of salts to alter the distribution of natural surfactants at the interface

IFT Reduction – Smart Water

Molecular Level Review:



$2RCOO^- + Ca^{2+} \Longleftrightarrow (RCOO)_2Ca$

Asphaltenes $\longleftrightarrow$ $\longleftrightarrow RCOO^- + Na^+ \Longleftrightarrow RCOONa$

$(RCOOH)_0 \longleftrightarrow (RCOOH)_{aq} \Longleftrightarrow RCOO^- + H^+$

Figure 4: Mechanism of natural surfactant generation in oil-water-clay system [15 and 16]

IFT Reduction – Smart Water

Increasing the pH can:

- **Increase the surface active behavior of asphaltenes** [17],
- **Is favorable for dissociation of naphthenic acids** [18],
- **Increases the in-situ sapnification** [19].

(Relatively high pH (greater than 9, compared to reservoir pH range of 5-7 [21]) is required for the mentioned phenomena to become dominant [19 and 20]. Hence, the role of pH at IFT reduction due to the three mentioned mechanism is unlikely to be significant in the practical applications.)

- **The pH increases can increase the detachment of organic materials from the rock surface**.

(Since the pH increase can occur locally in the vicinity of the clay surface due to the replacement of adsorbed Ca2+ ions by H+, this phenomena can happened in the broad ranges of pH. Its effectiveness depends on the cation exchange capacity of clay (ontmorillonite > illite > mica > kaolinite) [22].)

IFT Reduction – Smart Water

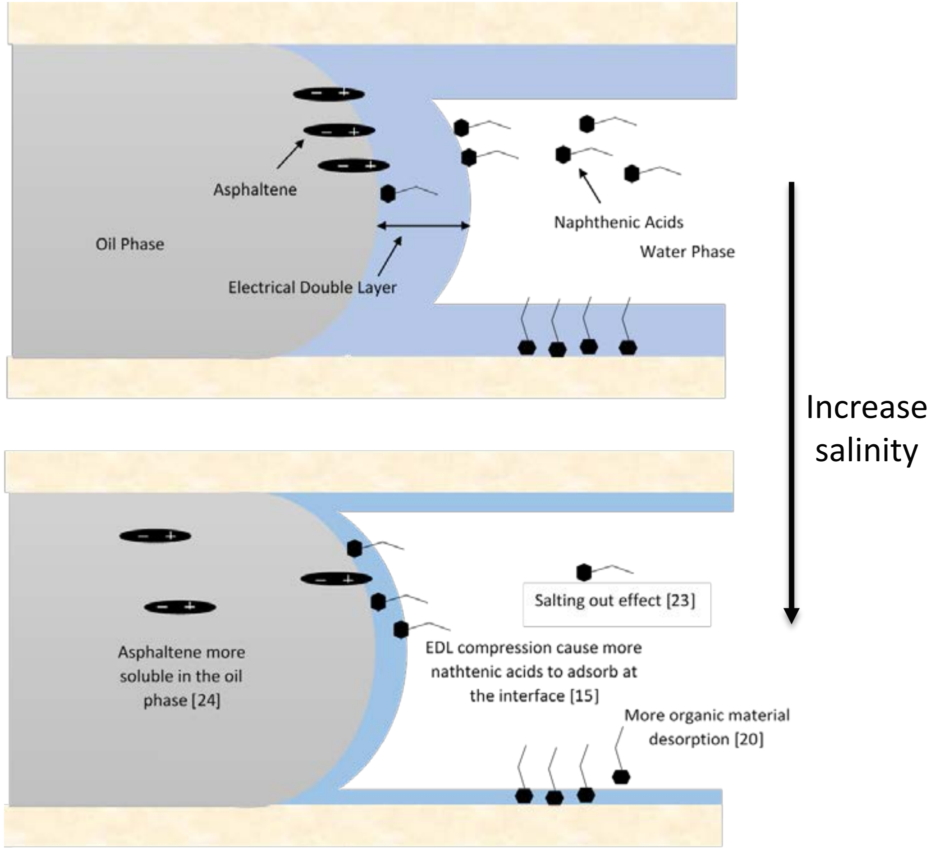


Figure 5: Salinity effect on the IFT reduction

IFT Reduction – Surfactants

Lab scale and molecular scale monitoring:

Surfactants can reduce the IFT value with the following trend:

IFT reduces by Increasing surfactant concentration up to the critical micelle concentration (CMC). Adding surfactant behind CMC does not have significant effect on the IFT [23].

