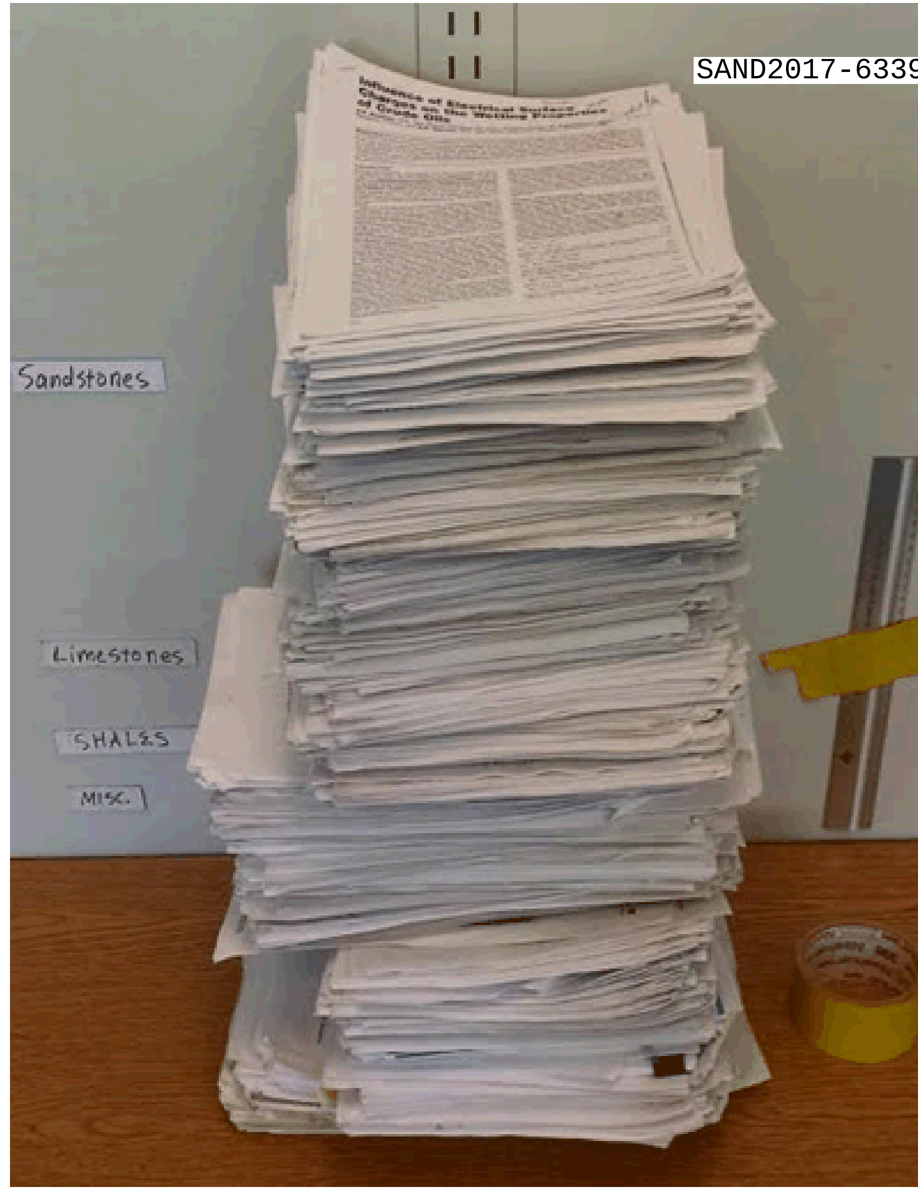
SAND2017-6339PE

Review of Low Salinity Recovery Mechanisms

Pat Brady, Senior Scientist, Sandia National Laboratories, Albuquerque, New Mexico, USA

5th TU Delft Summer School on Wettability and Low Salinity Waterflooding, Department of Geosciences and Engineering, Delft, The Netherlands, July 3-7, 2017.



12” ruler for scale

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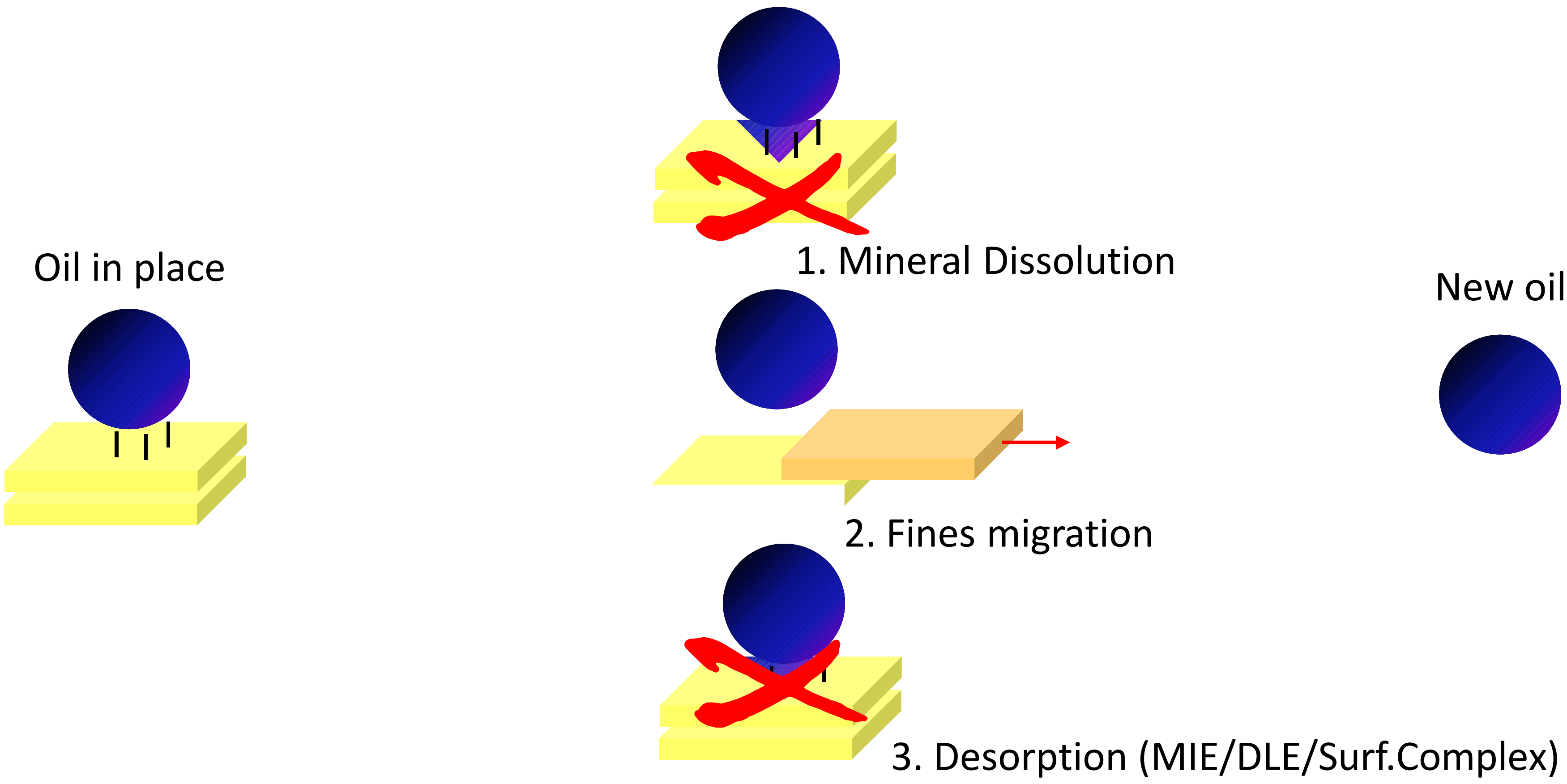
Waterflood chemical effects



In 2012 ...

Table 5. Proposed Low Salinity Mechanisms

Wettability Alteration	Webb et al. 2006, Patil et al. 2008, Berg et al. 2009, Vledder et al. 2010, Ashraf et al. 2010, Chen et al. 2010, Emadi and Sohrabi, 2013, Mahani et al. 2013, Romero et al. 2013, Al-Shalabi et al. 2014, Aghaeifar et al. 2015, Yang et al. 2015
Surface reactions/MIE	Lager et al. 2006, Austad et al. 2010, Sorbie and Collins, 2010, RezaeiDoust et al. 2011, RezaeiDoust et al. 2010, Austad et al. 2013, Brady et al. 2012, Fjelde et al. 2012, Brady et al. 2015
Fines migration	Tang and Morrow 1999, Pu et al. 2010, Fogden et al. 2011, Zeinijahromi et al. 2013, Hamouda and Valderhaug, 2014
IFT	McGwire et al. 2005, Alotaibi and Nasr-El-Din, 2010, Alvarado et al. 2014, Moeini et al. 2014
Double layer expansion	Ligthelm et al. 2009, Lee et al. 2010, Suijkerbuijk et al. 2013
Mineral Dissolution	Hiorth et al. 2010, Pu et al. 2010b
Salting in	RezaeiDoust et al. 2009
Micro-dispersions	Emadi and Sohrabi, 2013
Asperites	Brady et al 2015, Schmatz et al 2015

+ Osmosis (Sandengen, 2015)
+ Microdispersions (Alvarado, Sohrabi)
+ Oil film rigidity alteration (Ayirala et al).

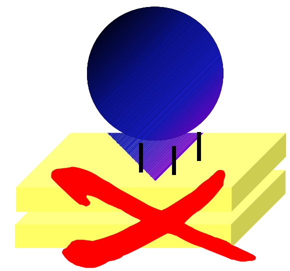
From: Thyne, Geoffrey. "Wettability Alteration in Reservoirs: How it Applies to Alaskan Oil Production." In *SPE Western Regional Meeting*. Society of Petroleum Engineers, 2016.

Mineral Dissolution
Osmosis
Multi-component Ion Exchange (MIE)
Surface Complexation
Double Layer Expansion
Fines Migration
IFT/Oil film/Micro-dispersions

When they happen: Why they happen: How hard they are to predict

Seconds | Minutes | Years

More dilute waterfloods dissolve parts of the host mineral.

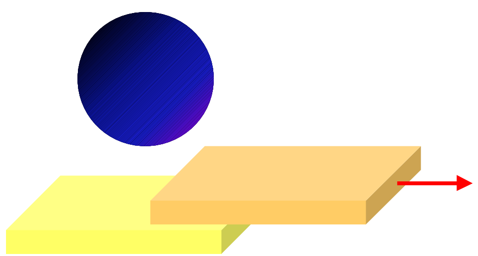


Mineral Dissolution

Sulfates ← Carbonates → Silicates

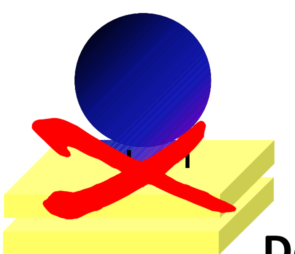
Easy

Changes in waterflood chemistry reverse the bonds of fines-reservoir adhesion.



Fines migration

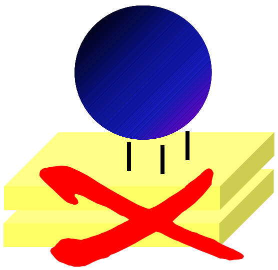
Hard



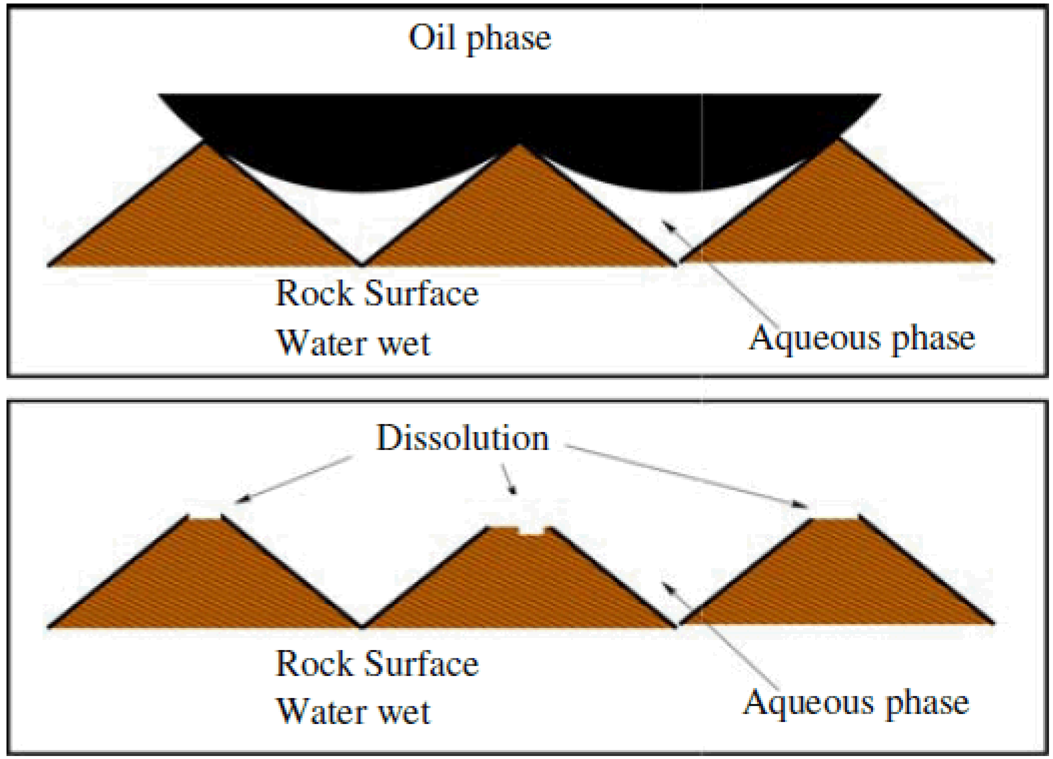
Desorption

Changes in waterflood chemistry reverse the bonds of oil-reservoir adhesion.

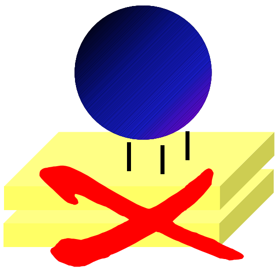
"Better"



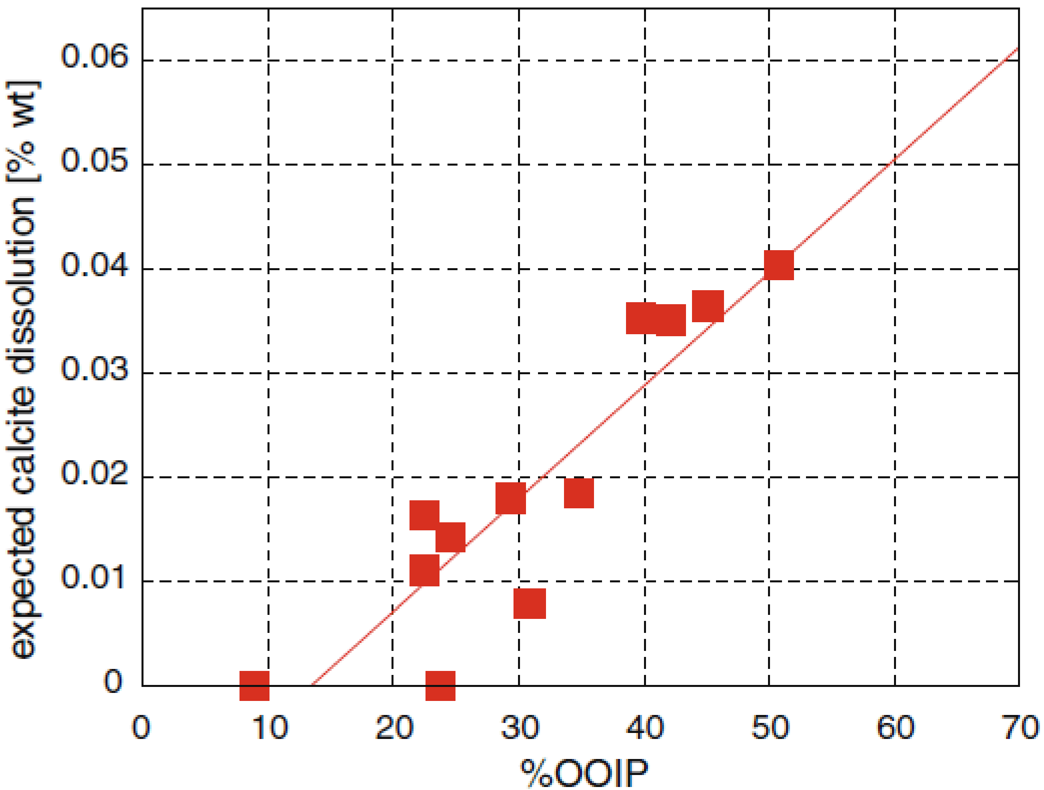
Mineral Dissolution



From: Hiorth, A., L. M. Cathles, and M. V. Madland. "The impact of pore water chemistry on carbonate surface charge and oil wettability." *Transport in porous media* 85, no. 1 (2010): 1-21.

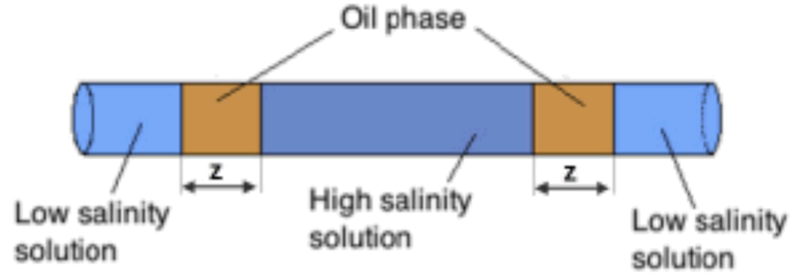


Mineral Dissolution

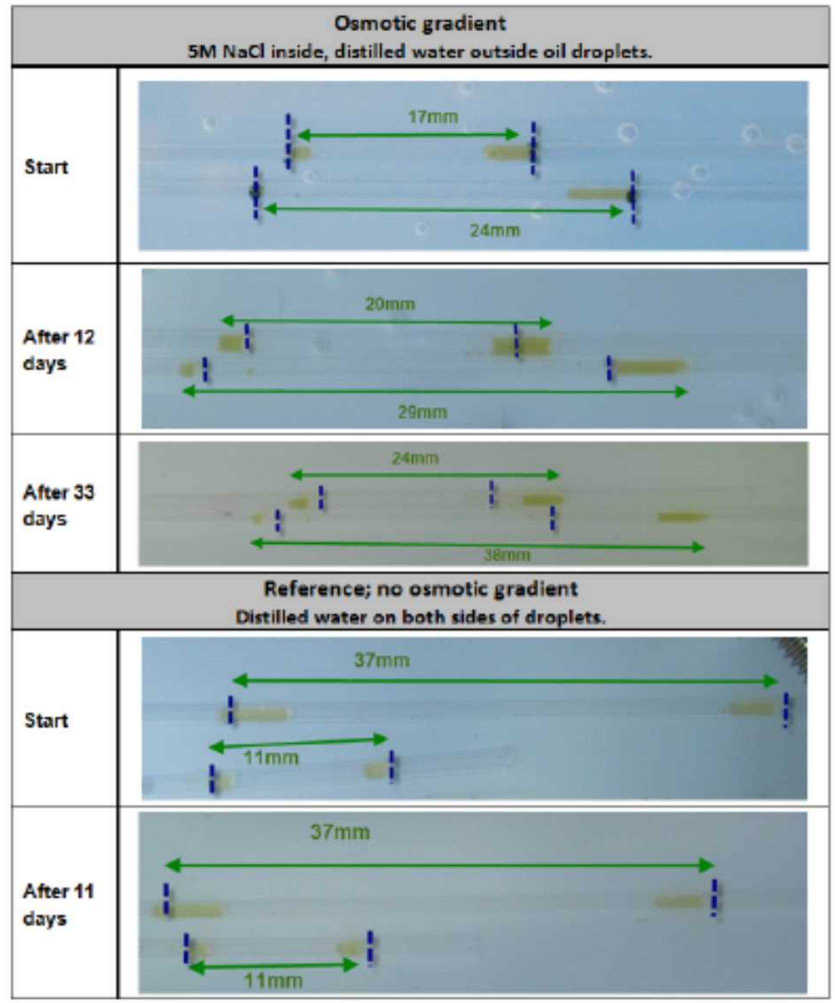


From: Hiorth, A., L. M. Cathles, and M. V. Madland. "The impact of pore water chemistry on carbonate surface charge and oil wettability." *Transport in porous media* 85, no. 1 (2010): 1-21.

Osmosis

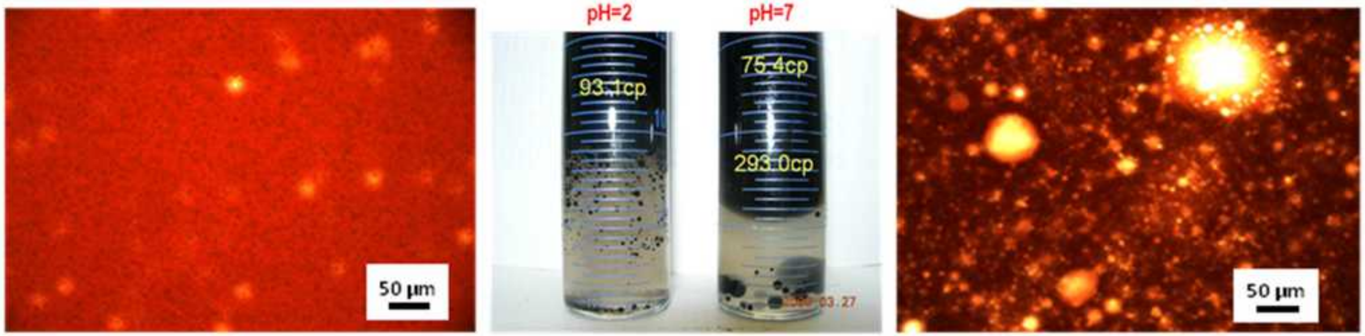


Sandengen, K., and O. J. Arntzen. "Osmosis during low salinity water flooding." *IOR 2013-17th European Symposium on Improved Oil Recovery*. 2013.



Other Oil-Water Approaches

Low salinity triggers water-in-oil (pickering) microdispersions which improves mobility (Alvarado, Sohrabi et al.),



From: Wang, Xiuyu, and Vladimir Alvarado. "Kaolinite and silica dispersions in low-salinity environments: Impact on a water-in-crude oil emulsion stability." *Energies* 4, no. 10 (2011): 1763-1778.

Oil film becomes less rigid to more quickly form an oil bank (Ayirala et al.)

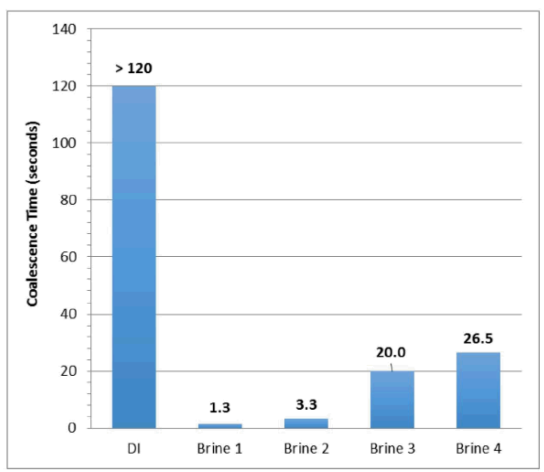
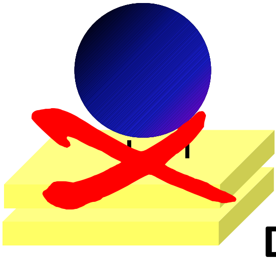


Figure 16—Coalescence Time of Oil Droplets in Different Brines/DI Water

Ayirala, Subhash C., Ali A. Al Yousef, Zuoli Li, and Zhenghe Xu. "Water Ion Interactions at Crude Oil-Water Interface: A New Fundamental Understanding on SmartWater Flood." In *SPE Middle East Oil & Gas Show and Conference*. Society of Petroleum Engineers, 2017.