Increase the salinity reduces the IFT value due to the decrease in the the electrostatic repulsion between the interface and surfactant ions, consequently increase the adsorption of surfactants on the interface [15]

Effective Parameters:

1. Concentration of surfactants in the bulk solution
2. Salinity of the bulk solution

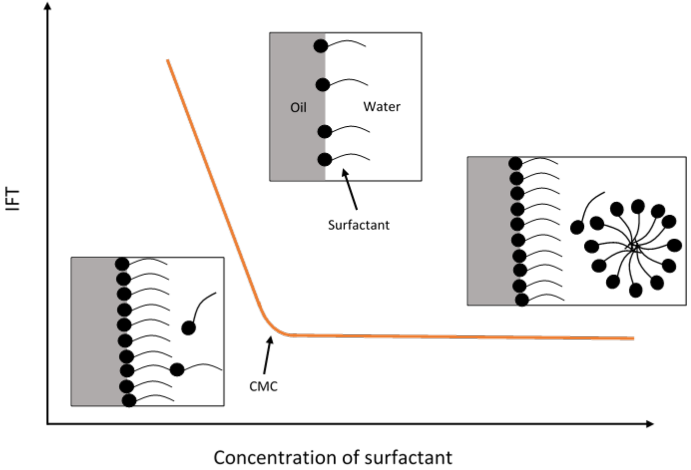


Figure 9: Schematic effect of surfactants on the IFT value [31]

IFT Reduction – Nanoparticle Fluids

Lab Scale Monitoring:

1. Without Surfactant Case:

Effect of the nanoparticles on the IFT is not conclusive: Some researchers have shown that nanoparticles can reduce the oil-water interfacial tension [25-26], but opposing results can also be found in the literature [27-29].

2. With Surfactant:

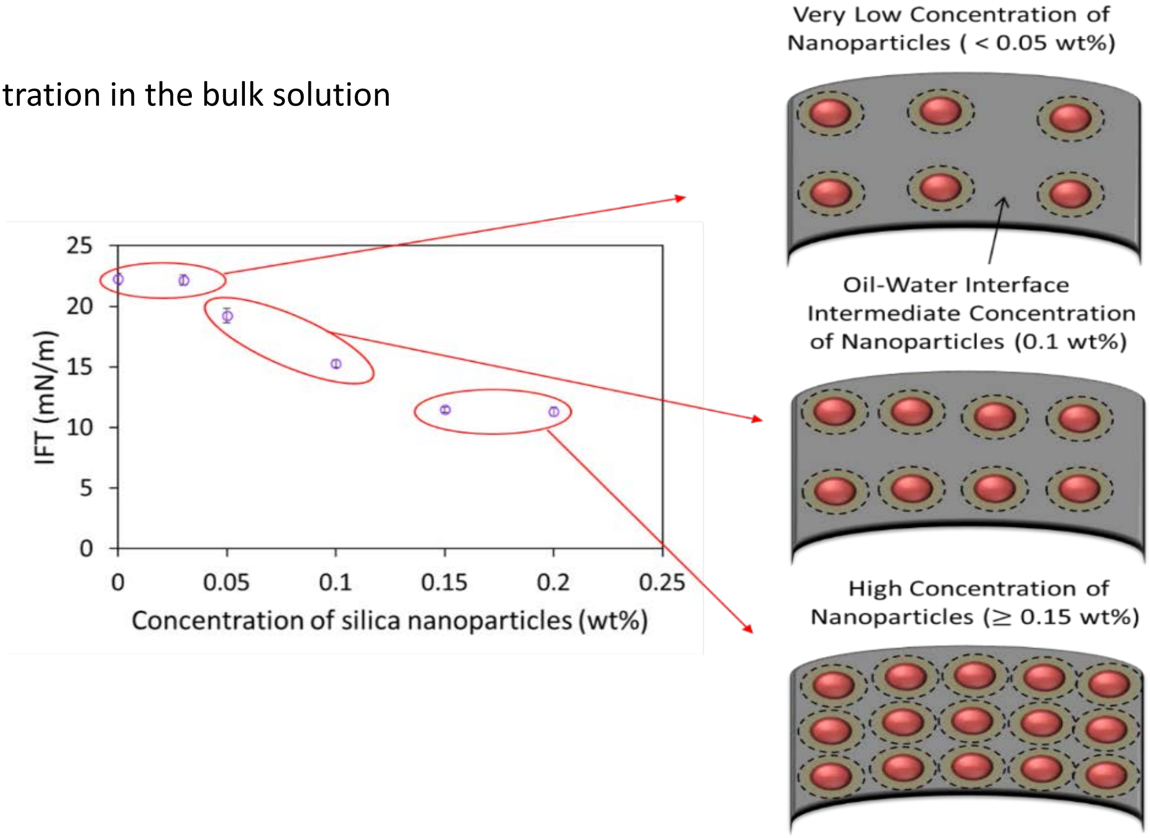
By increasing the concentration of surfactant in the solution, the adsorption of surfactant as individual ions changes the wettability of particles and provides a partially hydrophobic and a partially hydrophilic character to the surface, thus nanoparticles can be adsorbed at the interface and reduce the oil-water interfacial tension [27].

Effective Parameters:

1. Concentration of nanoparticles in the bulk solution
2. Size of nanoparticles
3. Charge of nanoparticles (pH depended)
4. Salinity of the bulk solution

IFT Reduction – Nanoparticle Fluids

Nano Scale Monitoring:
Effect of the nanoparticles 'concentration in the bulk solution



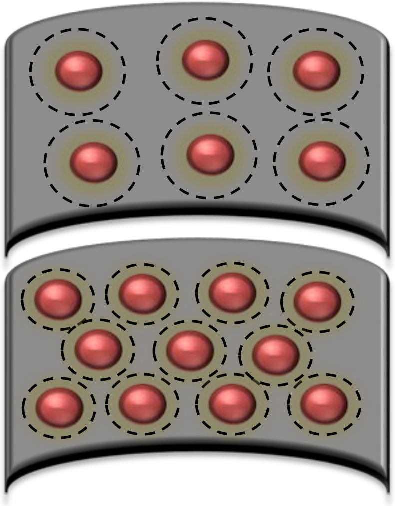
Very Low Concentration of Nanoparticles (< 0.05 wt%)

Oil-Water Interface

Intermediate Concentration of Nanoparticles (0.1 wt%)

High Concentration of Nanoparticles (≥ 0.15 wt%)

IFT Reduction – Nanoparticle Fluids



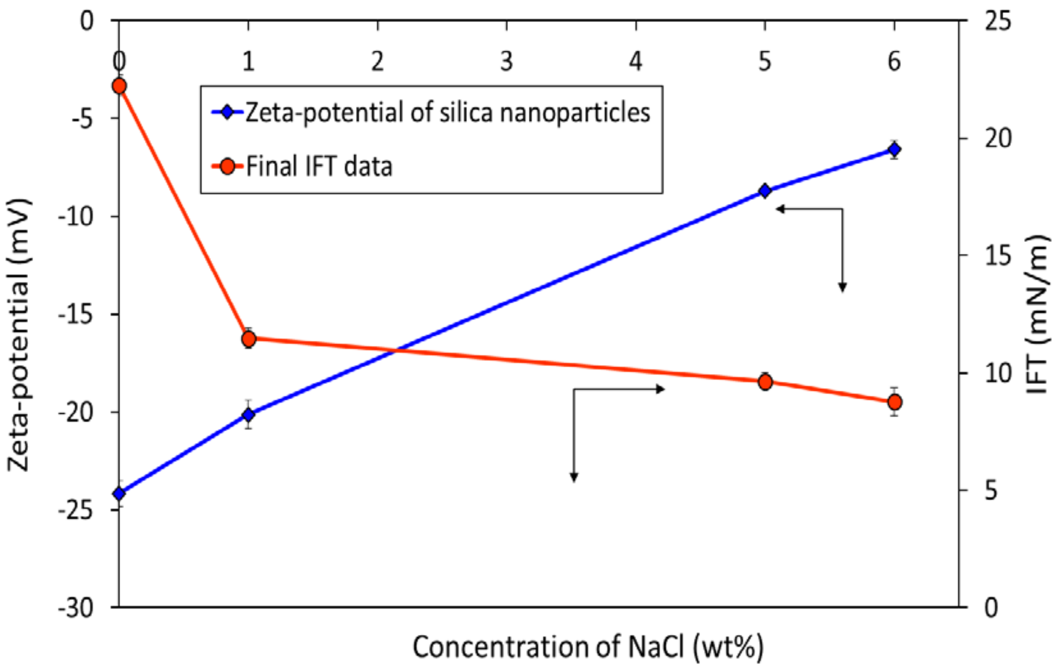
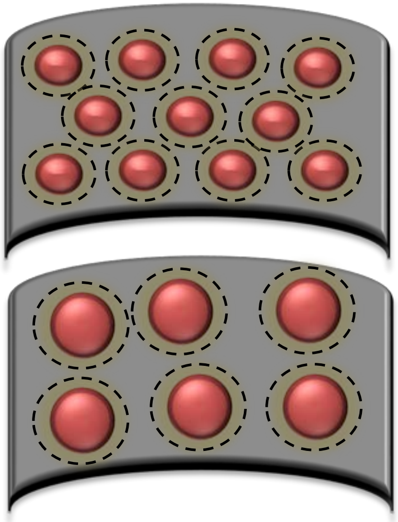


Figure 7: Zeta-potential and final IFT value for 0.15 wt% silica nanoparticles in different concentrations of NaCl solution [10]