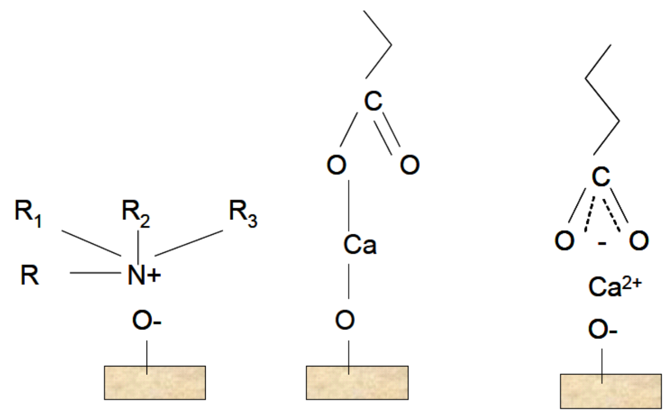
Desorption

Multi-component Ion Exchange

Mechanism	Organic functional group involved
Cation exchange	Amino, ring NH, heterocyclic N (aromatic ring)
Protonation	Amino, heterocyclic N, carbonyl, carboxylate
Anion exchange	Carboxylate
Water bridging	Amino, Carboxylate, carbonyl, alcoholic OH
Cation bridging	Carboxylate, amines, carbonyl, alcoholic OH
Ligand exchange	Carboxylate
Hydrogen bonding	Amino, carbonyl, carboxyl, phenolic OH
Van der Waals interaction	Uncharged organic units

Table 1, Mechanism of association between organic functional groups and soil minerals (from Sposito, 1989)

From: Lager, A., K. J. Webb, and C. J. J. Black. "Impact of brine chemistry on oil recovery." In *IOR 2007-14th European Symposium on Improved Oil Recovery*. 2007.



Cation exchange

Ligand bridging

Simplest Case: Oil-Quartz

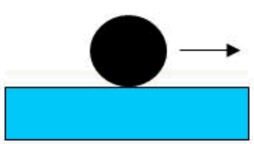
What we see

Oil wet

Adhesion

────

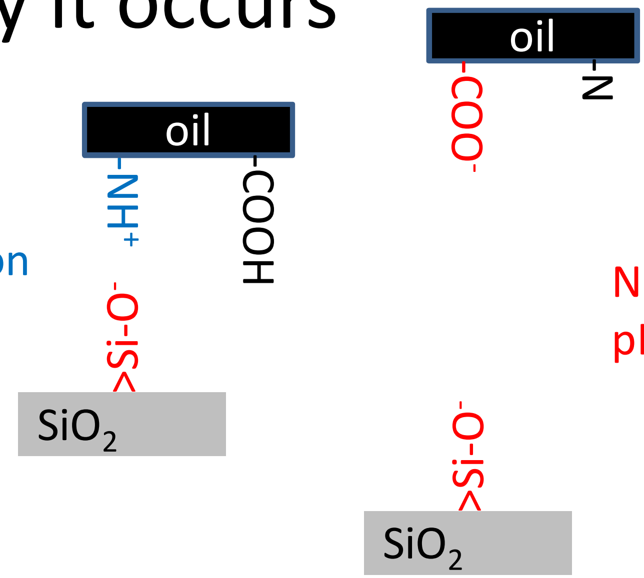
Water wet



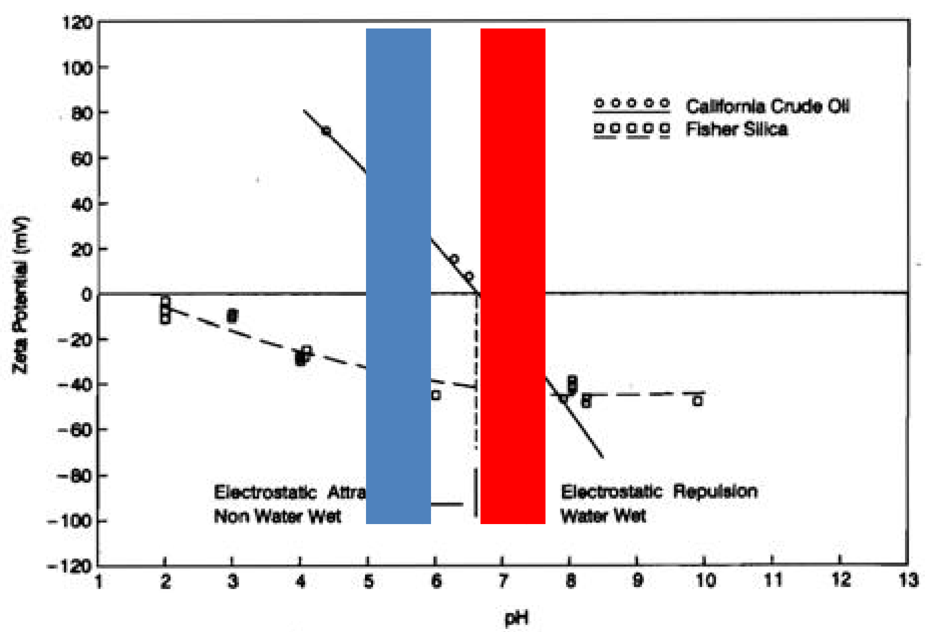
Non-adhesion

Why it occurs

Attraction
pH 5

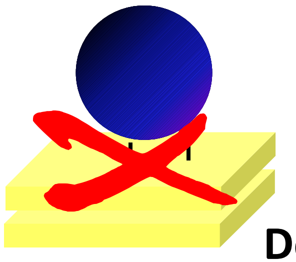


No attraction
pH 7



from Dubey and Doe (1993) *Base number and wetting properties of crude oil*. SPE Reservoir Engineering, 8 (195-200).

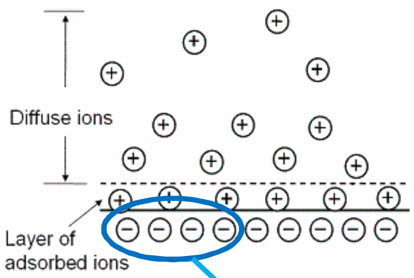
Double Layer Expansion and Surface Complexation



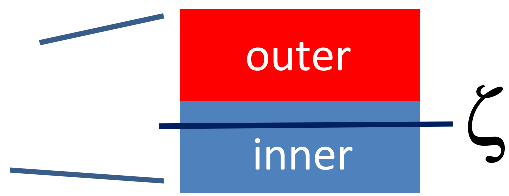
Desorption

Coulomb's Law; $F = kZ_1Z_2/d^2$

Double Layer Expansion



Electric Double Layer



+NaCl

$+CaCl_2$

N_s = # of charged (inner) surface sites

Surface Complexation

+NaCl

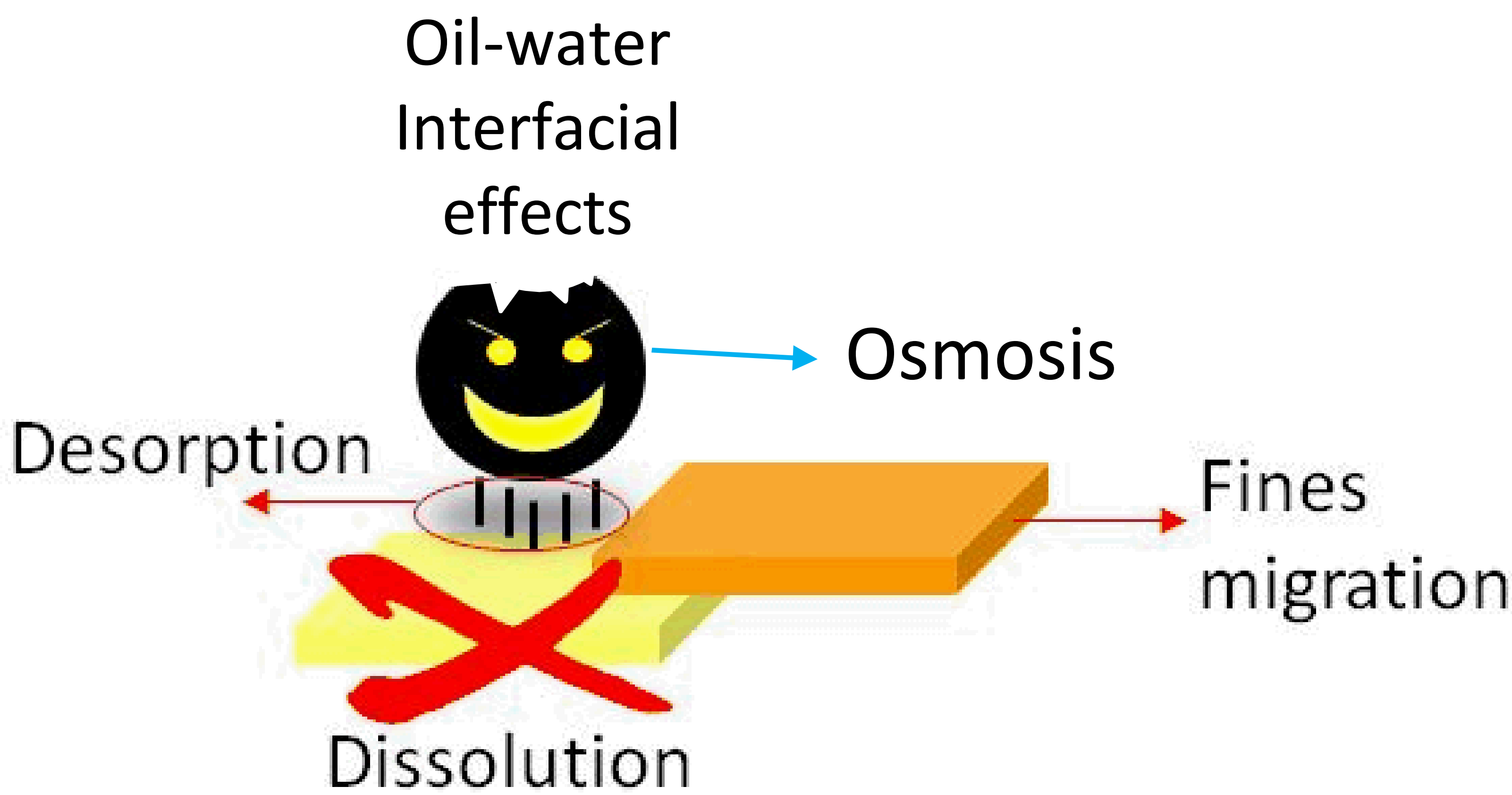
$N_s \uparrow$

$+CaCl_2$

$N_s \downarrow$

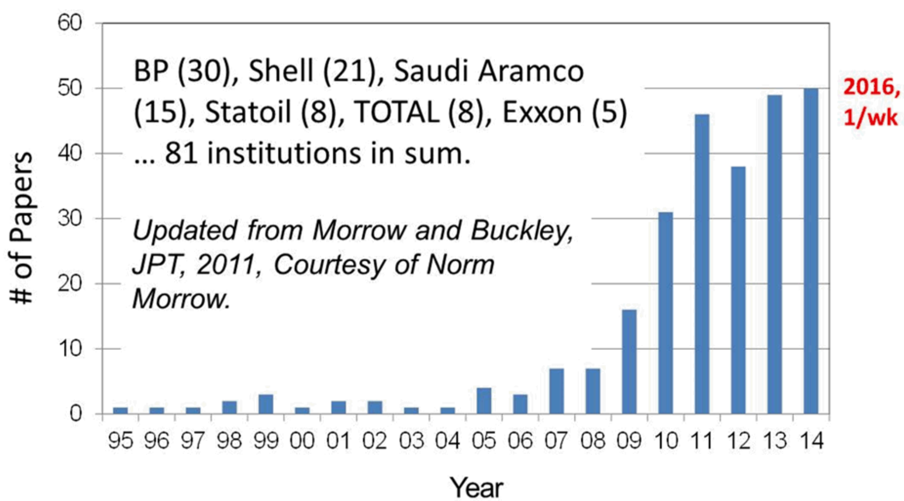
e.g. $-COO^- + Ca^{+2} \leftrightarrow -COOCa^+$

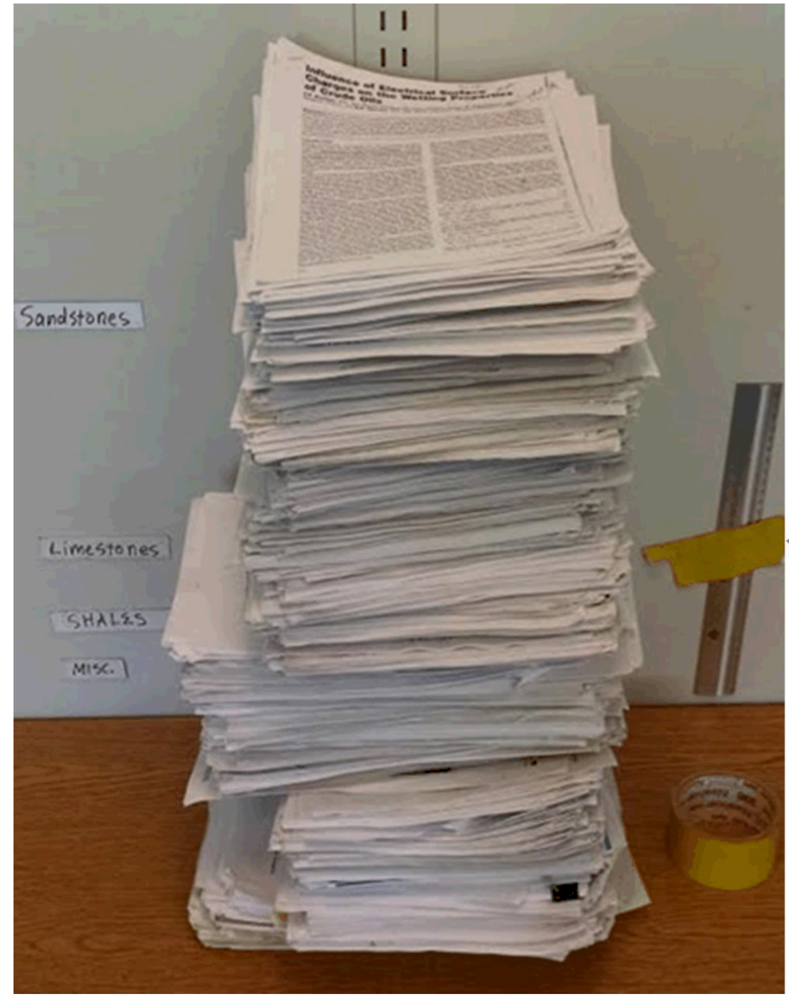
Source: http://microfluidics.stanford.edu/Projects/Archive/bioanal.htm


Oil-water
Interfacial
effects
Osmosis
Desorption
Fines
migration
Dissolution

Introduction to Electrostatics and Wettability

Pat Brady, Sandia Labs





12" ruler for scale

… in the April 30, 2016 issue of The Economist

The Economist | World politics | Business & finance | Economics | Science & technology | Culture | Blogs | Debate | Multimedia | Print edition

Viral infections

General knowledge

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Progress towards a broad antiviral treatment

Apr 30th 2016 | From the print edition

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IN THE medical armoury vaccines are a wonderful piece of ammunition. But they are like bullets that can hit one target only. Different vaccines are needed to prevent specific viral infections. If a person is already ill, vaccines won't help. Various antiviral drugs might, shortening the time people are ill or preventing serious complications. The trouble is viruses are a moving target because they can evolve rapidly. Researchers have tinkered with some antiviral treatments that might work against a wide spectrum of diseases, but all have had shortcomings. Now one group thinks they have found a method that might protect cells in the body from a viral invasion.

The new research, led by James Hedrick of the IBM Almaden Research Center in California, Naoki Yamamoto of the National University of Singapore and Yi Yan Yang of the Institute of Bioengineering and Nanotechnology, also in Singapore, stems from an old tactic that has been problematic in the past. All viruses depend upon similar electrical charges at their surfaces to connect to the cells that they are trying to infect. If the charges on viruses and cells could somehow be meddled with, it should make things harder for the virus to infect the host.

Lots of experiments have demonstrated that the theory is sound. Unfortunately, many of the materials used to interfere with the electrical charges have also been toxic to the cells they are supposed to protect. Dr Hedrick and his colleagues speculated that it might be possible to work around this problem with polyethylenimine. Previous work has shown

In this section

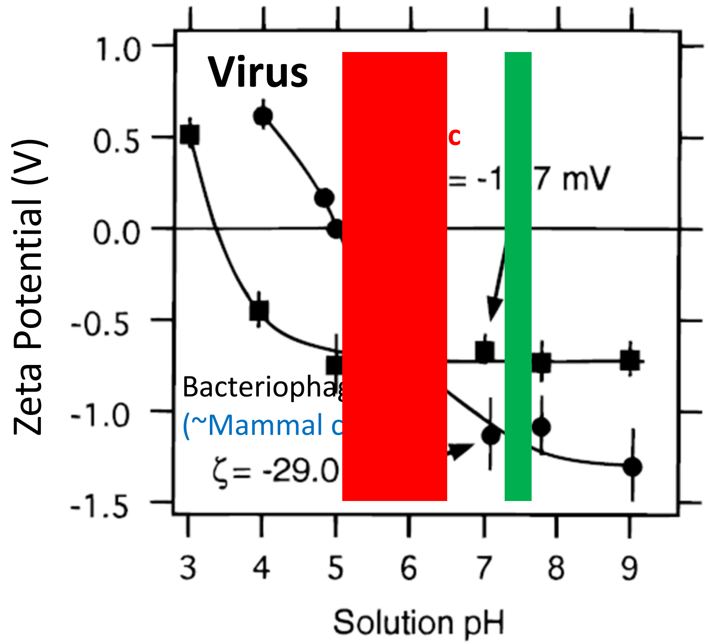
A printed smile
Getting the pulse racing
General knowledge
Buddy, can you spare a

Follow The

… All viruses depend upon similar electrical charges at their surfaces to connect to the cells that they are trying to infect. If the charges on viruses and cells could somehow be meddled with, it should make things harder for the virus to infect the host…

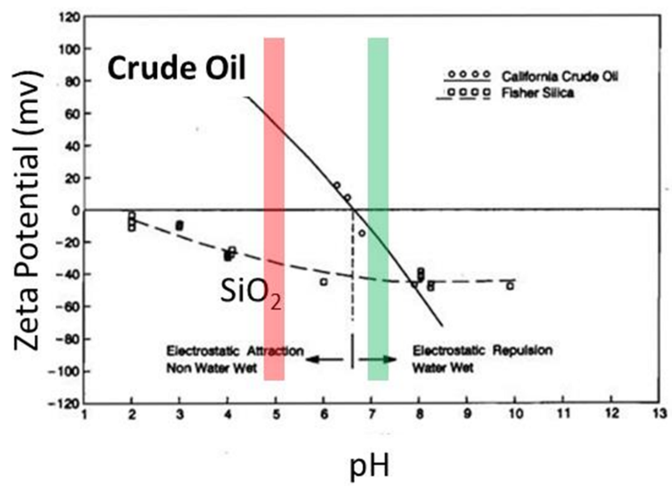
Endosomal pH 5-6.5 Physiological fluid pH 7.4

Virus on Cell



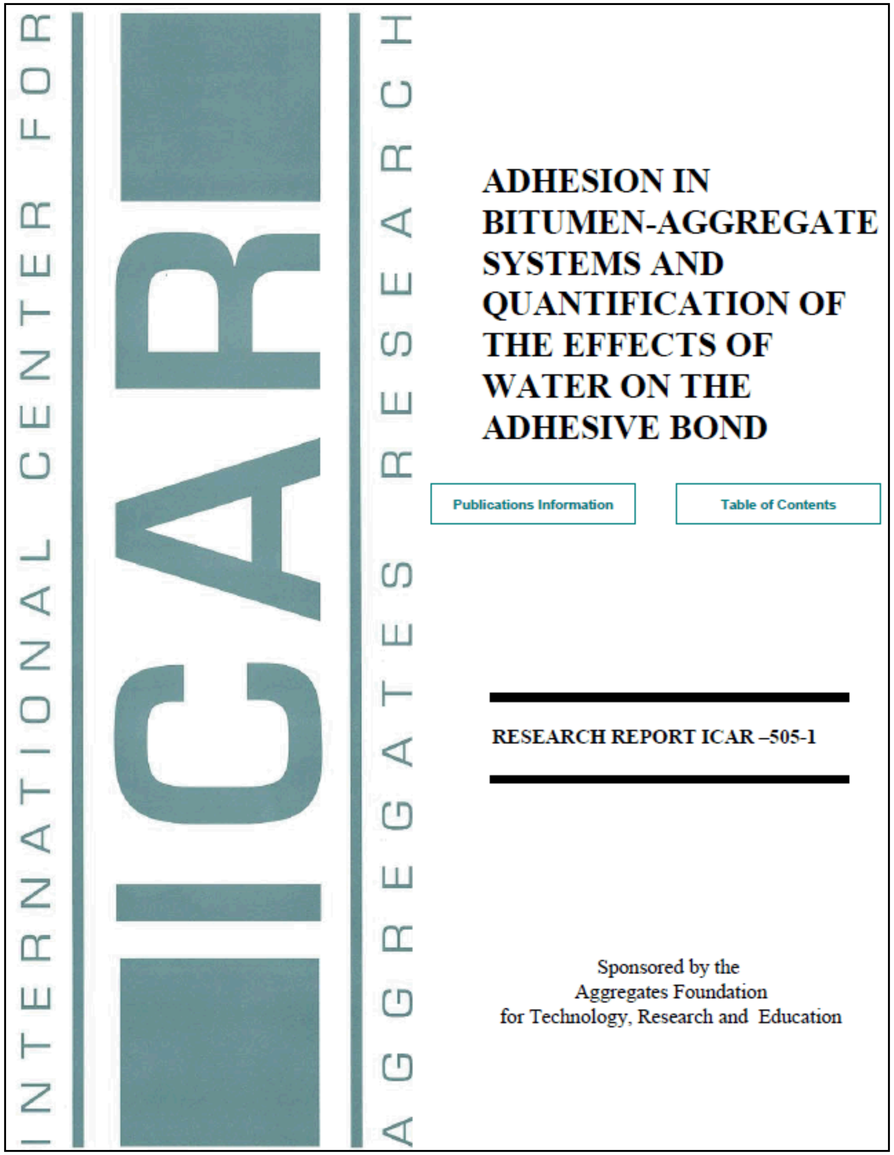
From Redman et al., 1997 ES&T

Oil on Rock



from Dubey and Doe (1993) *Base number and wetting properties of crude oil.* SPE Reservoir Engineering, 8 (195-200).

Pothole Formation



INTERNATIONAL CENTER FOR AGGREGATES RESEARCH

ICAR

ADHESION IN BITUMEN-AGGREGATE SYSTEMS AND QUANTIFICATION OF THE EFFECTS OF WATER ON THE ADHESIVE BOND

Publications Information

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RESEARCH REPORT ICAR –505-1

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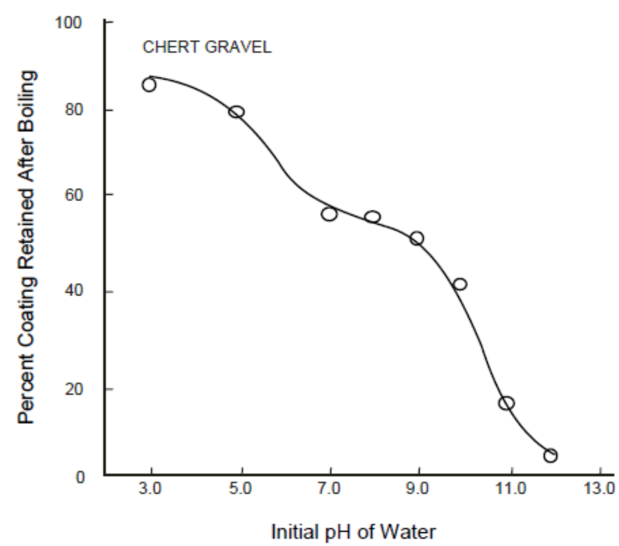
The addition of adhesion promoters to bitumen is common practice and numerous research papers and reviews have been published on different compounds used and the effects of anti-strip agents on performance of asphalt mixes. Basic, amine anti-strip agents are generally used to improve adhesion of bitumen with siliceous aggregates. Logaraj (2002) states that the two main characteristics of anti-strip additives are (a) they have a polar amine end group which will chemically bond with the siliceous aggregate surface, and (b) they have a hydrocarbon chain with similar properties to that of the bitumen so that they will interact and become part of the bitumen. A primary amine (RNH_2) and tertiary amine (NR_3) are schematically illustrated in Figure 15.



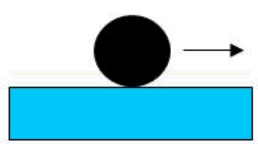
Simplest Case: Oil-Quartz

What we see

Oil wet

Adhesion

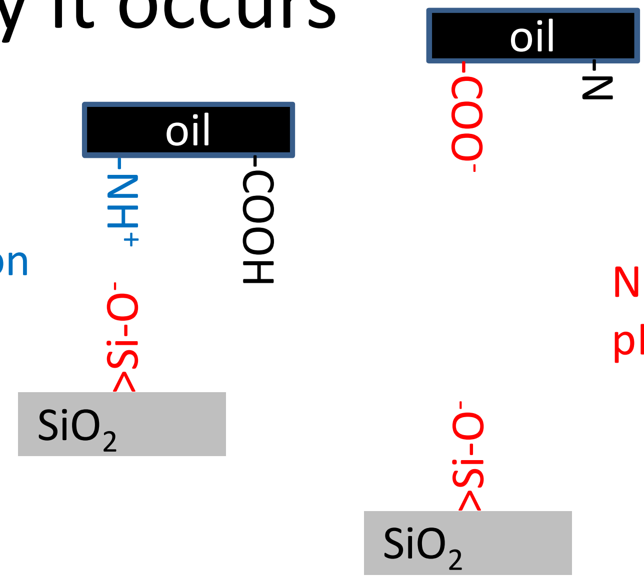
Water wet



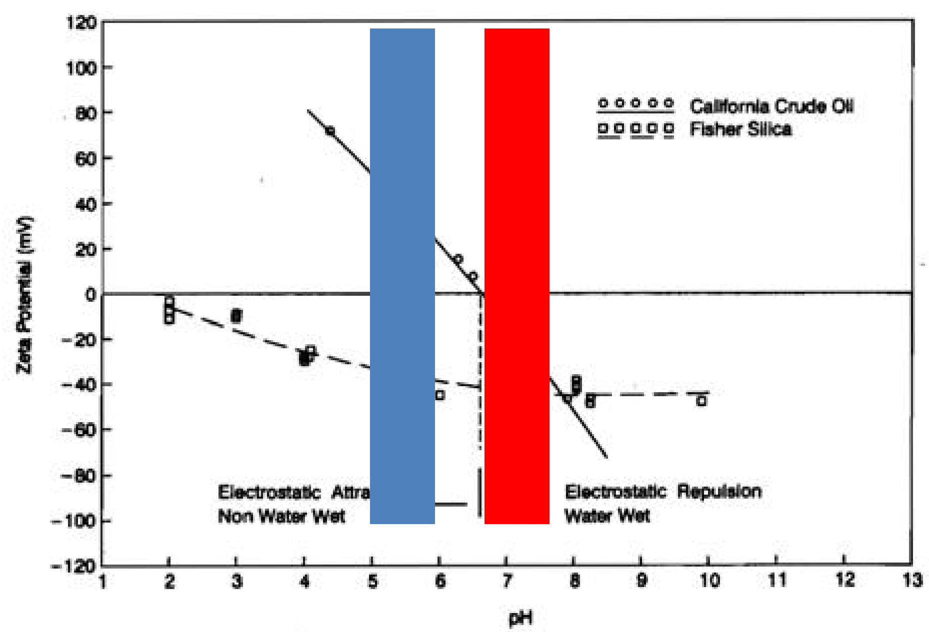
Non-adhesion

Why it occurs

Attraction
pH 5



No attraction
pH 7



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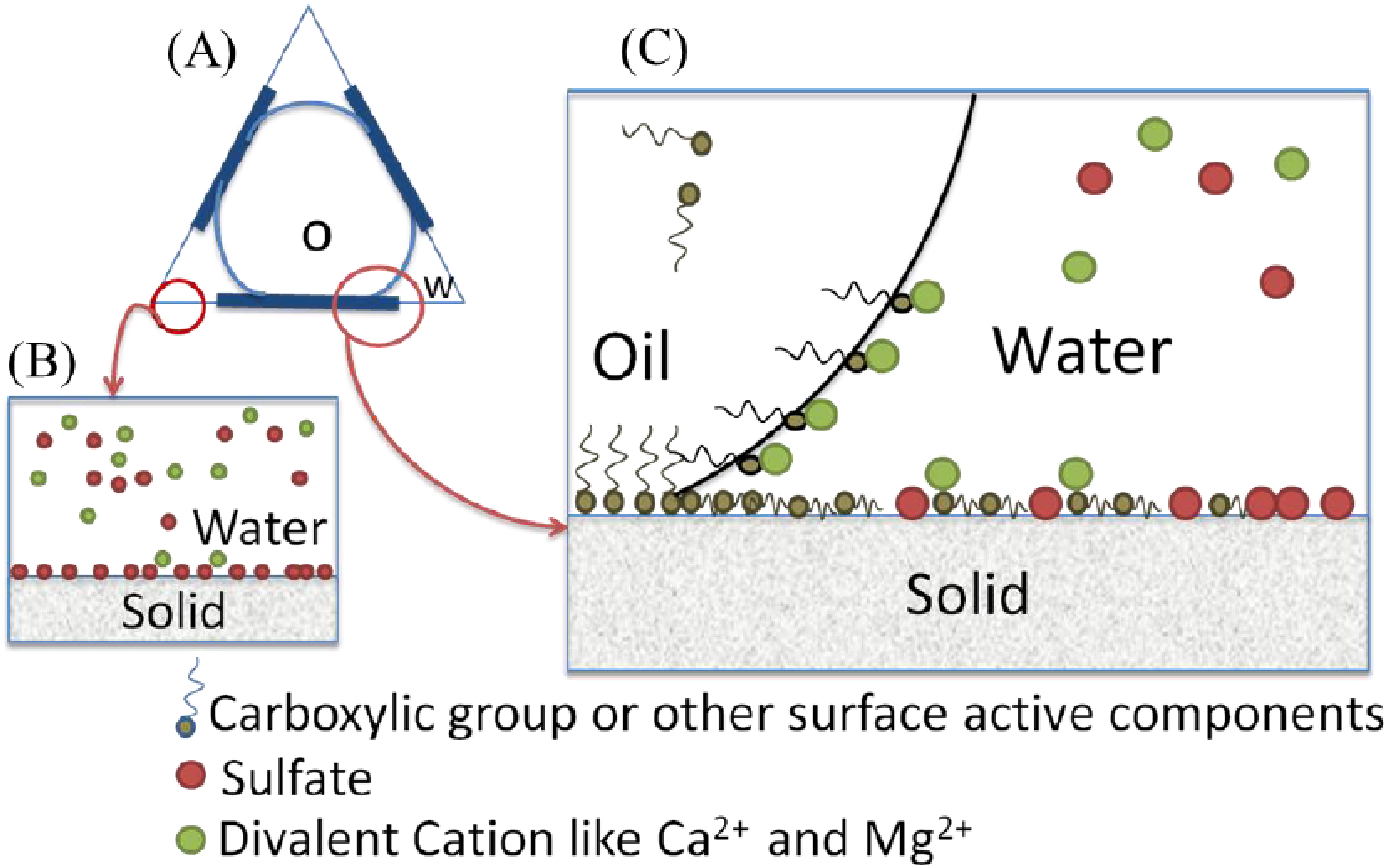
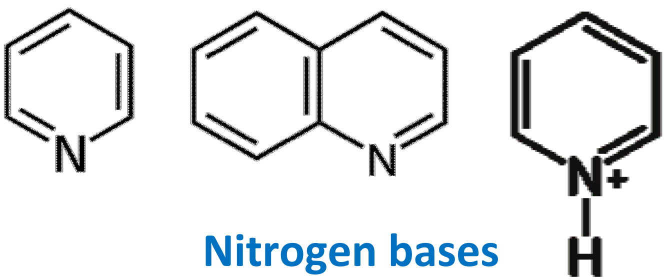
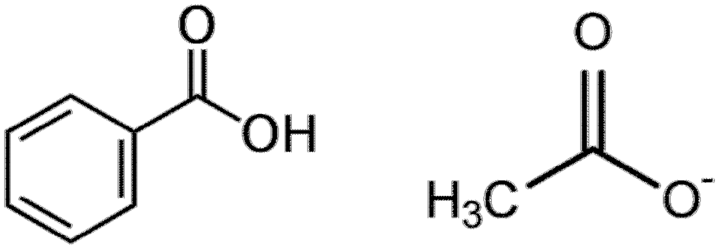


From: Qiao, C., L. Li, R. T. Johns, and J. Xu. "A Mechanistic Model for Wettability Alteration by Chemically Tuned Water Flooding in Carbonate Reservoirs. Paper SPE-170966 presented at the SPE Annual Technical Conference and Exhibition Amsterdam, The Netherlands, 27-29 October.

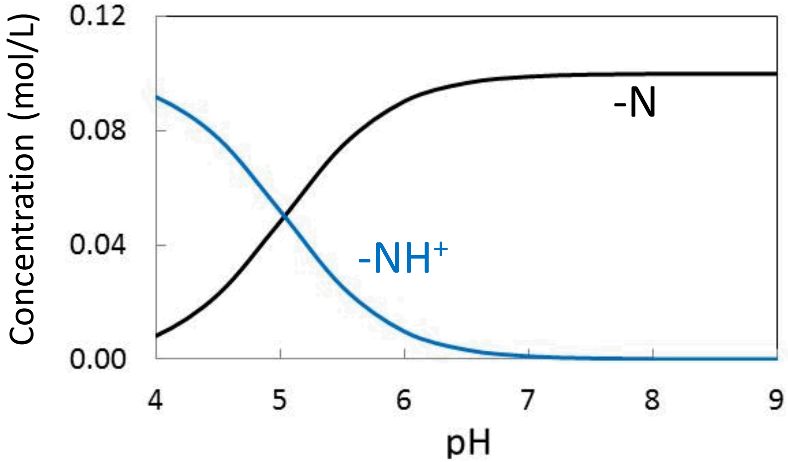
Oil Surface Chemistry

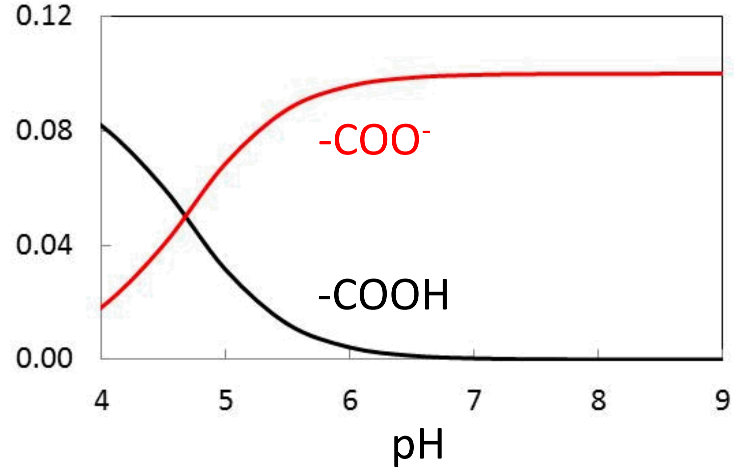


Nitrogen bases



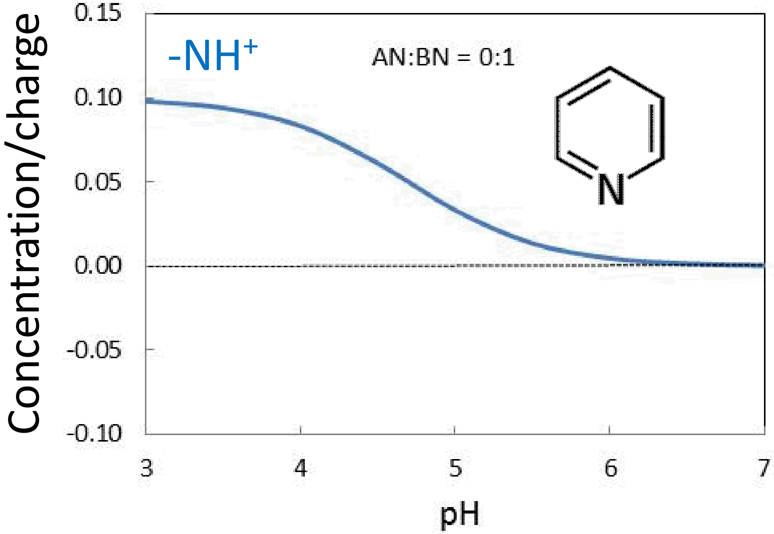
Carboxylic acids

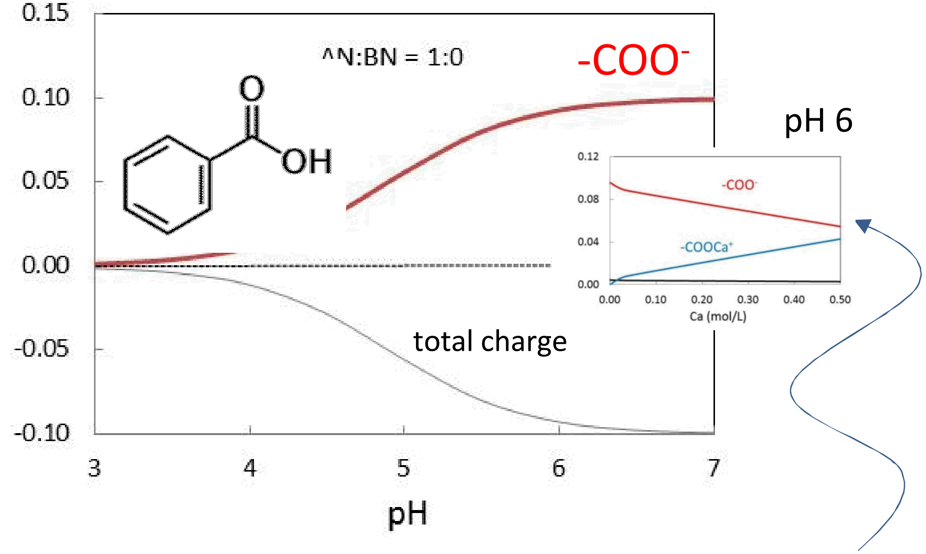




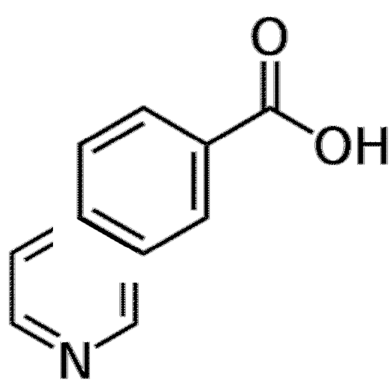
$-NH^+ \leftrightarrow -N + H^+$ $K_A \sim 10^{-5}$, 25°C

$-COOH \leftrightarrow -COO^- + H^+$ $K_A \sim 10^{-5}$, 25°C

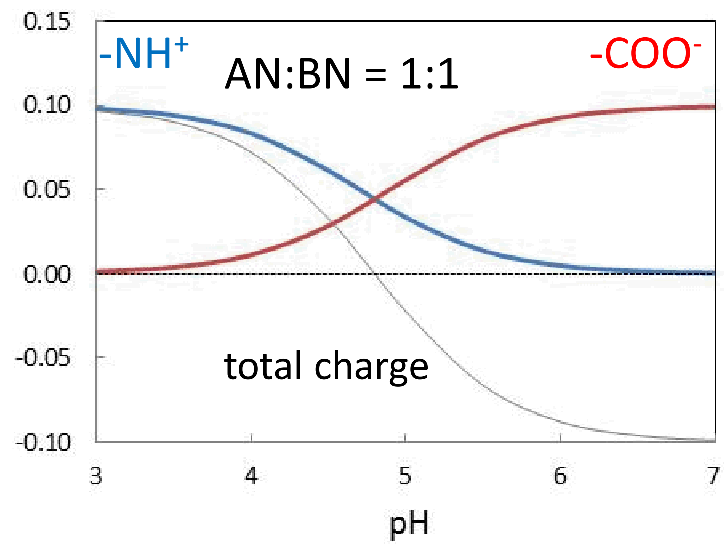




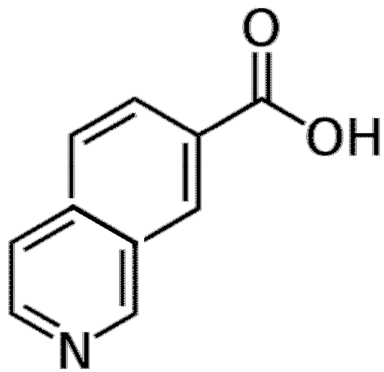
$-COO^{-} + Ca^{++} \leftrightarrow -COOCa^{+}$



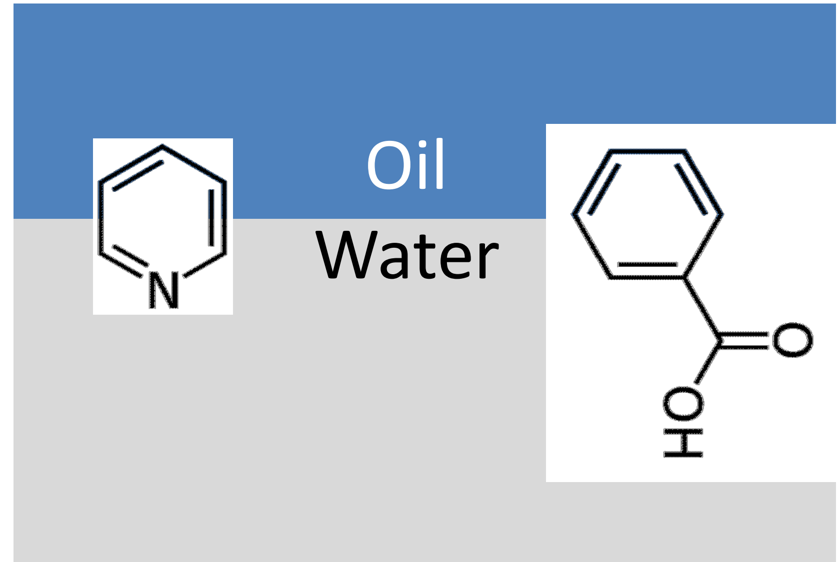
Proto-oil zwitterion

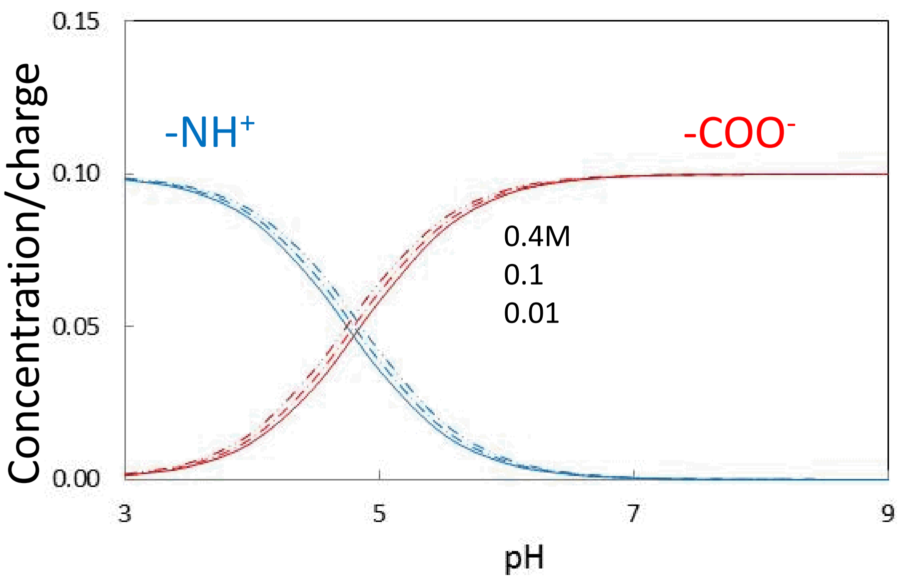


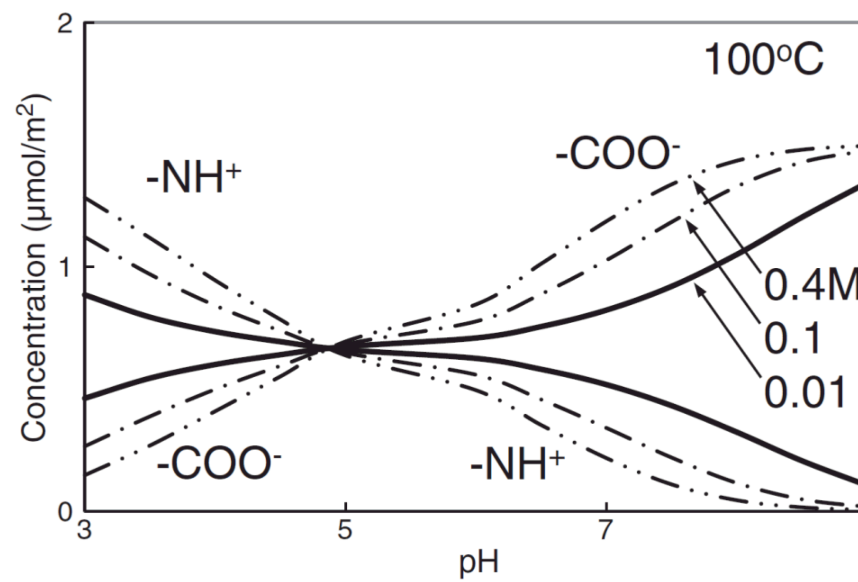
Aqueous species



Macromolecule







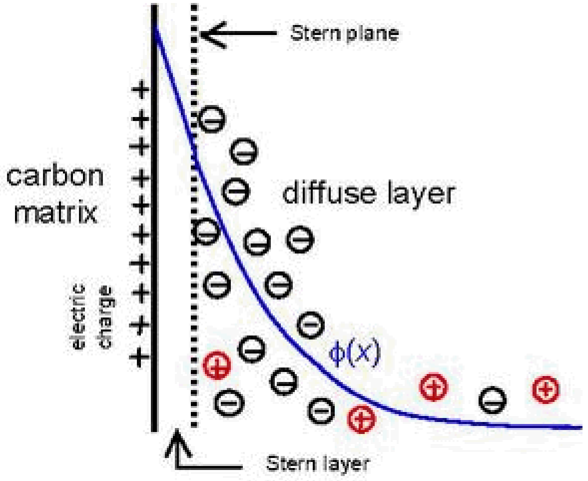
From: Brady, Patrick V., and James L. Krumhansl. "A surface complexation model of oil–brine–sandstone interfaces at 100° C: Low salinity waterflooding." *Journal of Petroleum Science and Engineering* 81 (2012): 171-176.