IFT Reduction – Nanoparticle Fluids



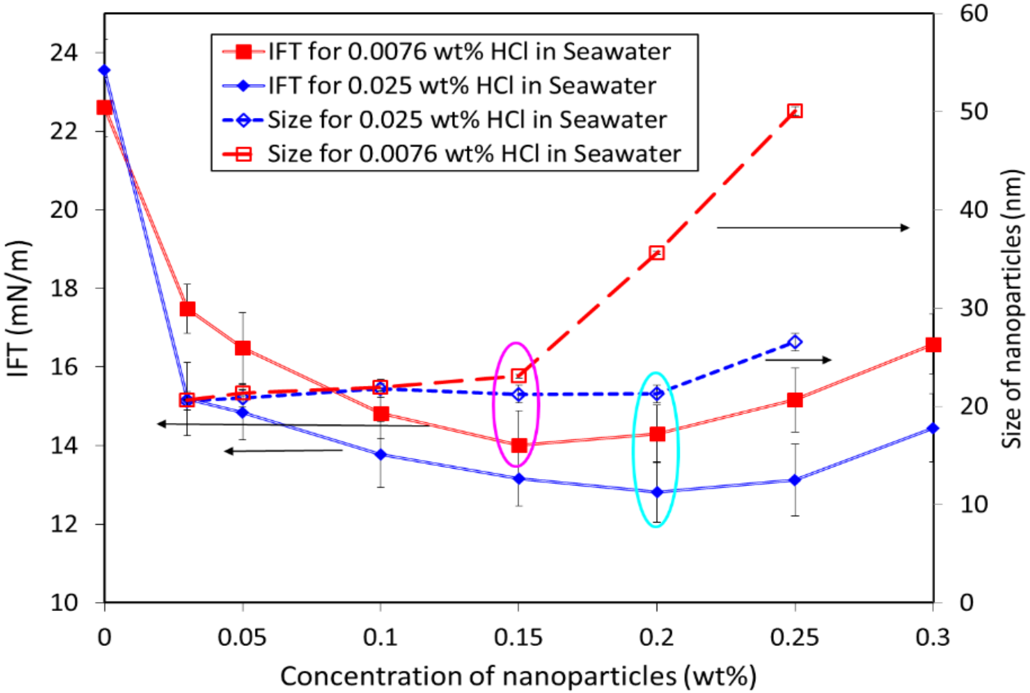


Figure 8: Oil-water interfacial tension and hydrodynamic size of silica nanoparticles in seawater in different concentrations of nanoparticles [10]

Wettability Alteration

- **Nanoparticle Fluids**

Wettability Alteration

Smart Water

Nanoparticles

Surfactants

1. **Lab scale experiments** for all cases show wettability alteration toward more water-wet condition, which might be favorable for oil production [34-41].
2. Competition between disjoining pressure, capillary pressure, and naphthenic acids removal from the rock surface defines the ultimate wettability of the reservoir rock after smart IOR.
3. Smart water alters disjoining pressure by altering electrostatic repulsion force [35] and Naphthenic acids removal by ion exchange mechanism [35]
4. nanoparticles alters disjoining pressure by structural disjoining pressure at wedge-film [36]
5. Surfactants (micellar solutions) can alter the rock wettability by naphthenic acids removal [40] and structural disjoining pressure [41]