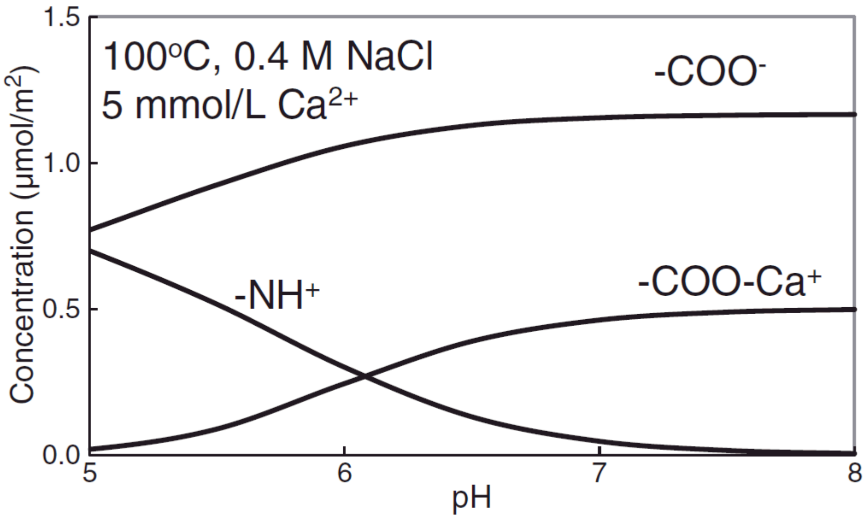
Diffuse Double Layer Model of Oil Surface

1. $-NH^{+} \leftrightarrow -N + H^{+} \; K_{NH} = [-N]$ [redacted] $a_{H+}/[-NH^{+}]$

2. $-COOH \leftrightarrow -COO^{-} + H^{+} \; K_{COOH}$
$=$ [redacted] $[-COO^{-}]a_{H+}/[-COOH]$

3. $-COOH + Ca^{2+} \leftrightarrow -COOCa^{+} + H^{+} \; K_{COOH}$
$= [-COOCa^{+}]$ [redacted] $a_{H+}/[-COOH]$





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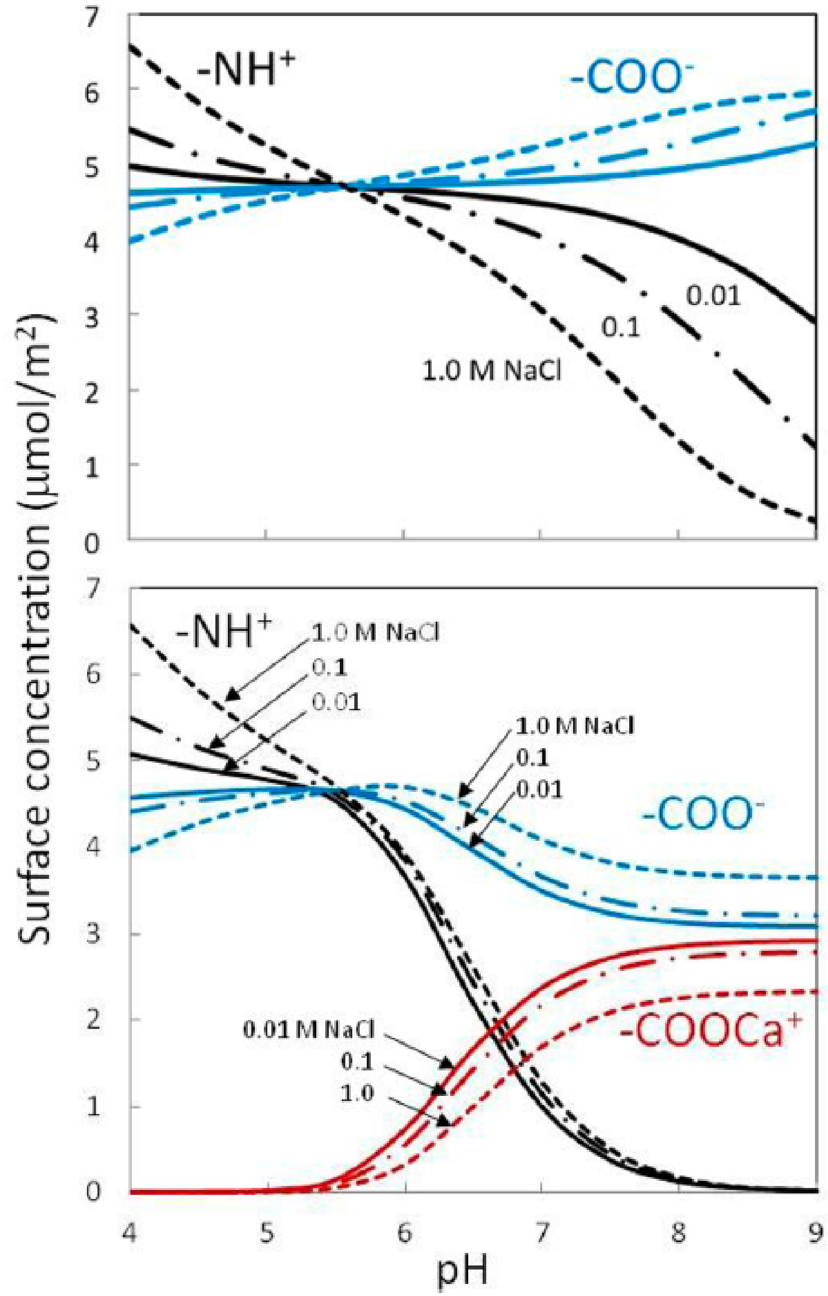


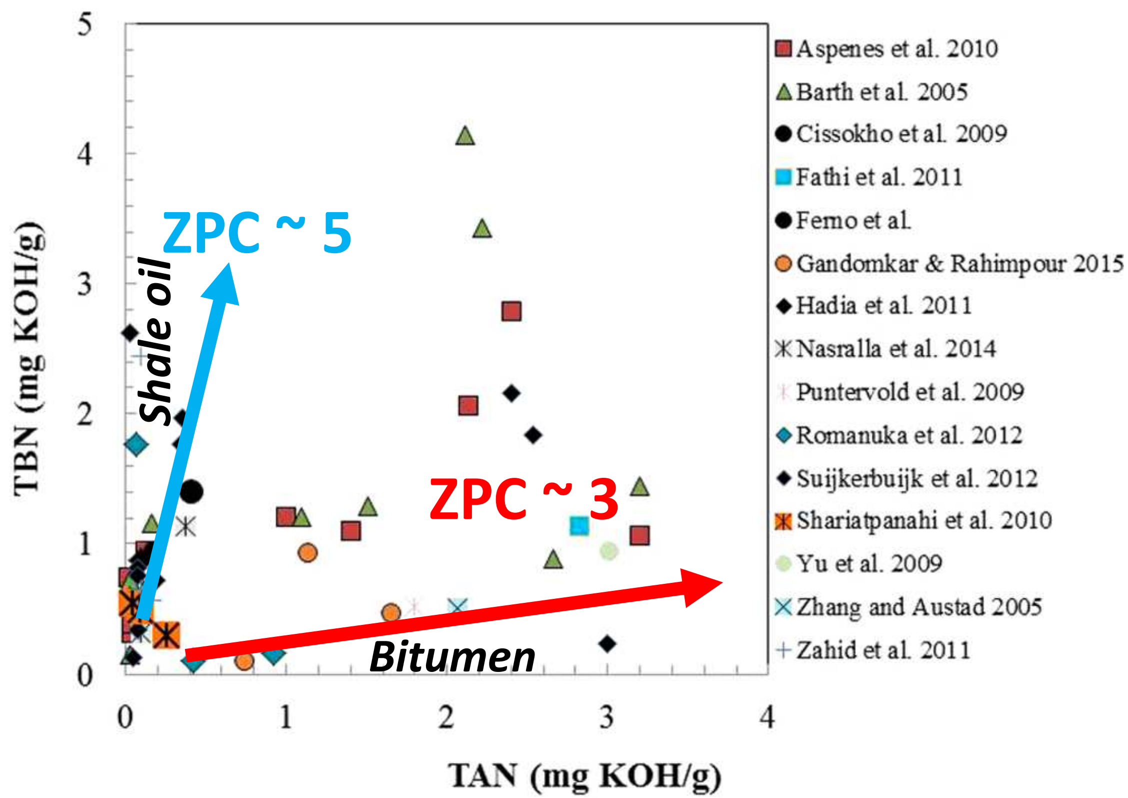
From: Brady, Patrick V., Norman R. Morrow, Andrew Fogden, Vivianne Deniz, and Nina Loahardjo. "Electrostatics and the low salinity effect in sandstone reservoirs." *Energy & Fuels* 29, no. 2 (2015): 666-677.

Oil Acid and Base Numbers

Table 1. Acid and Base Numbers

Crude Oil	Acid # (mg KOH/g oil)	Base # (mg KOH/g oil)
A-90	0.24 ± 0.04*	1.99 ± 0.09
A-93	0.14 ± 0.04*	2.42 ± 0.33
A-93**	0.12 ± 0.02	2.80 ± 0.08
A-93 n-C_6 asphaltenes	unable to measure*	9.82 ± 0.44
A-93 n-C_6 maltenes	0.18 ± 0.02	1.38 ± 0.03
A-95	0.24 ± 0.05*	2.20 ± 0.01
Brookhaven	0.18 ± 0.03	0.46 ± 0.05
California	0.39 ± 0.03*	5.19 ± 0.10
CS	0.33 ± 0.03	1.16 ± 0.18
Dagang	0.66 ± 0.08*	4.67 ± 0.17
EMSU	0.55 ± 0.02	0.80 ± 0.04
Lagrave	0.29 ± 0.02*	0.65 ± 0.02
Maljamar	0.12 ± 0.04	0.72 ± 0.06
Moutray	0.55 ± 0.10	0.81 ± 0.09
NBU	0.09 ± 0.03	
Schuricht	0.28 ± 0.12*	2.09 ± 0.06
Spraberry	0.32 ± 0.02	2.83 ± 0.05
ST-86	0.48 ± 0.06	1.07 ± 0.07
ST-87	0.29 ± 0.06	1.17 ± 0.01
ST-88	0.24 ± 0.01	0.53 ± 0.06
ST-89	0.10 ± 0.01	0.92 ± 0.01
SQ-94	0.45 ± 0.05*	0.24 ± 0.14
SQ-95	0.16 ± 0.03*	0.62 ± 0.03
Tensleep	0.16 ± 0.03	0.96 ± 0.01
Wassan	0.32 ± 0.09	0.97 ± 0.06

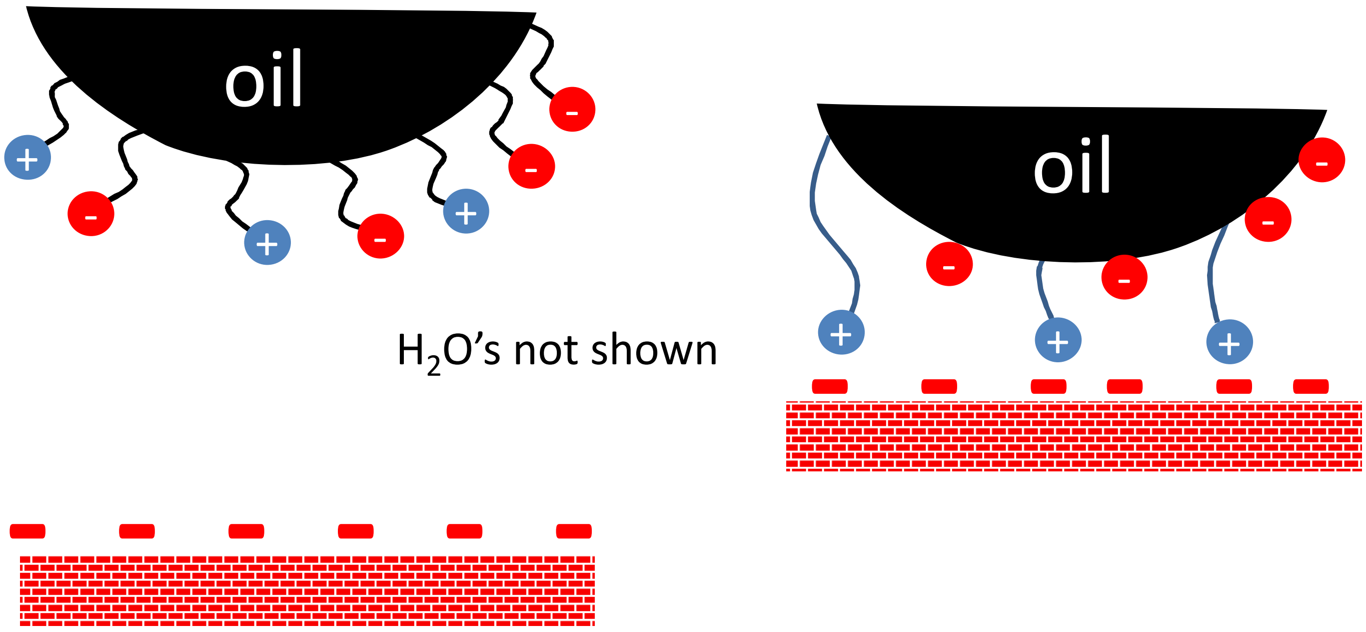
Courtesy of Jill Buckley and Norm Morrow



Underlying figure courtesy of Geoff Thyne

Oil Surface Chemistry Peculiarities

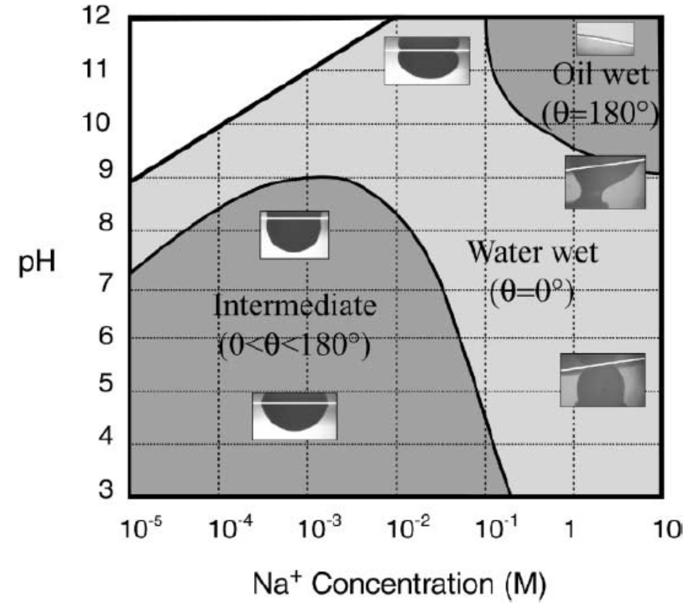
1. Smudged pK_a's,
2. Self-association of acids and bases,
3. Other surface groups.
4. "Hairiness".



After Somasundaran et al., 1993

Hairy DLVO

Drummond and Israelachivilli (2004) “It is important to emphasize that the results obtained with this crude oil cannot be explained in terms of the DLVO theory alone, and it is necessary to invoke polymer-like steric and bridging interactions, to quantitatively describe the measured force profiles”



Drummond, Carlos, and Jacob Israelachvili. "Fundamental studies of crude oil–surface water interactions and its relationship to reservoir wettability." *Journal of Petroleum Science and Engineering* 45, no. 1 (2004): 61-81.

From Somasundaran et al. 1998, Role of reconformation of hairs in anomalous deposition of zwitterionic latex particles. Colloids and Surfaces.

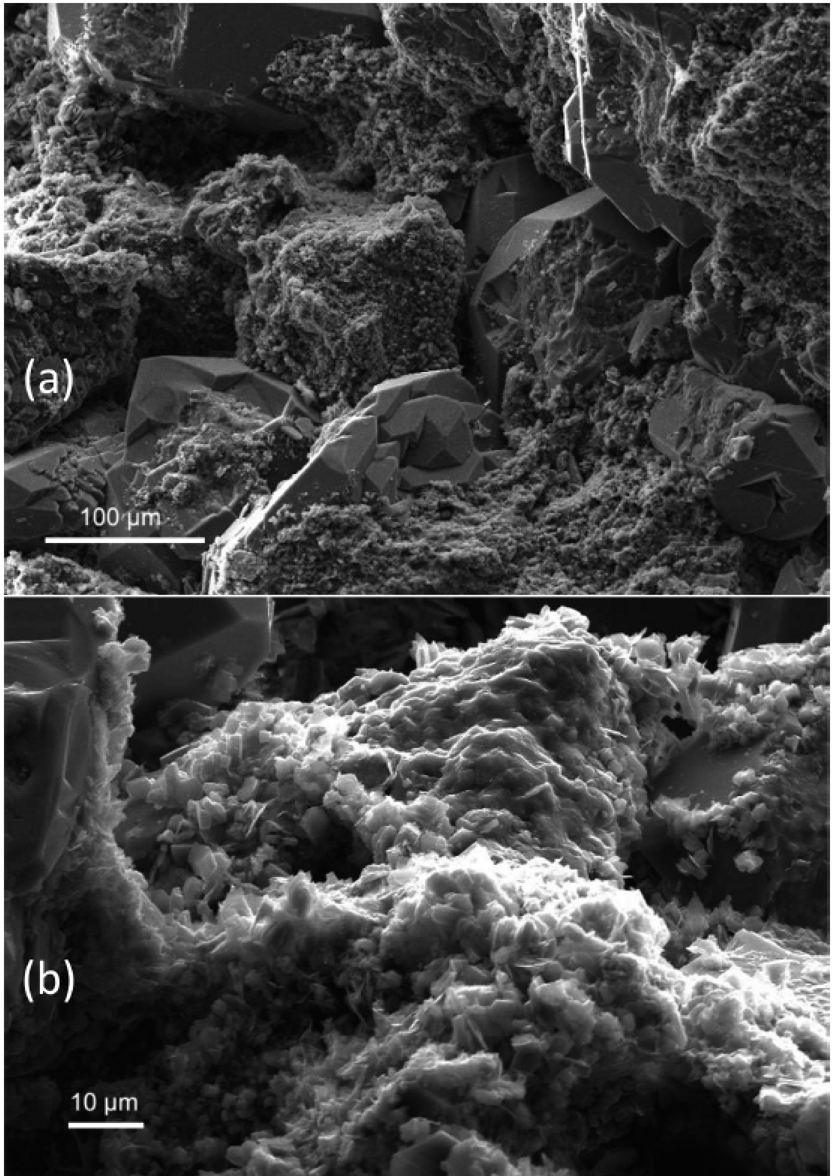
5. Unconventional deposition of zwitterionic latex particles

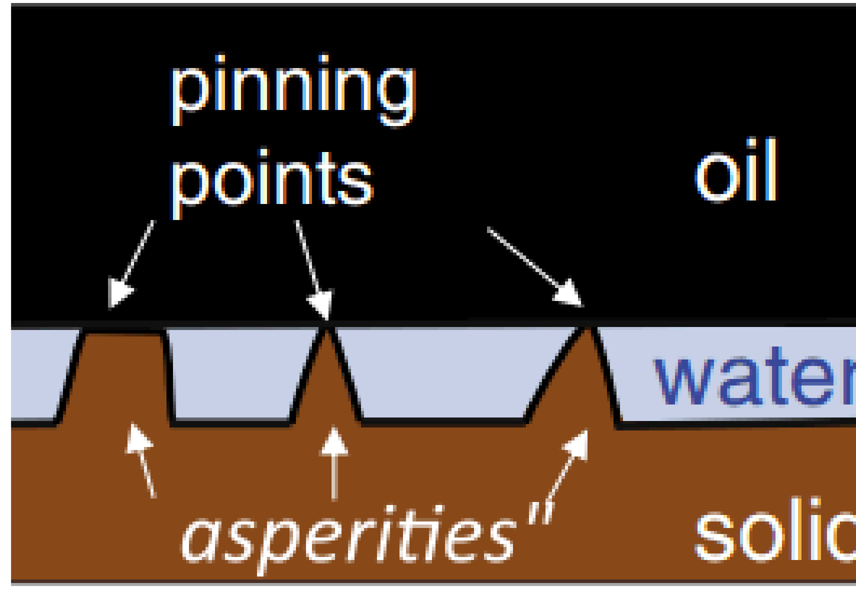
It is proposed that the deposition of the zwitter-ionic latex particles to be due to the rearrangement of the mixed charge groups present in the latex surface in such a manner that the positive charge sites are extended towards the glass surface and the negative ones retracted away from it. Thus even though the overall average zeta potential is negative, the hairy charges are proposed to recon-figure when the two surfaces begin to feel each other.