Wettability – Smart Water

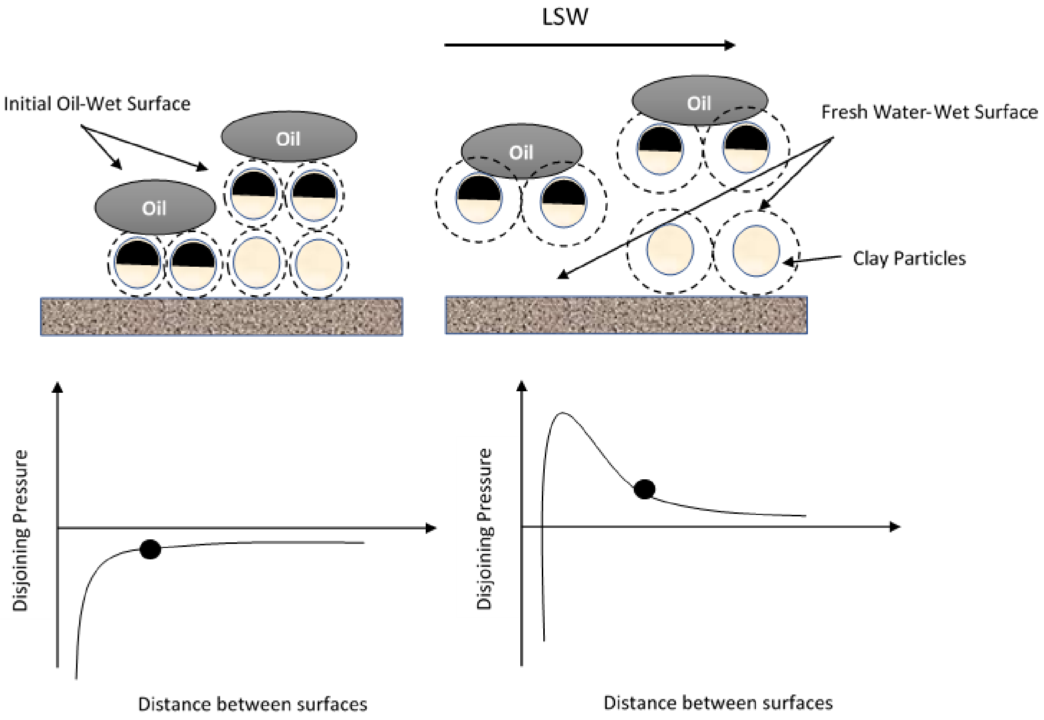


Figure 11 :Schematic diagram of removing mixed-wet particles [37]

1. Removing mixed-wet particles [37]
2. Change in disjoining pressure by expanding electrical double layer (connate water required) [35]
3. Naphthenic acids removal by ion exchange mechanism [35] (Similar mechanism as discussed in the IFT section)

Wettability – Smart Water

Change in disjoining pressure by expanding electrical double layer (connate water required)

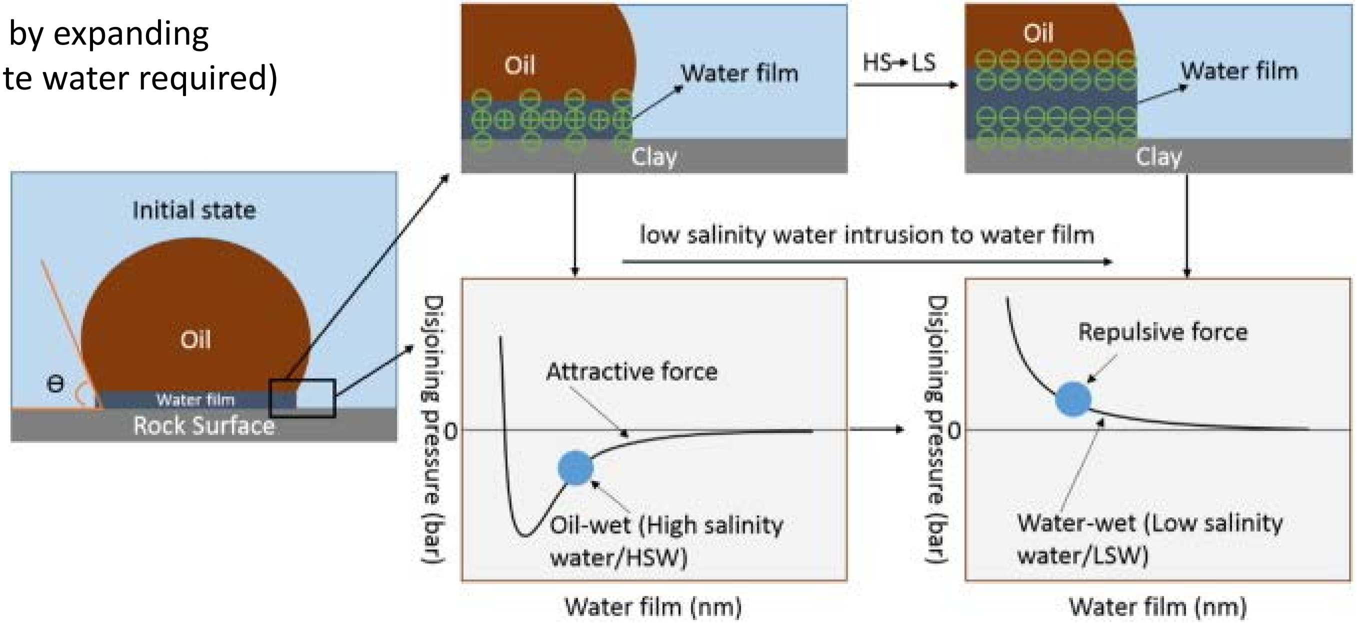


Figure 12. Scheme of the interaction of Crude Oil/Brine/Rock (COBR) system with the presence of either high salinity water or low salinity water [38].

Wettability – Nanoparticle Fluids

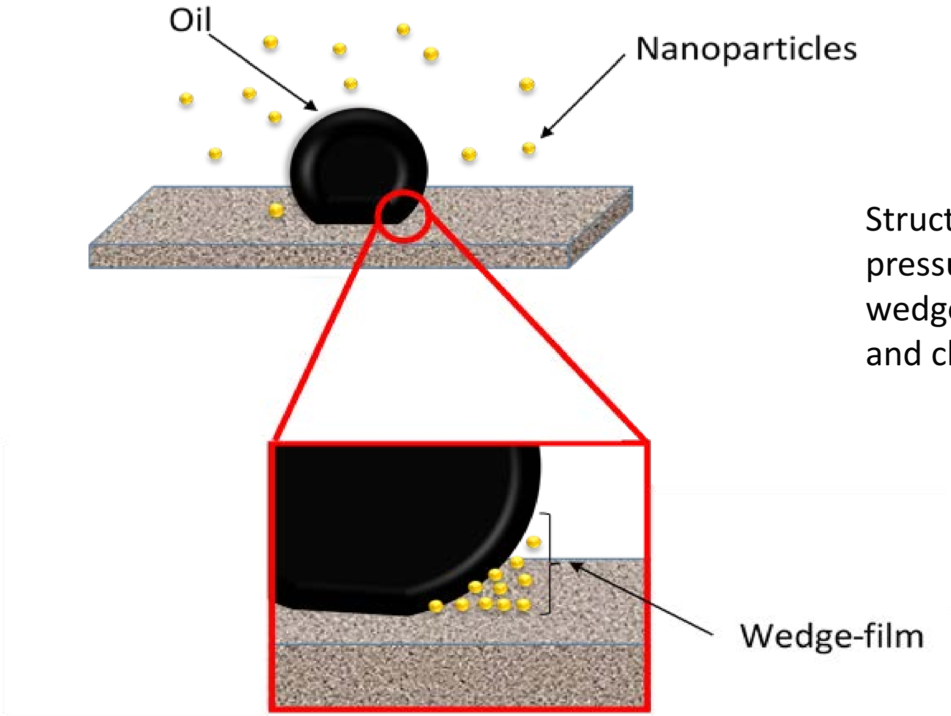


Figure 13: nanoparticle assembling is wedge film causes to structural disjointing pressure [39]

Structural disjointing pressure at wedge-film: Excess pressure due to accumulation of nanoparticles in the wedge-film causes to overcome the Van der Waals forces and change the wettability

Wettability – Nanoparticle Fluids

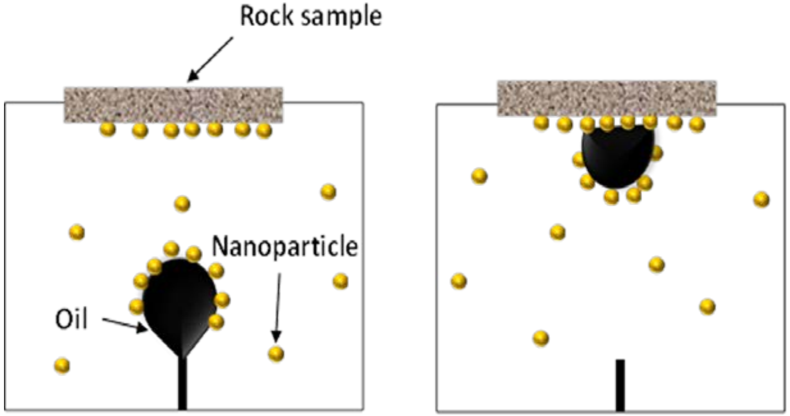


Figure 14a: Conventional Contact Angle Measurements

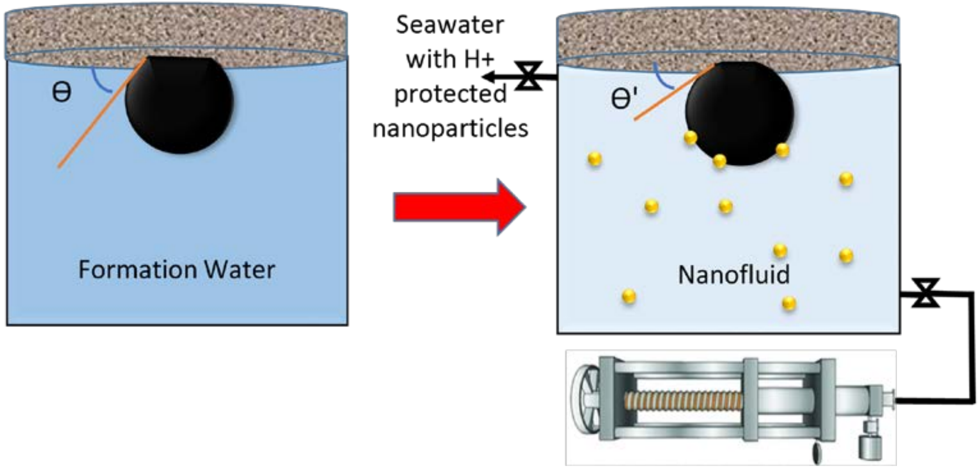


Figure 14a: Contact Angle Measurements using the Displacement Method

Wettability – Nanoparticle Fluids

Water-wet conditions (original)