Zeta Potentials tell only a small part of the story

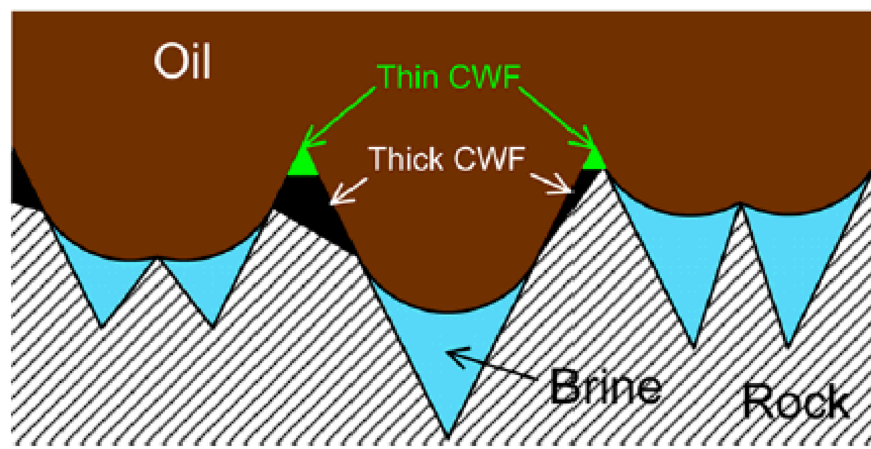
Mineral Surface Chemistry

Pat Brady, Sandia Labs

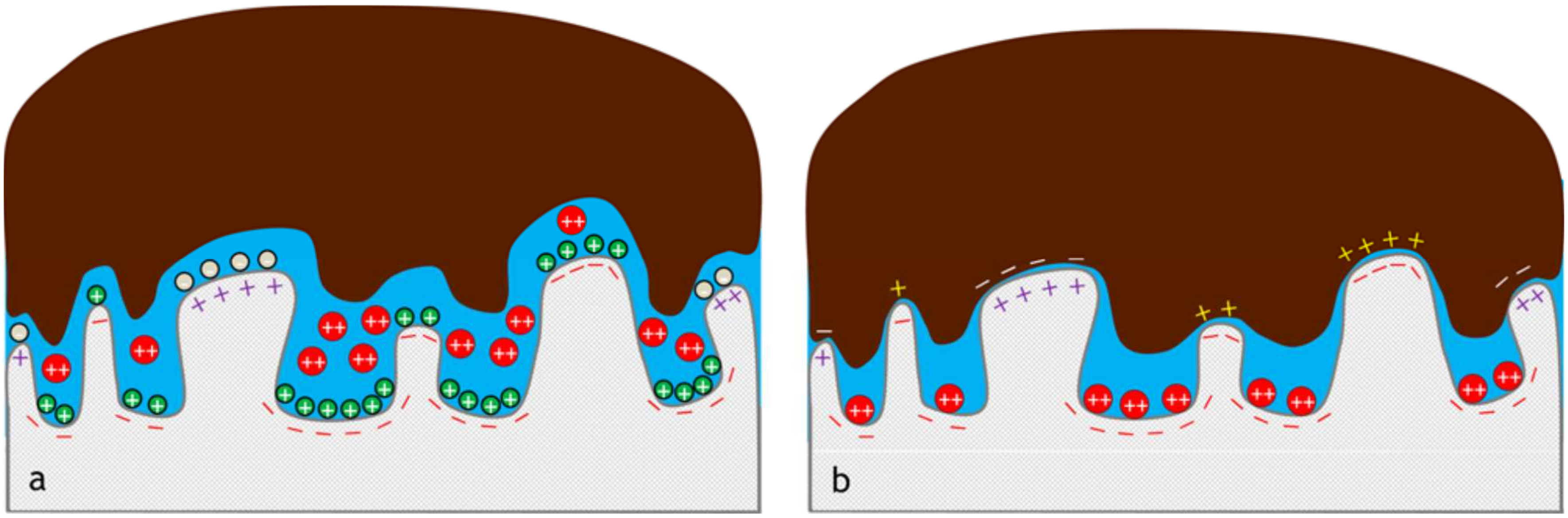




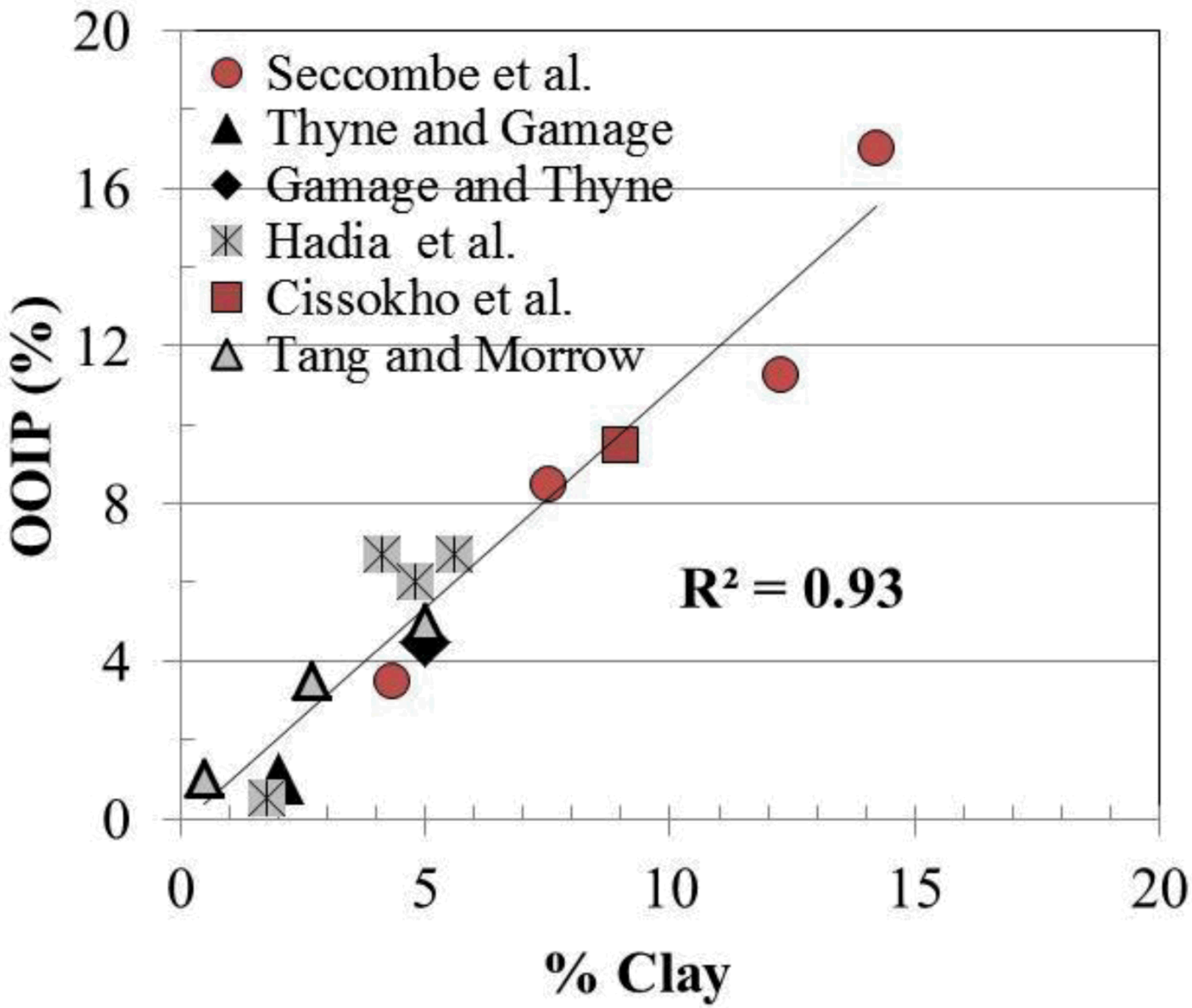
Schmatz, Joyce, Janos L. Urai, Steffen Berg, and Holger Ott. "Nanoscale imaging of pore-scale fluid-fluid-solid contacts in sandstone." *Geophysical Research Letters* 42, no. 7 (2015): 2189-2195.



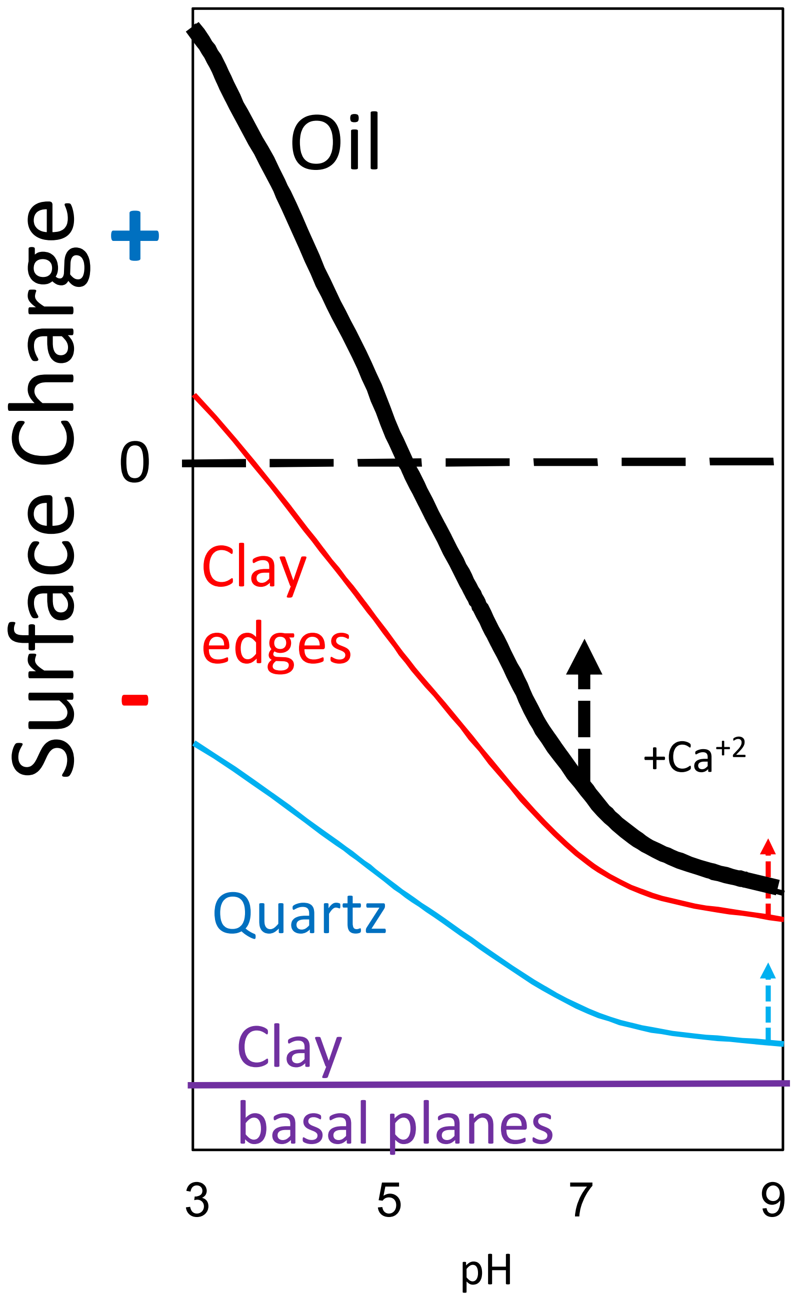
From Brady, P. V., Morrow, N. R., Fogden, A., Deniz, V., & Loahardjo, N. (2015). Electrostatics and the low salinity effect in sandstone reservoirs. *Energy & Fuels*, *29*(2), 666-677.



From: Farajzadeh, Rouhi, Hua Guo, Julia van Winden, and J. Bruining. "Cation exchange in the presence of oil in porous media." *ACS Earth and Space Chemistry* (2017).



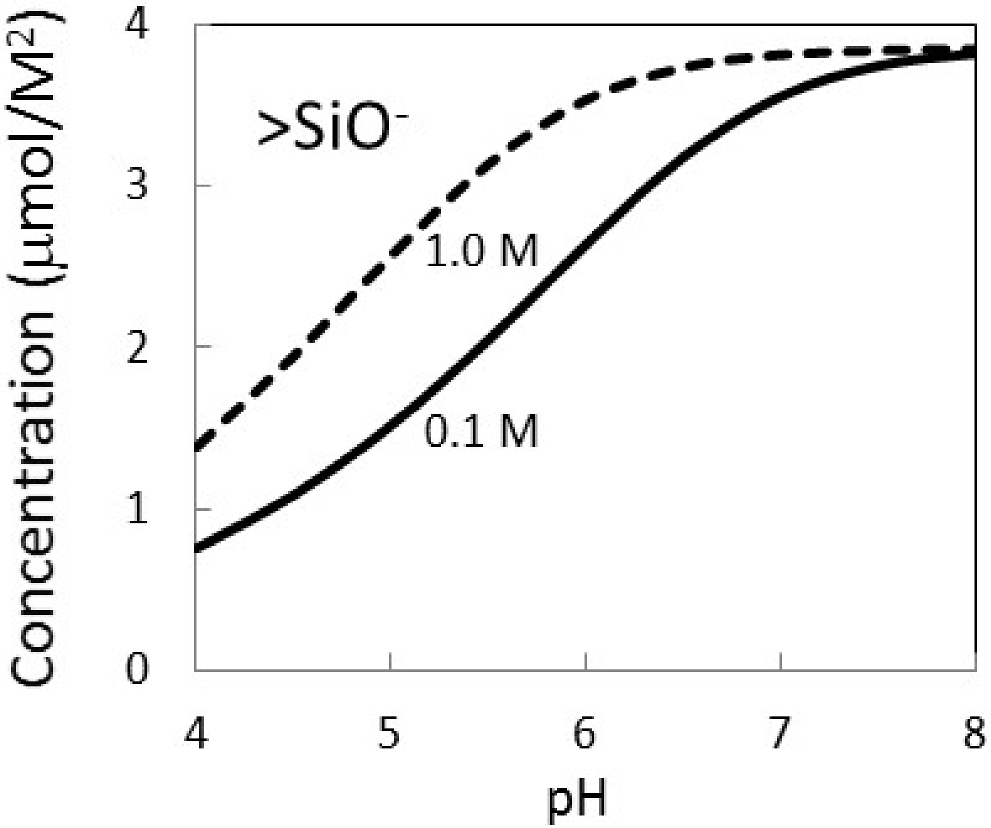
From: Thyne, Geoffrey. "Wettability Alteration in Reservoirs: How it Applies to Alaskan Oil Production." In *SPE Western Regional Meeting*. Society of Petroleum Engineers, 2016.

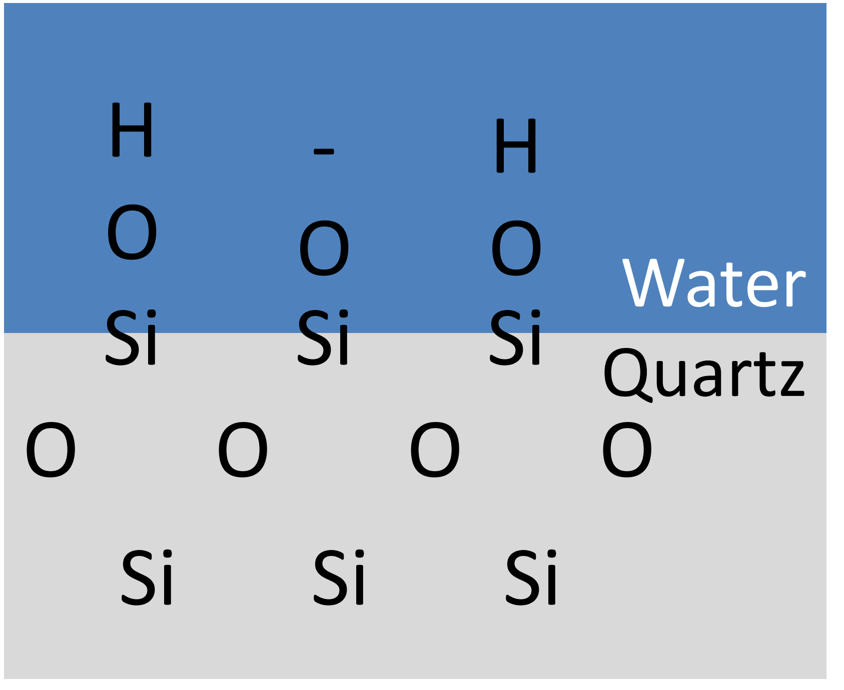

Surface Charge
+
0
-
Oil
Clay
edges
Quartz
Clay
basal planes
+Ca+2
3
5
7
9
pH

Quartz

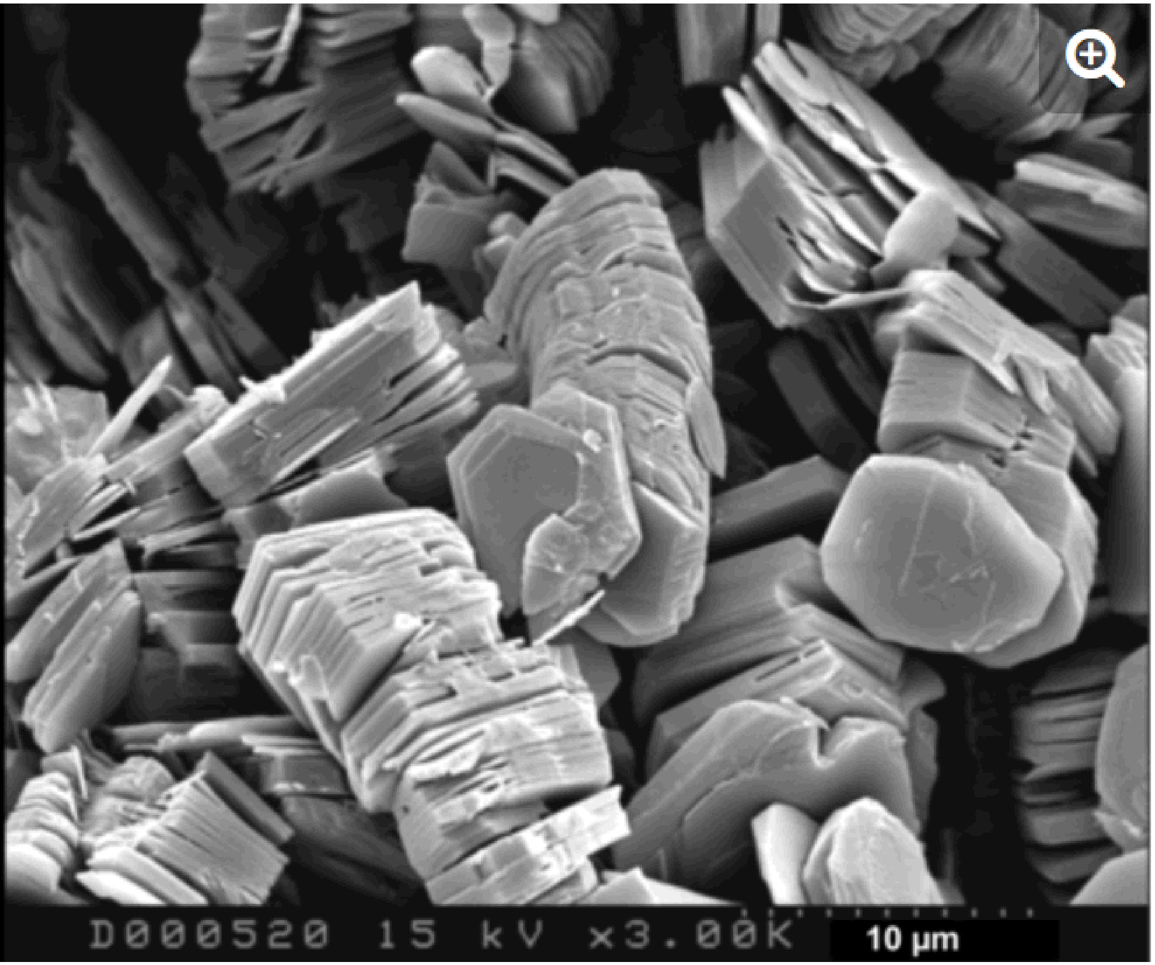
Silicic acid: $H_4SiO_4 \leftrightarrow H_3SiO_4^- + H^+$

SiO_2 surface: $>SiOH \leftrightarrow >SiO^- + H^+$

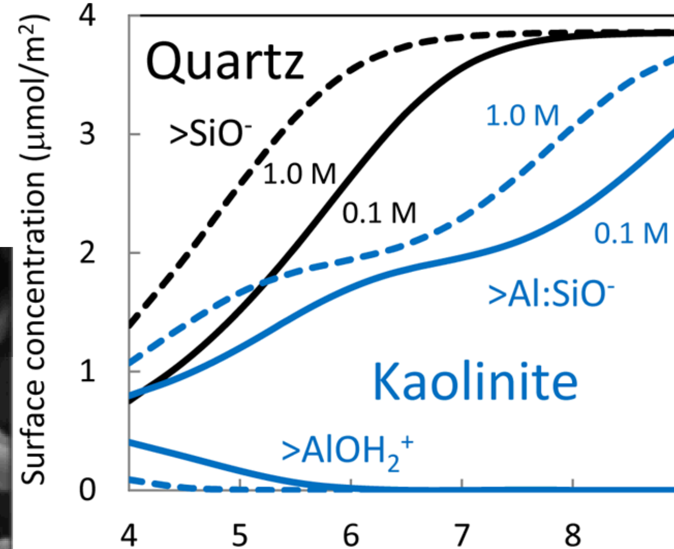




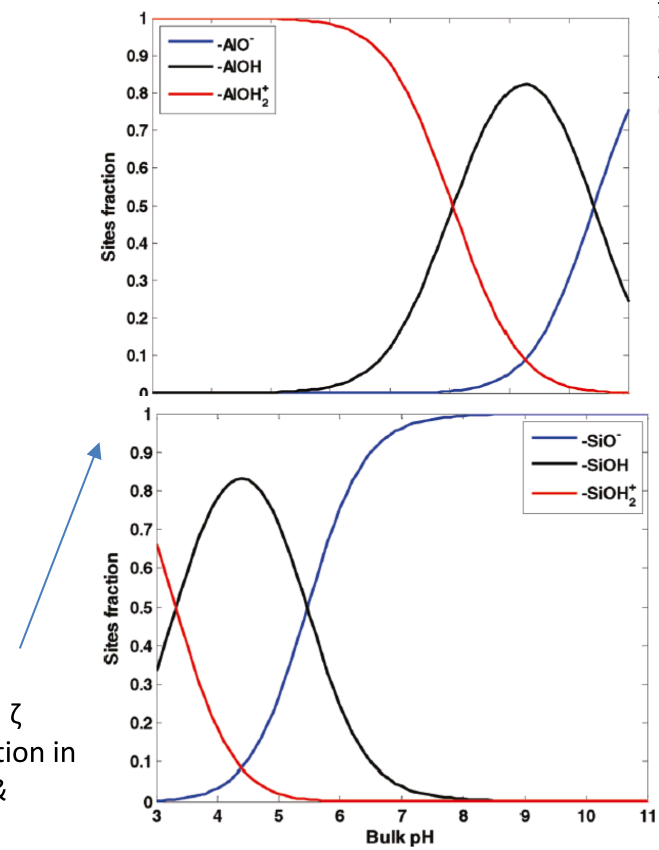
Kaolinite (clay edges)



From: Wilson, M. J., L. Wilson, and I. Patey. "The influence of individual clay minerals on formation damage of reservoir sandstones: a critical review with some new insights." *Clay Minerals* 49.2 (2014): 147-164.



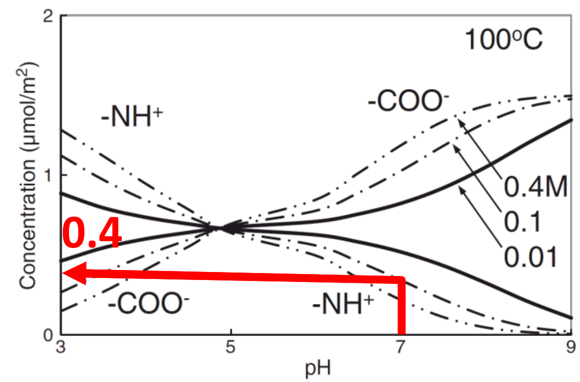
Brady, Patrick V., Norman R. Morrow, Andrew Fogden, Vivianne Deniz, and Nina Loahardjo. "Electrostatics and the low salinity effect in sandstone reservoirs." *Energy & Fuels* 29, no. 2 (2015): 666-677.

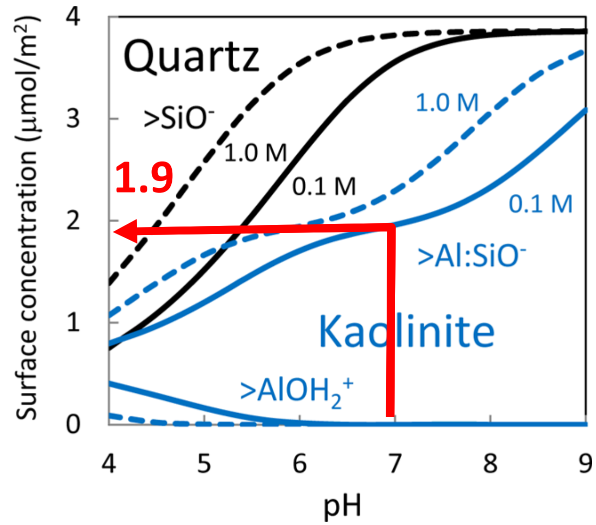


From: Jiang, Tianmin, George J. Hirasaki, and Clarence A. Miller. "Characterization of kaolinite ζ potential for interpretation of wettability alteration in diluted bitumen emulsion separation." *Energy & Fuels* 24, no. 4 (2010): 2350-2360.