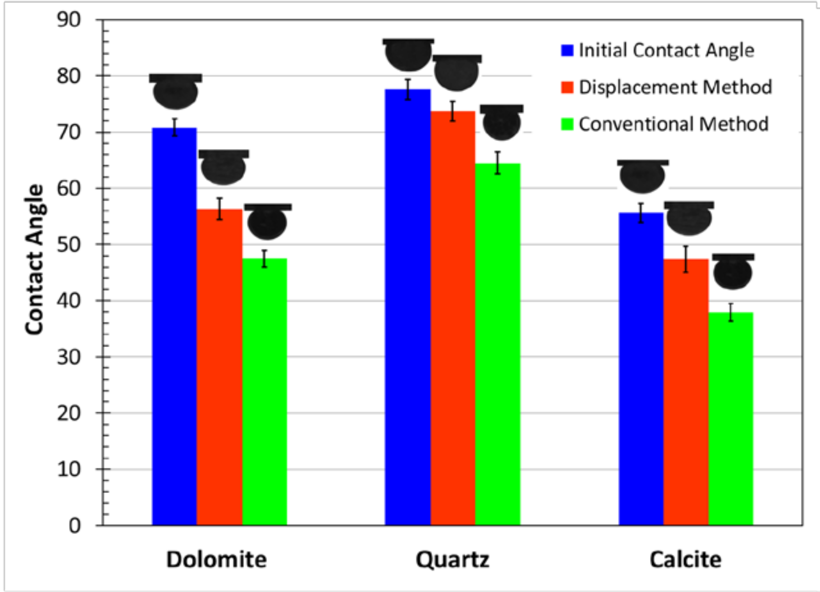


Fig. 15a: Contact θ measurements in simple (silica NPs in NaCl brine, n-decane, mineral) water-wet conditions

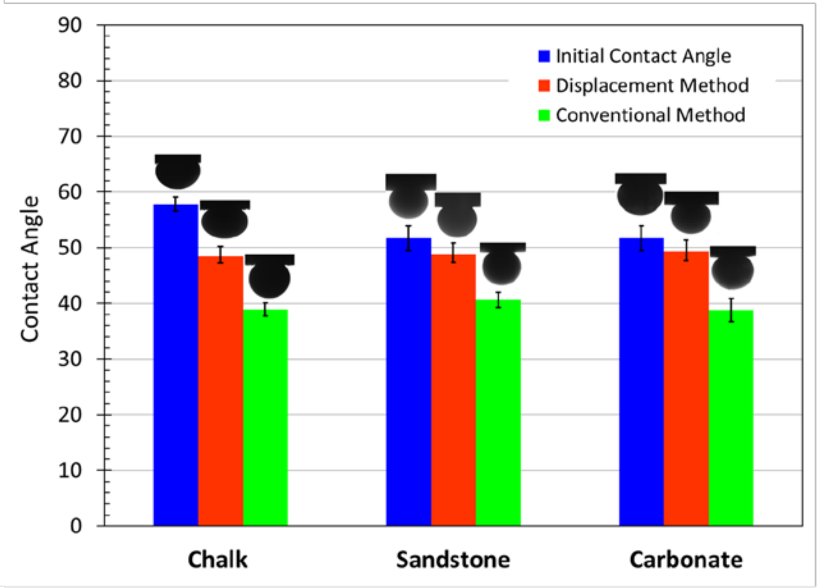


Fig. 15b: Contact θ measurements in complex (H+ protected silica NPs in seawater, 35°API crude oil, reservoir rock) water-wet conditions

Wettability – Nanoparticle Fluids

Oil-wet conditions (after 4 weeks of aging)