How to Model Oil-Clay Adhesion?

- Disjoining pressure
- Zeta potentials
- **Bond product sum**

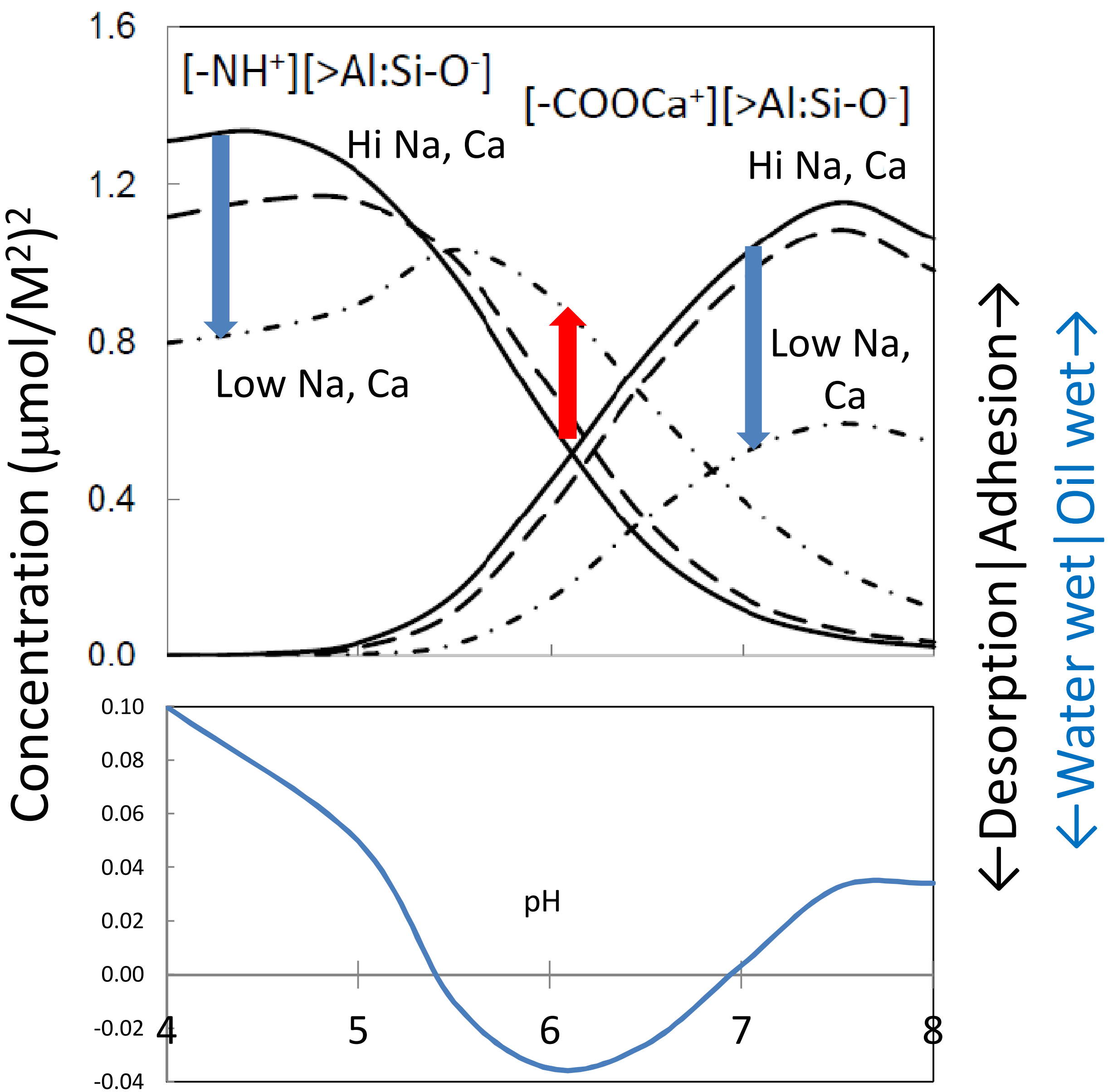


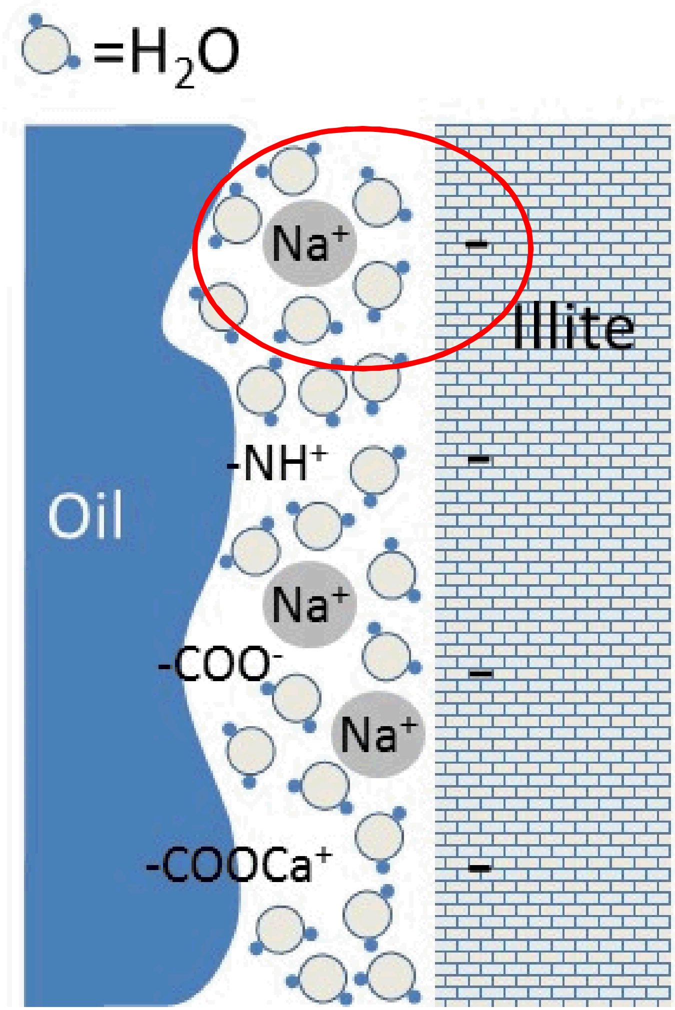


Example: Oil-NH^+ to Kaolinite $>AlO^-$, pH 7, 0.1M NaCl, 100°C.

Bond product = $[-NH^+][>AlO^-]$ = $0.4*1.9 = 0.76\ (\mu mol/M^2)^2$

Kaolinite-Oil Adhesion





Clay Ion Exchange

= "Basal plane sorption"

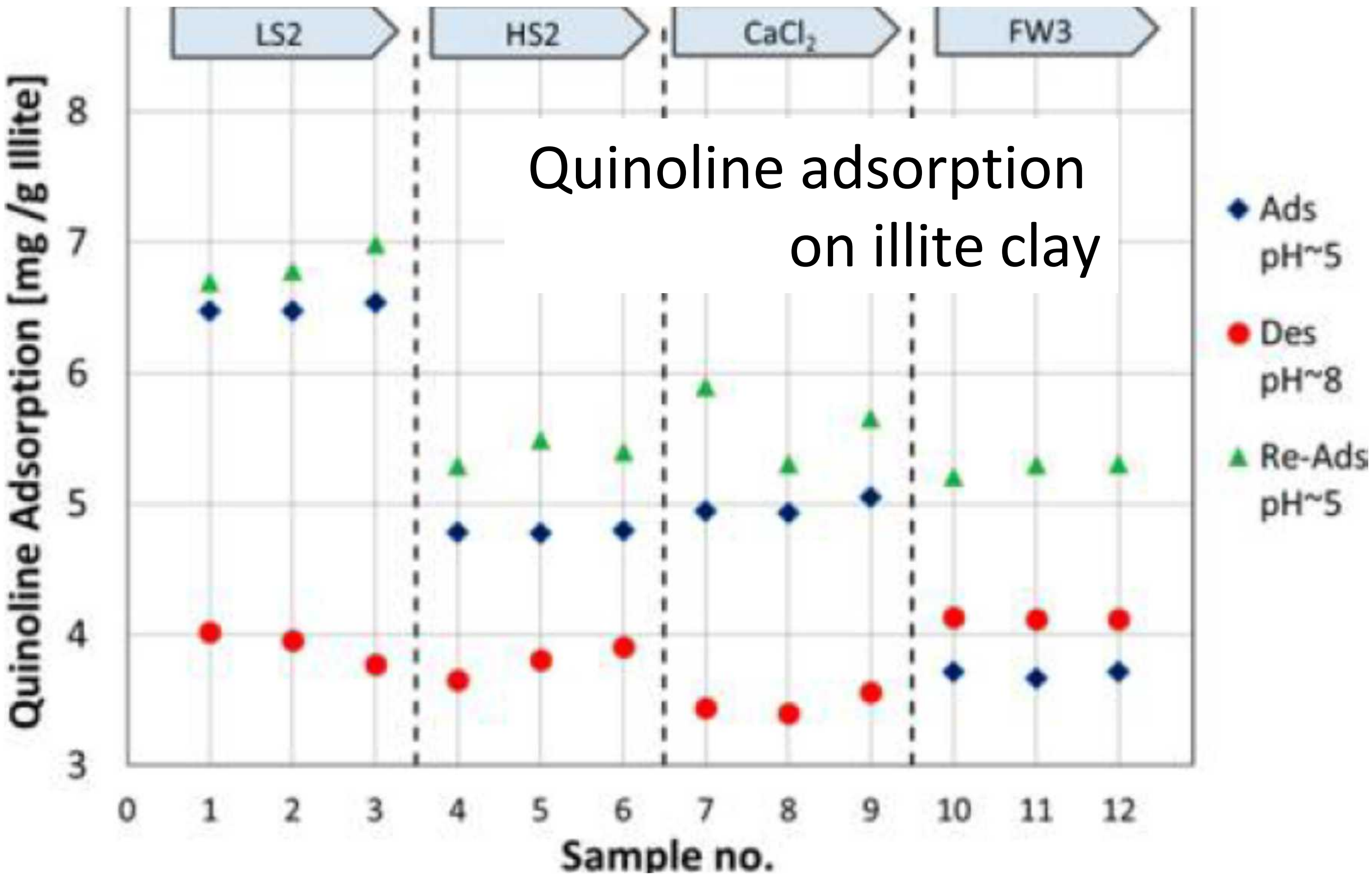
$$>Na + H^+ \leftrightarrow >H + Na^+$$

$$2>Na + Ca^{+2} \leftrightarrow >Ca + 2Na^+$$

Cation Exchange Capacity, CEC (meq/100g)

$$= >Na + >H + 2>Ca$$

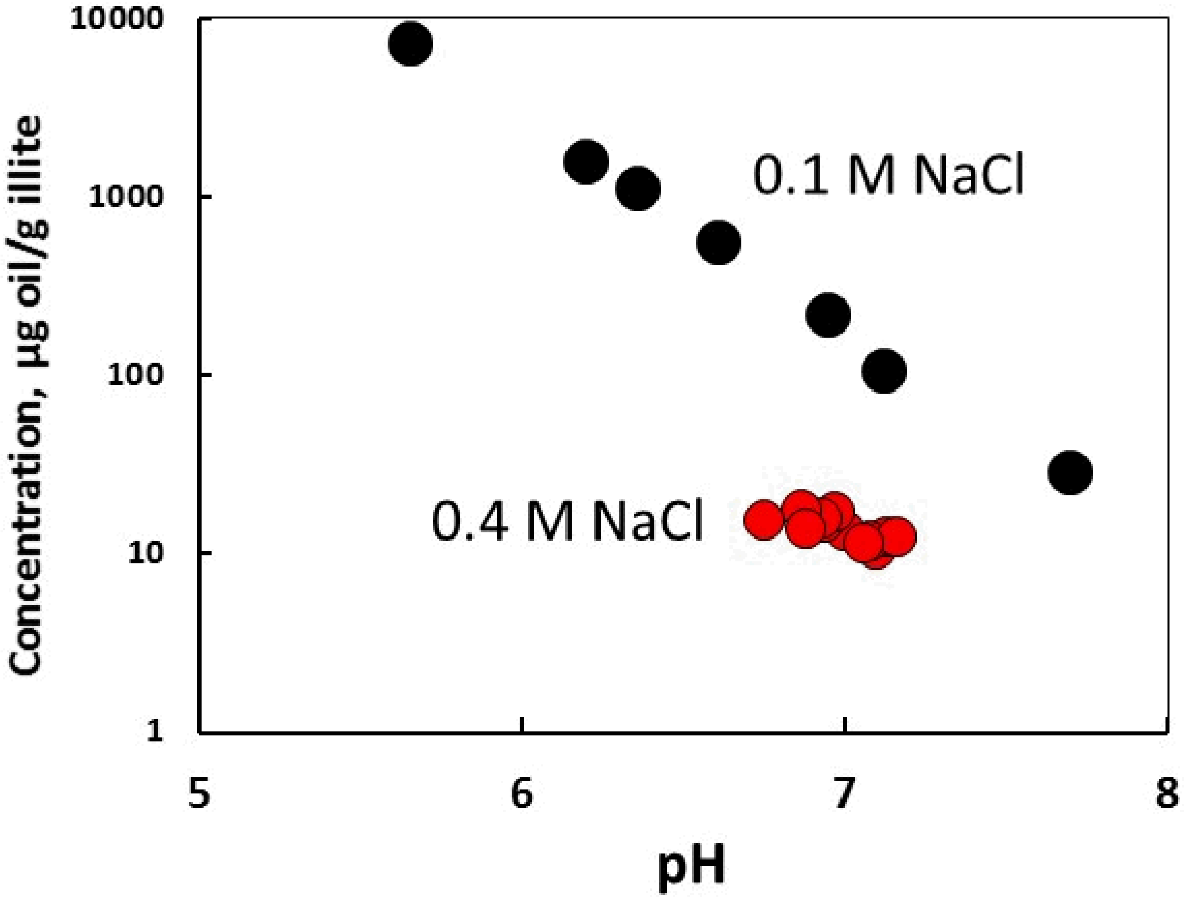
CEC: Smectite > Illite/Chlorite > Kaolinite



From: Aghaeifar, Zahra, Skule Strand, Tor Austad, Tina Puntervold, Hakan Aksulu, Kine Navratil, Silje Storås, and Dagny Håmsø. "Influence of Formation Water Salinity/Composition on the Low-Salinity Enhanced Oil Recovery Effect in High-Temperature Sandstone Reservoirs." *Energy & Fuels* 29, no. 8 (2015): 4747-4754.

Oil Adsorption on Illite

Source: C.R. Bryan, Sandia Labs



Both Oil and Illite have negative zeta potentials, but there is still sorption.

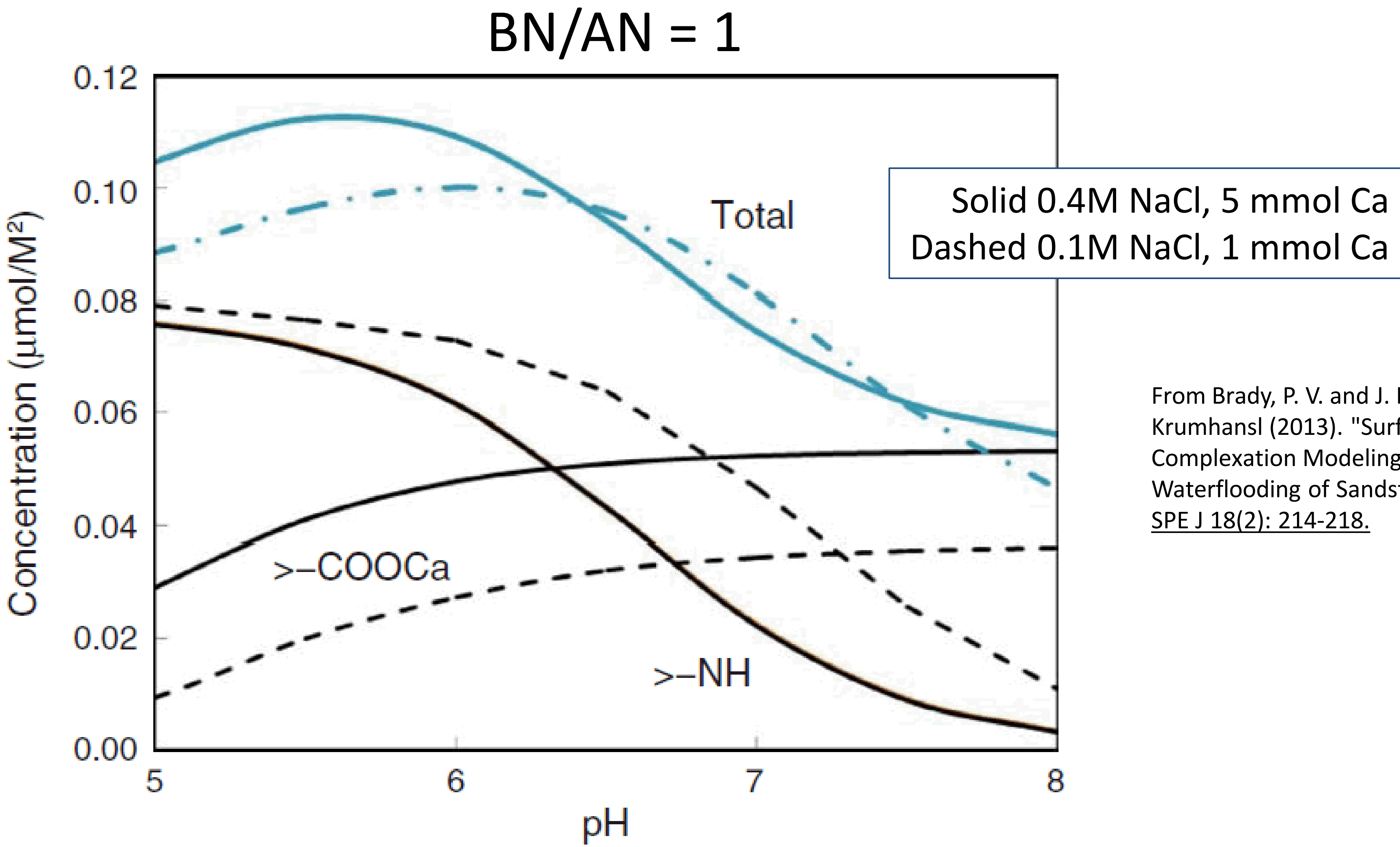
Decreased ionic strength thickens the double layer, but increases oil sorption.

Something besides classical DLVO is controlling wettability.

Oil from West Pearl Queen Field, Hobbs, New Mexico

TBN/TAN ~ 1.3

Oil-Illite Adhesion at 100°C

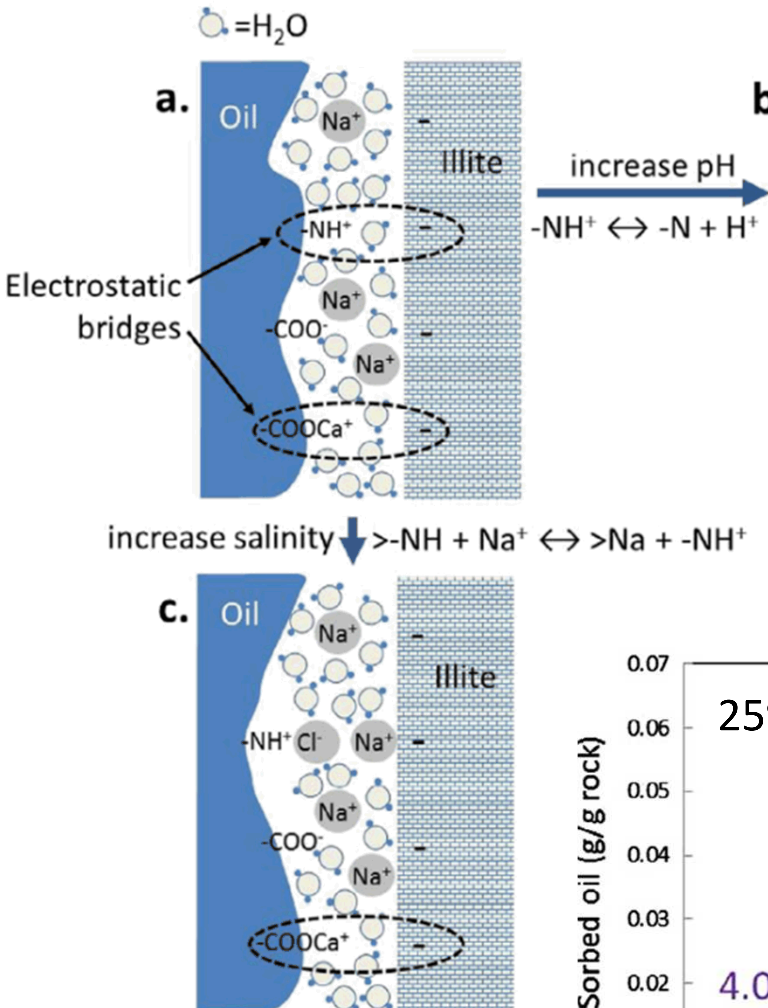


From Brady, P. V. and J. L. Krumhansl (2013). "Surface Complexation Modeling for Waterflooding of Sandstones." SPE J 18(2): 214-218.

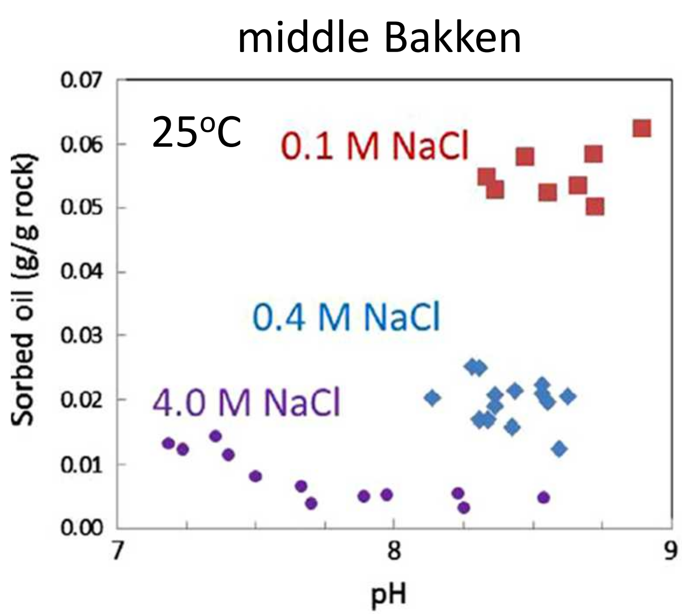
Basin	Production (mbbl/d)	% Carbonate	% Clay	% Kerogen	Dominant clay
Permian	2040	5–40	10–40	1–10	Illite
Bakken	1220	10–15	10–20	2–8	Illite
Eagle Ford	900	40–60	10–40	5–10	Smec/illite/kaol

[a] Balance is mostly quartz or biogenic silica.