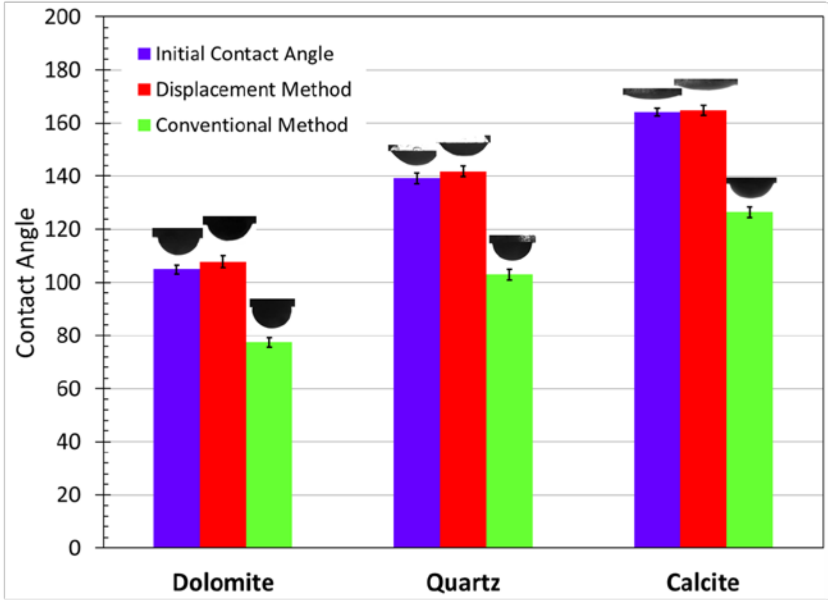


Fig. 16a: Contact θ measurements in simple (silica NPs in NaCl brine, n-decane, mineral) oil-wet conditions

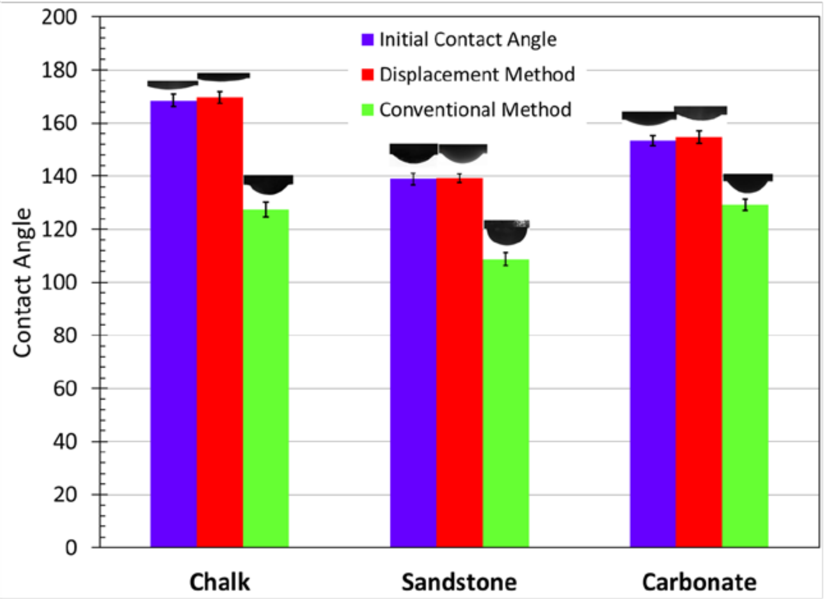


Fig. 16b: Contact θ measurements in complex (H+ protected silica NPs in seawater, 35°API crude oil, reservoir rock) oil-wet conditions

Conclusions

- **Smart Water makes sense especially for the offshore:**
  - minimal OPEX for materials/chemicals and supply is unlimited (seawater)
- **Smart SCAL includes determining how our complex, multi-component, multi-phase systems impact reservoir properties:**
  - Understand pore scale mechanisms
  - Design specific EOR processes
  - Reduce cost
  - Improve recovery
- **Systematic, smart, intelligent approach to understanding of fluid-fluid and fluid-rock interactions:**
  - Simple systems
  - Complex systems
  - Consider temperature and pressure

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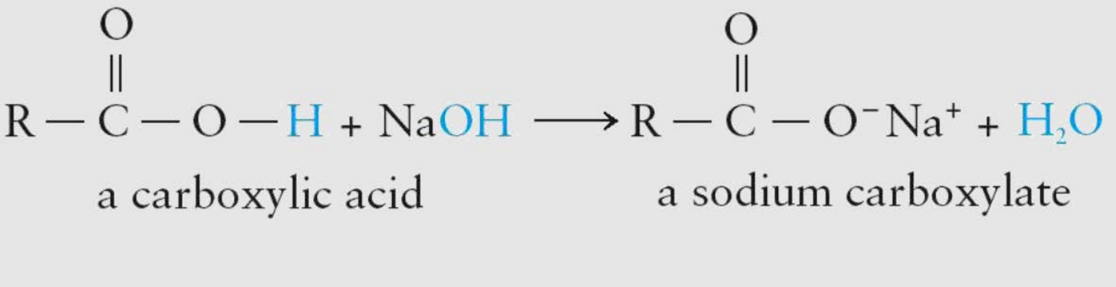
Saponification



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{-}Na^{+} + H_2O$$

a carboxylic acid

a sodium carboxylate

Carboxylic acid only dissacociates in the presence of basic solutions w presence of OH
Sodium carboxylare acts as anionic surfactant

Or with Ca2+ from clays/cements