Oil-Illite Adhesion in Tight Formations

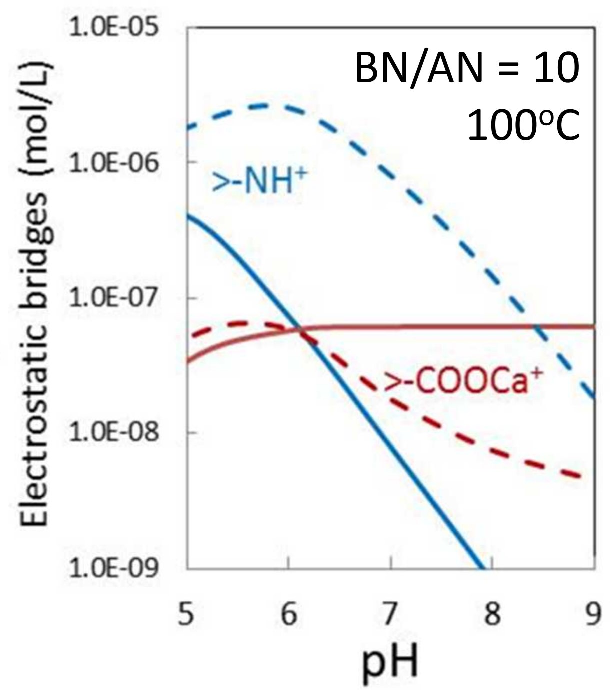


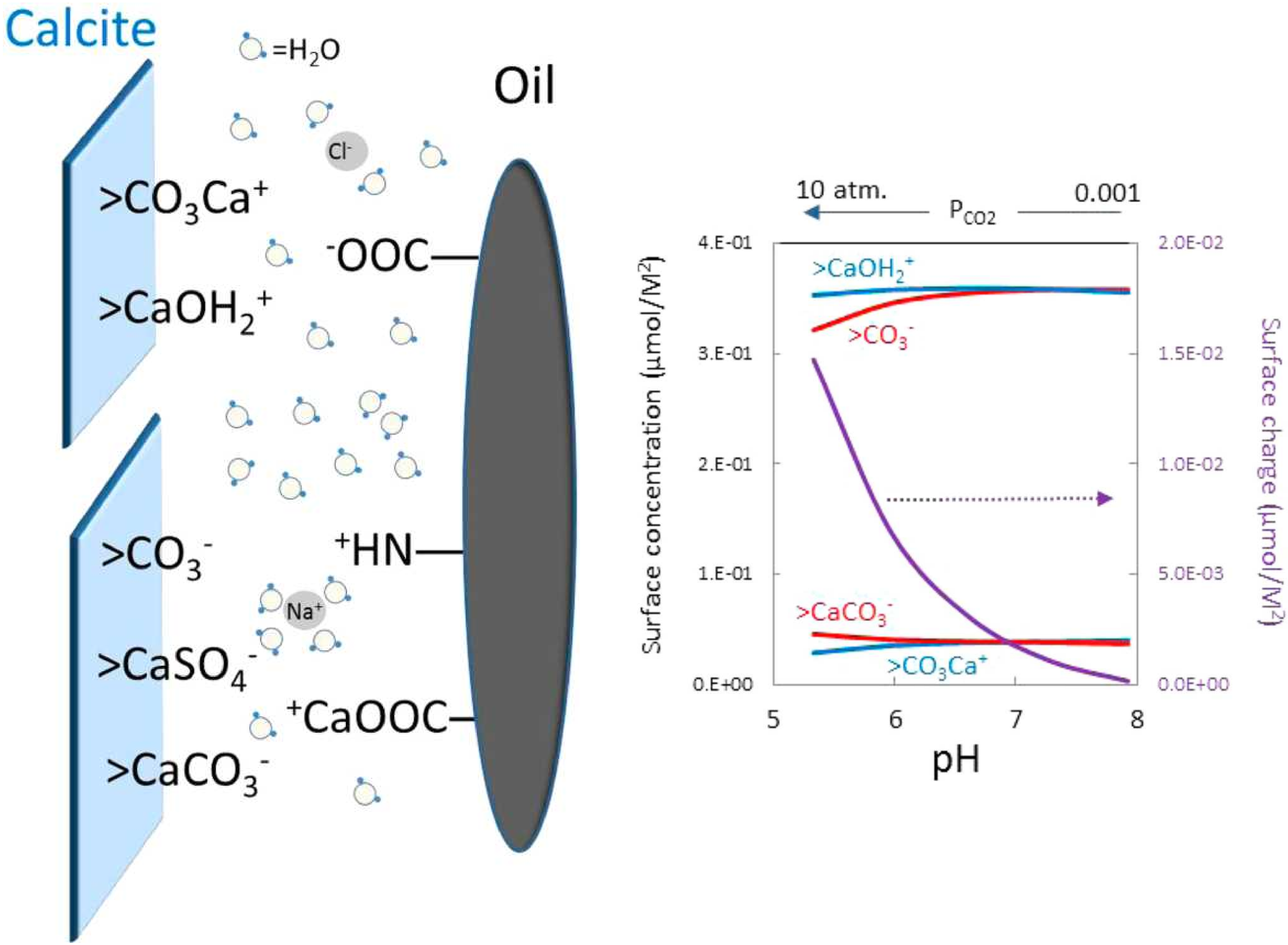
Brady et al. (2016) J. Unconventional Oil and Gas Resources



Solid = Hi TDS

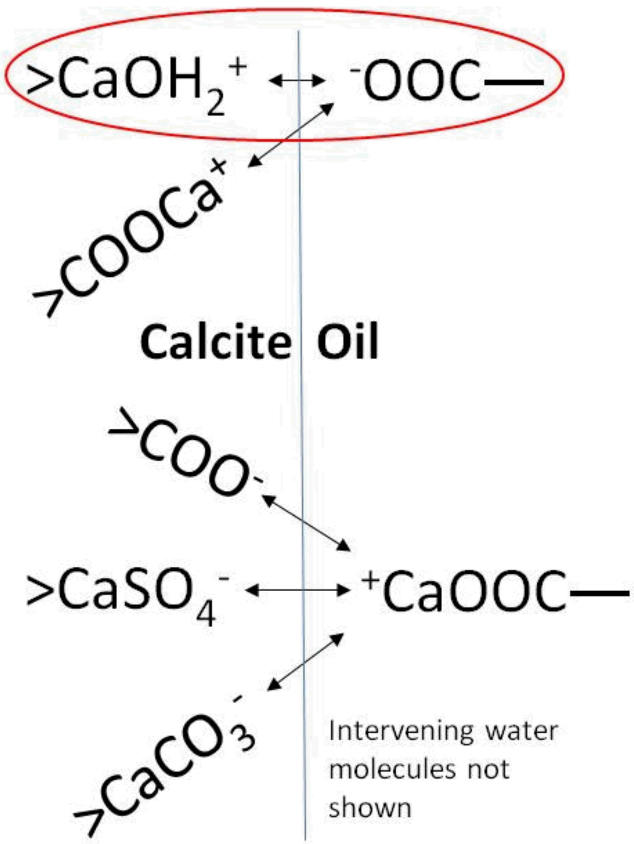
Dash = Low TDS

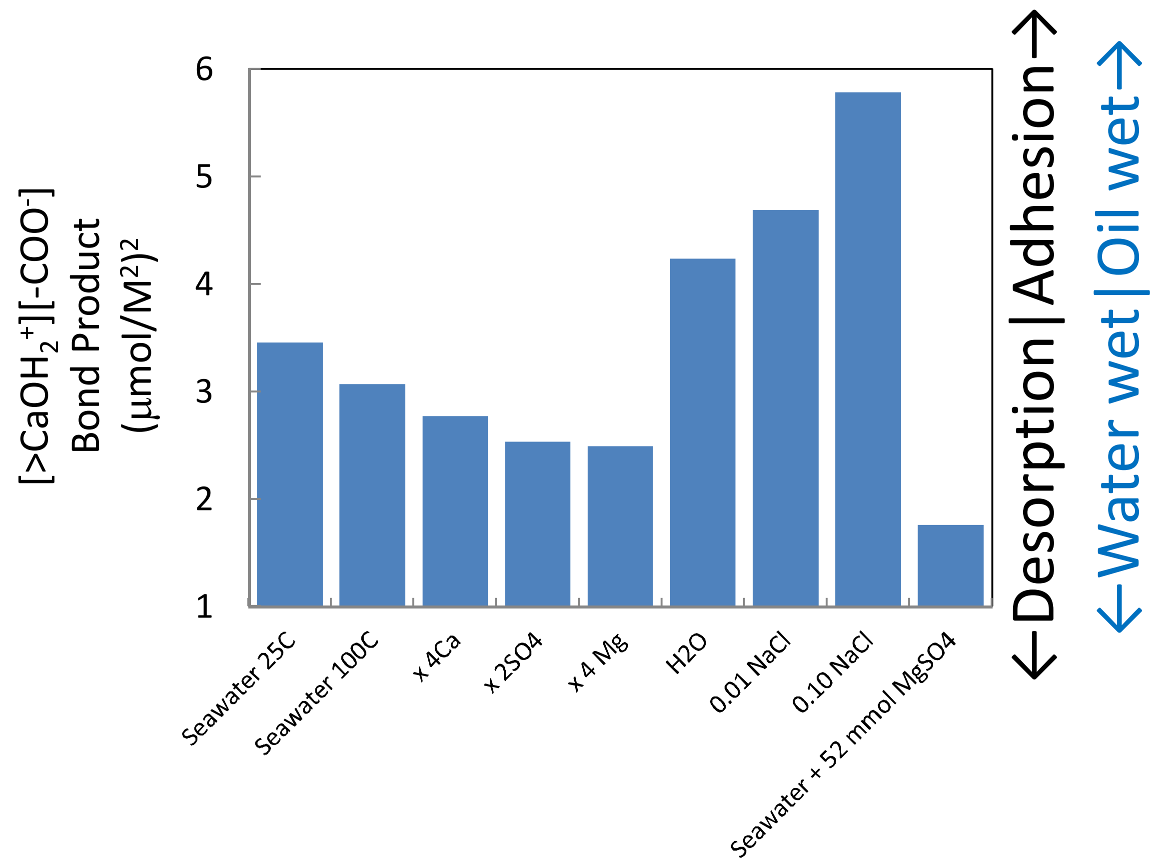




Calcite
=H2O
Oil
Cl-
>CO3Ca+
-OOC
>CaOH2+
>CO3-
+HN
Na+
>CaSO4-
+CaOOC
>CaCO3-
10 atm.
PCO2
0.001
Surface concentration (µmol/M2)
Surface charge (µmol/M2)
4.E-01
3.E-01
2.E-01
1.E-01
0.E+00
2.0E-02
1.5E-02
1.0E-02
5.0E-03
0.0E+00
>CaOH2+
>CO3-
>CaCO3-
>CO3Ca+
5
6
7
8
pH

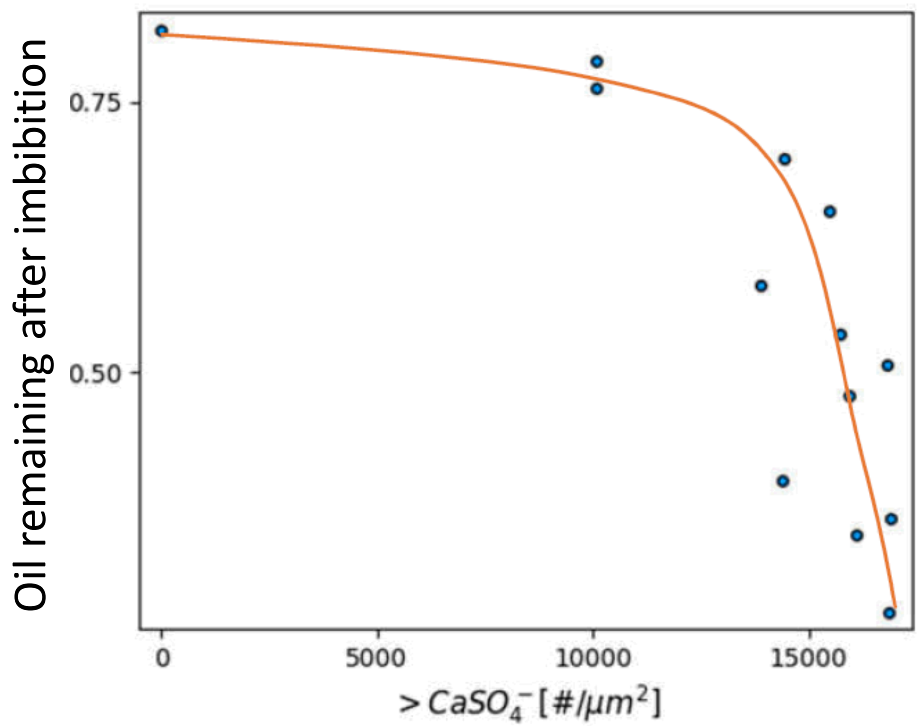
Oil-Limestone Adhesion

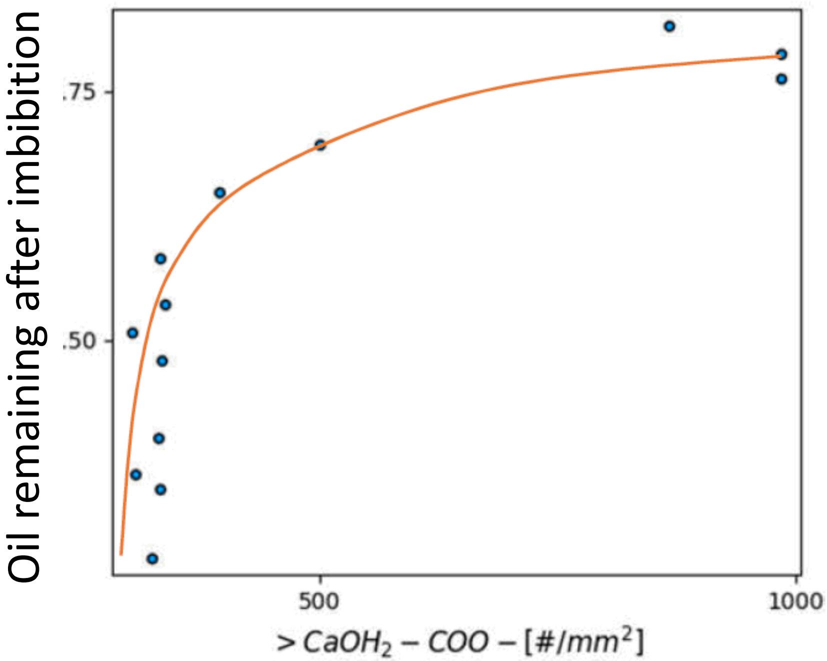




From: Brady, Patrick Vane, James L. Krumhansl, and Paul E. Mariner. "Surface complexation modeling for improved oil recovery." In *SPE Improved Oil Recovery Symposium*. Society of Petroleum Engineers, 2012.

Bond Products and imbibition





From: Eftekhari, A. A., H. Baghooee, M. la Cour Christensen, K. Thomsen, H. M. Nick, and E. Stenby. "Uncertainties in the Mechanistic Models of the Modified Brine Water-flooding of Chalk." In *IOR 2017-19th European Symposium on Improved Oil Recovery*. 2017.

Bond Products and Core floods

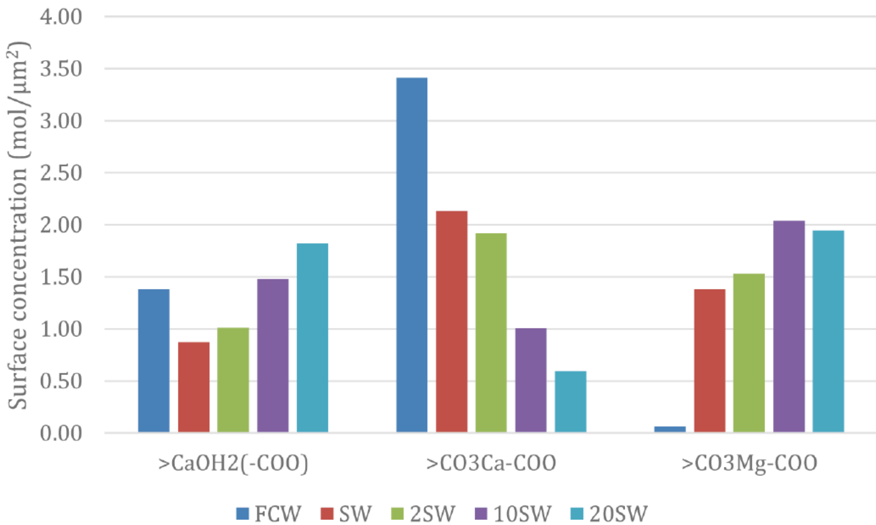
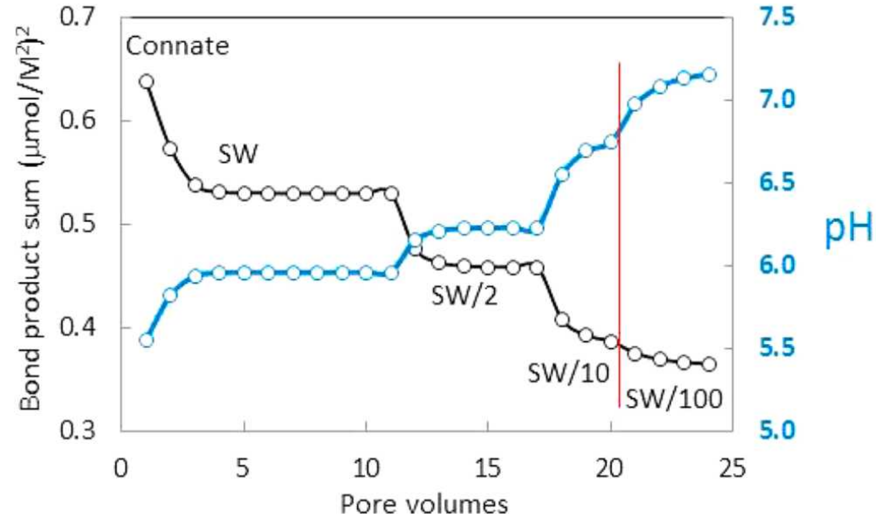
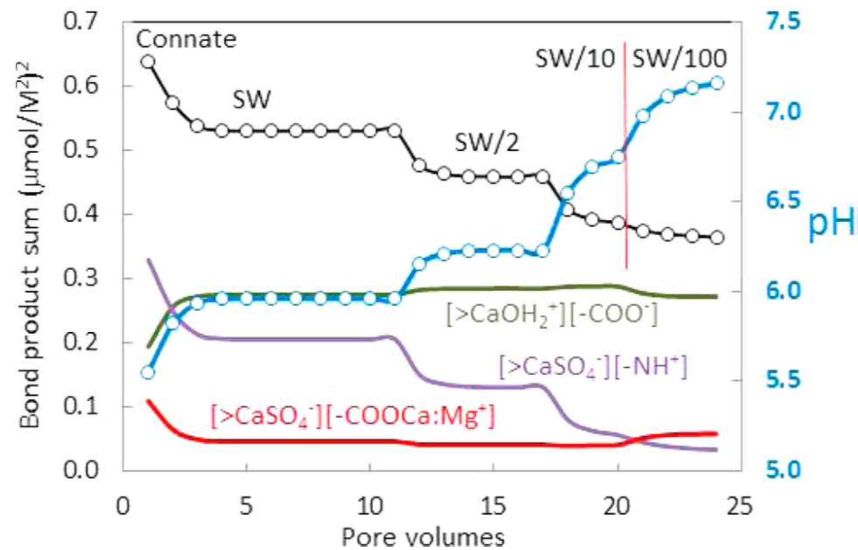


Figure 2—Calculated adsorbed carboxylic acid for brine in Yousef et al. (2010).

From: Qiao, Changhe, Li Li, Russell T. Johns, and Jinchao Xu. "A mechanistic model for wettability alteration by chemically tuned waterflooding in carbonate reservoirs." *SPE Journal* 20, no. 04 (2015): 767-783.





Brady, Patrick V., and Geoffrey Thyne. "Functional wettability in carbonate reservoirs." *Energy & Fuels* 30, no. 11 (2016): 9217-9225.

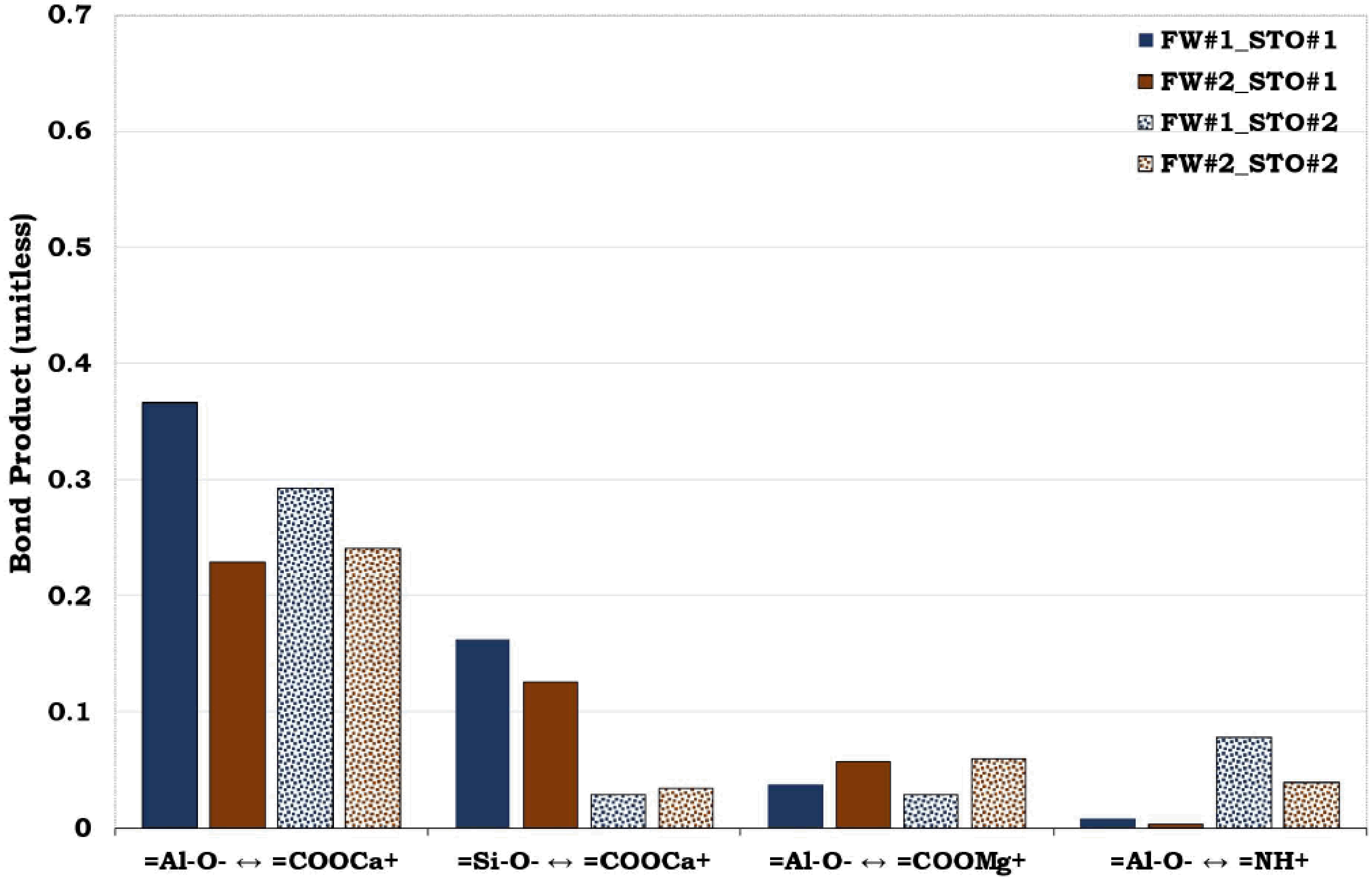
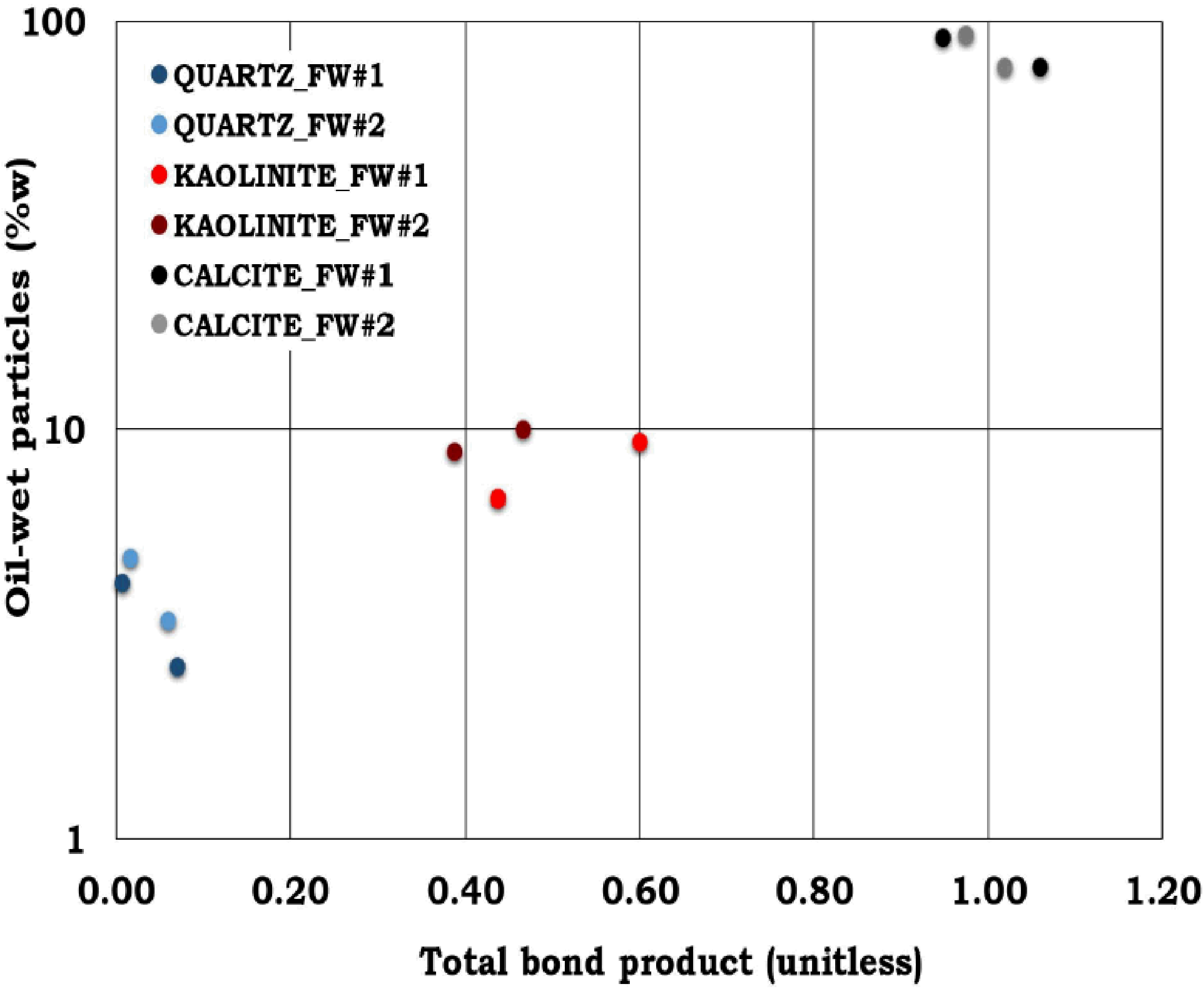


Figure 3—The bond product of the dominant electrostatic pair linkage in kaolinite

From: Erzuah, S., I. Fjelde, and A. V. Omekeh. "Wettability Estimation by Surface Complexation Simulations." In *79th EAGE Conference and Exhibition 2017-SPE EUROPEC*. 2017.



From: Erzuah, S., I. Fjelde, and A. V. Omekeh. "Wettability Estimation by Surface Complexation Simulations." In *79th EAGE Conference and Exhibition 2017-SPE EUROPEC*. 2017.

Kaolinite Edges

$>Al\text{-}O\text{-}H_2^+ \leftrightarrow >Al\text{-}O\text{-}H + H^+$

$>Al\text{-}O\text{-}H \leftrightarrow >Al\text{-}O^- + H^+$

Oil

$\text{-}NH^+ \leftrightarrow \text{-}N + H^+$

$\text{-}COOH \leftrightarrow \text{-}COO^- + H^+$

$\text{-}COOH + Ca^{+2} \leftrightarrow \text{-}COOCa^+ + H^+$

Illite, Smectite, Kaolinite Basal Planes

$Na + H^+ \leftrightarrow >H + Na^+$

$>Na + \text{-}NH^+ \leftrightarrow >\text{-}NH + Na^+$

$>Na + \text{-}COOCa^+ \leftrightarrow >\text{-}COOCa + Na^+$

$2>Na + Ca^{+2} \leftrightarrow >Ca + 2Na^+$

Calcite

$>CaOH + H^+ \leftrightarrow >CaOH_2^+$

$>CaOH + HCO_3^- \leftrightarrow >CaCO_3^- + H_2O$

$>CaOH_2^+ + SO_4^{-2} \leftrightarrow >CaSO_4^- + H_2O$

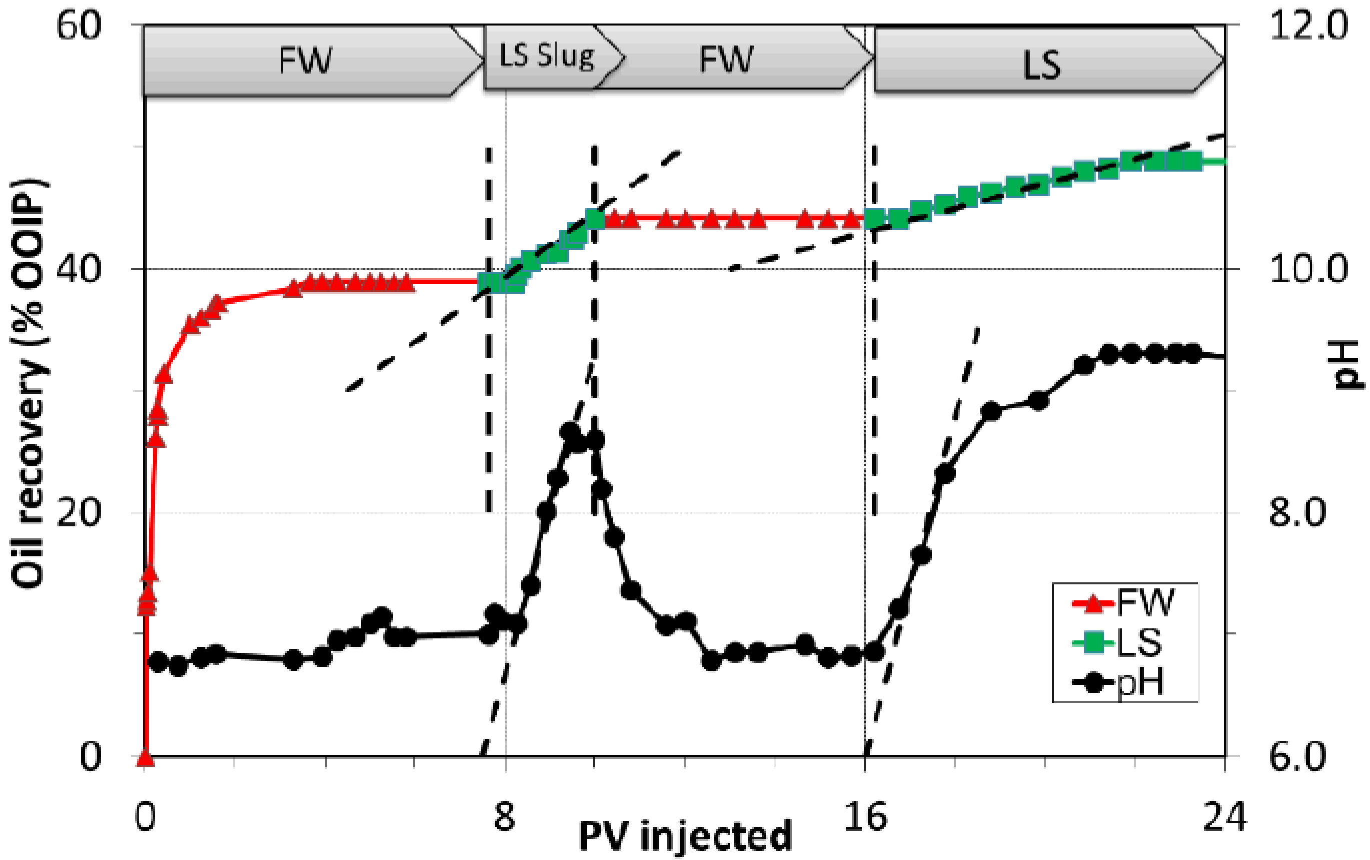
$>CO_3H \leftrightarrow >CO_3^- + H^+$

$>CO_3H + Ca^{+2} \leftrightarrow >CO_3Ca^+ + H^+$

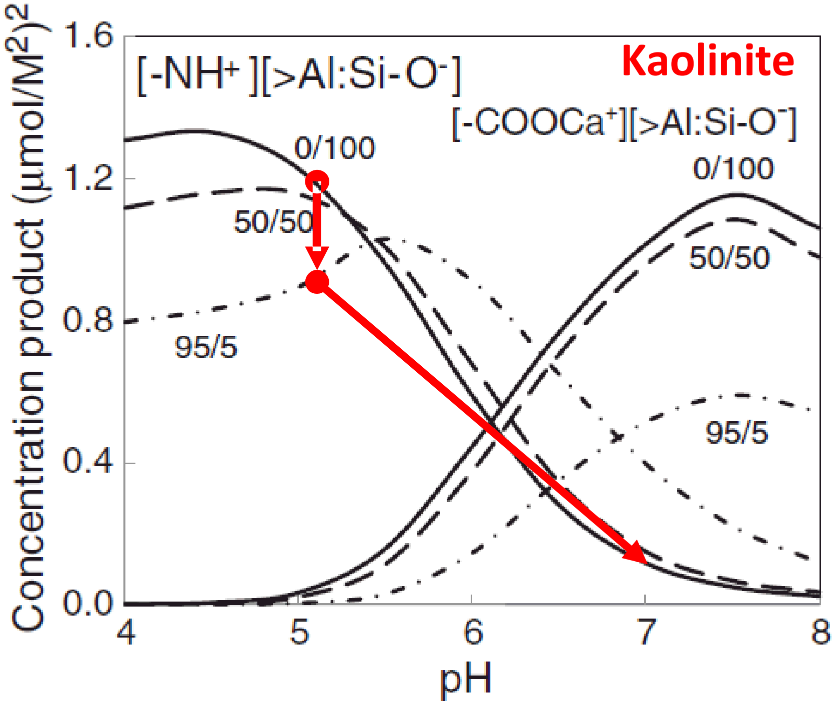
$>CO_3H + Mg^{+2} \leftrightarrow >CO_3Mg^+ + H^+$

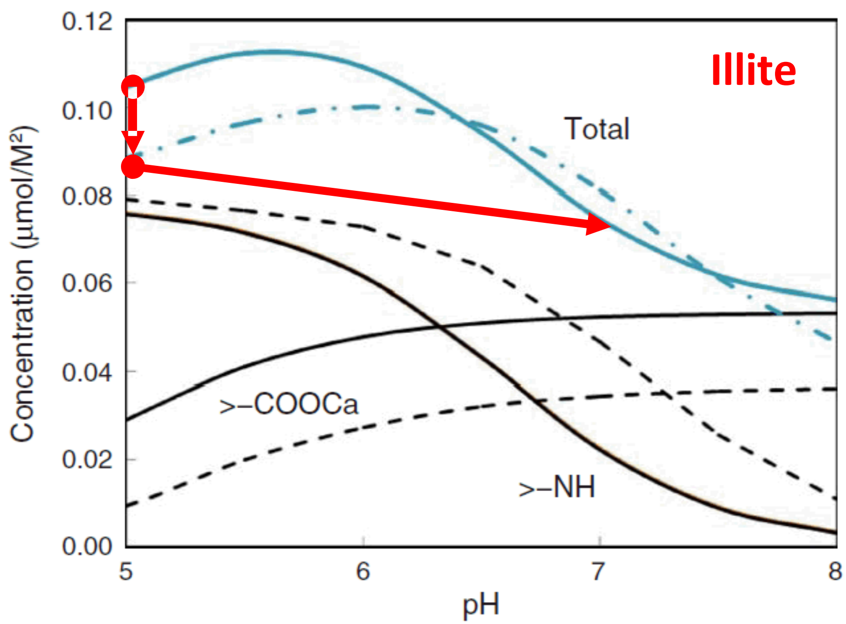
Reservoir Geochemistry: Predicting wettability alteration

Pat Brady, Sandia Labs



Ivan Pinerez Ph.D. Thesis, Univ. Stavanger, Enhanced oil recovery from Sandstones and Carbonates with "Smart Water" (2017).





Decreasing salinity increases pH which (usually) decreases the bond product, which usually makes more water wet, which usually means more oil.

1. What is the salinity?

2. What are initial pH, Ca+Mg, Sulfate and how will they change?

    What is the P_{CO2}?

    Which minerals will grow/dissolve?

    How much ion exchange?

3. How will the above affect oil-rock adhesion?

```
SOLUTION 1
# Connate water
-units mg/l
-temp  100
pH 7.0     charge
Ca 19040
Mg 2439
#C(4) 354   as HCO3
C(4) 354 as HCO3 CO2(g) -3.5
S(6) 350 as SO4
Na 59491
Cl 132060
```

```
EXCHANGE 1
X 0.068
-equilibrate with solution 1
```

```
USE SOLUTION 1
USE surface 1
EQUILIBRIUM_PHASES 1
Calcite 0.0 1.0
Anhydrite   0.0 1.0
Dolomite 0.0 1.0
```

Over water-flooding time-scales:

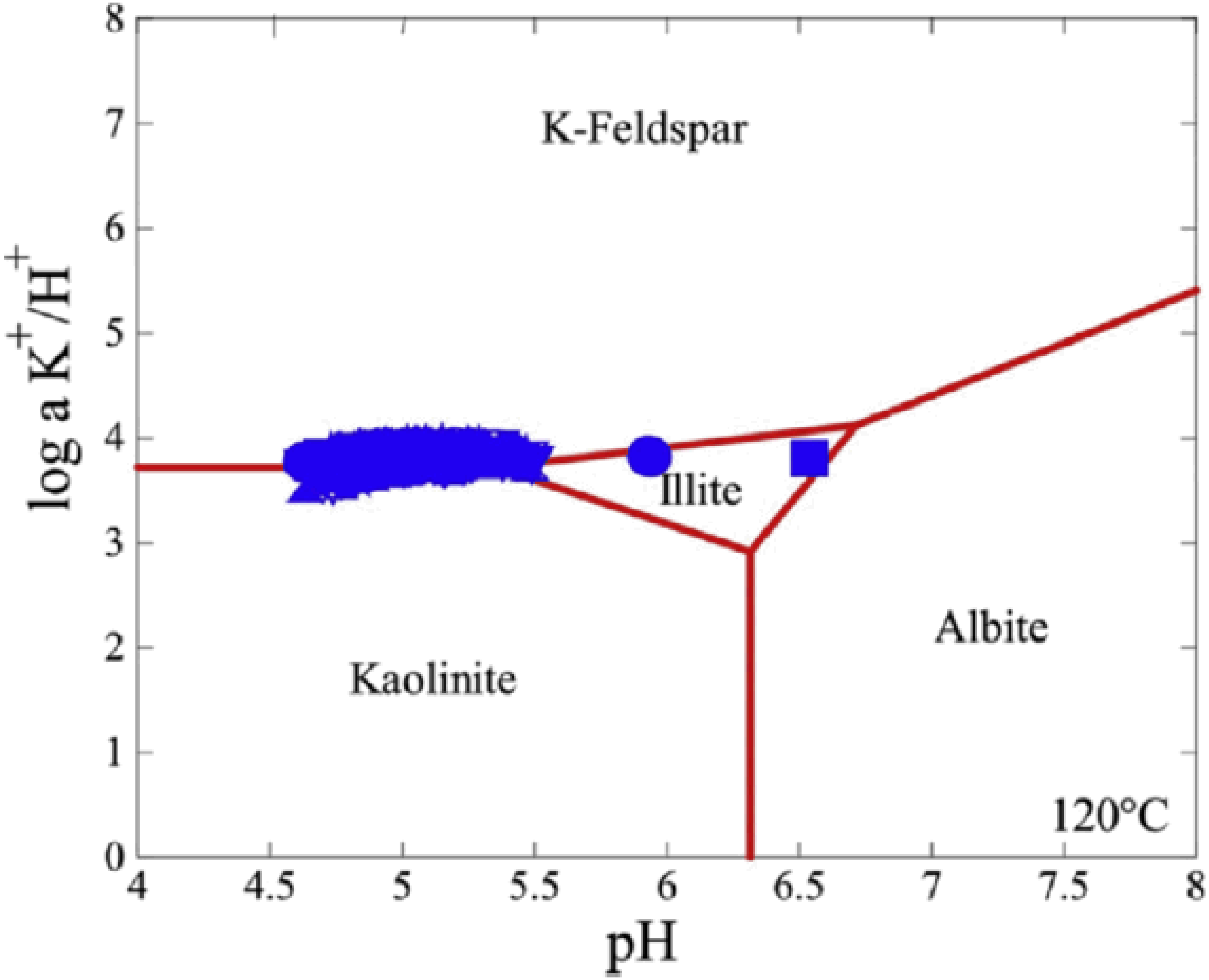
1. Salinity is what it is and won't change except through dilution, IX.
2. Calcium carbonate and sulfate minerals always at equilibrium.
3. Dolomite will only grow at T >100^{o}C.
4. Silicate minerals will neither grow nor dissolve.

Aqueous reactions
Ion Exchange
Oil/Mineral surface reactions
Oil Desorption
Carbonate/Sulfate reactions
At ~ 100^{o}C
Silicate reactions

Seconds Days Decades

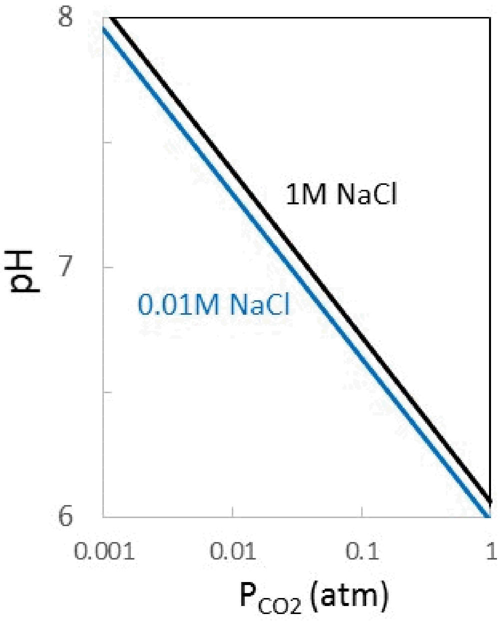
Why and how pH shifts

pH goes Up	
Calcite/Dolomite Dissolution	$H^+ + CaCO_3 \leftrightarrow Ca^{+2} + HCO_3^-$
CO_2 degassing	$H^+ + HCO_3^- \leftrightarrow CO_2\uparrow + H_2O$
Ion Exchange/Dilution	$>Na + H^+ \leftrightarrow >H + Na^+$
Albite dissolution	$NaAlSi_3O_8 + H^+ + H_2O \leftrightarrow Al(OH)_3 + 3SiO_2 + Na^+$
pH goes Down	
CO_2 increase – oxidation	$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$
CO_2 increase - salinity	$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$
Sulfide dissolution	$FeS_2 + 7/2O_2 + H_2O \leftrightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+$
Calcite/Dolomite Growth	$Ca^{+2} + HCO_3^- \leftrightarrow H^+ + CaCO_3$
Ion Exchange/Concentration	$>H + Na^+ \leftrightarrow >Na + H^+$



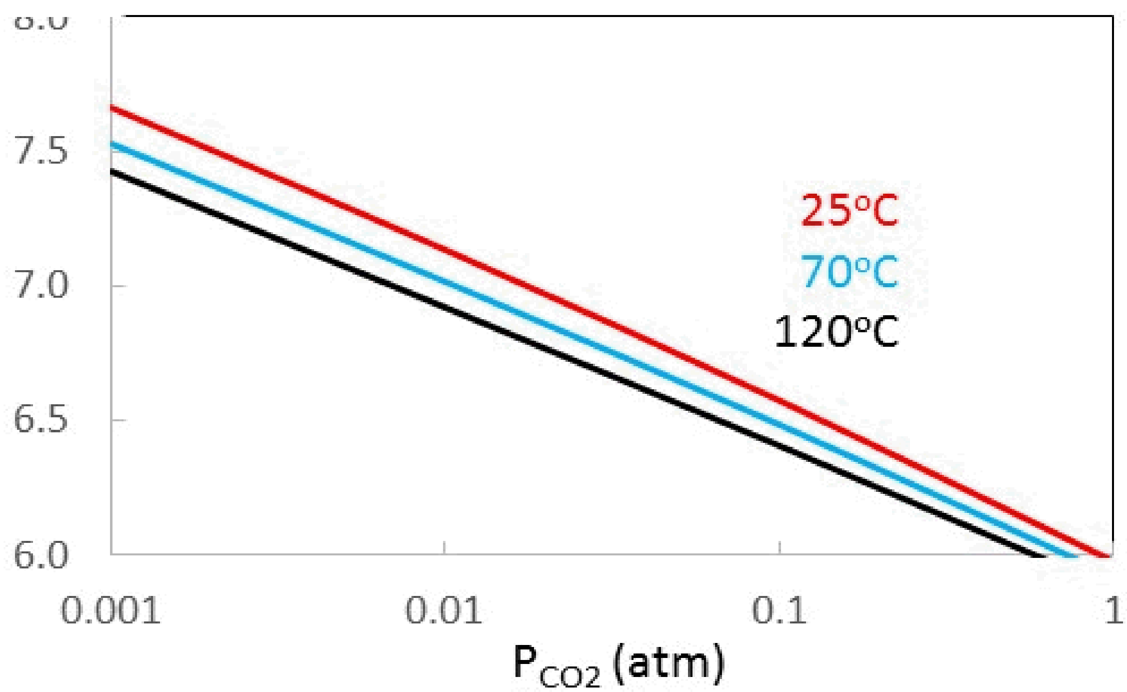
$$2KAlSi_3O_8 + H_2O + 2H^+ \leftrightarrow Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2K^+$$

From: Thyne, Geoffrey, and Patrick Brady. "Evaluation of formation water chemistry and scale prediction: Bakken Shale." *Applied Geochemistry* 75 (2016): 107-113.

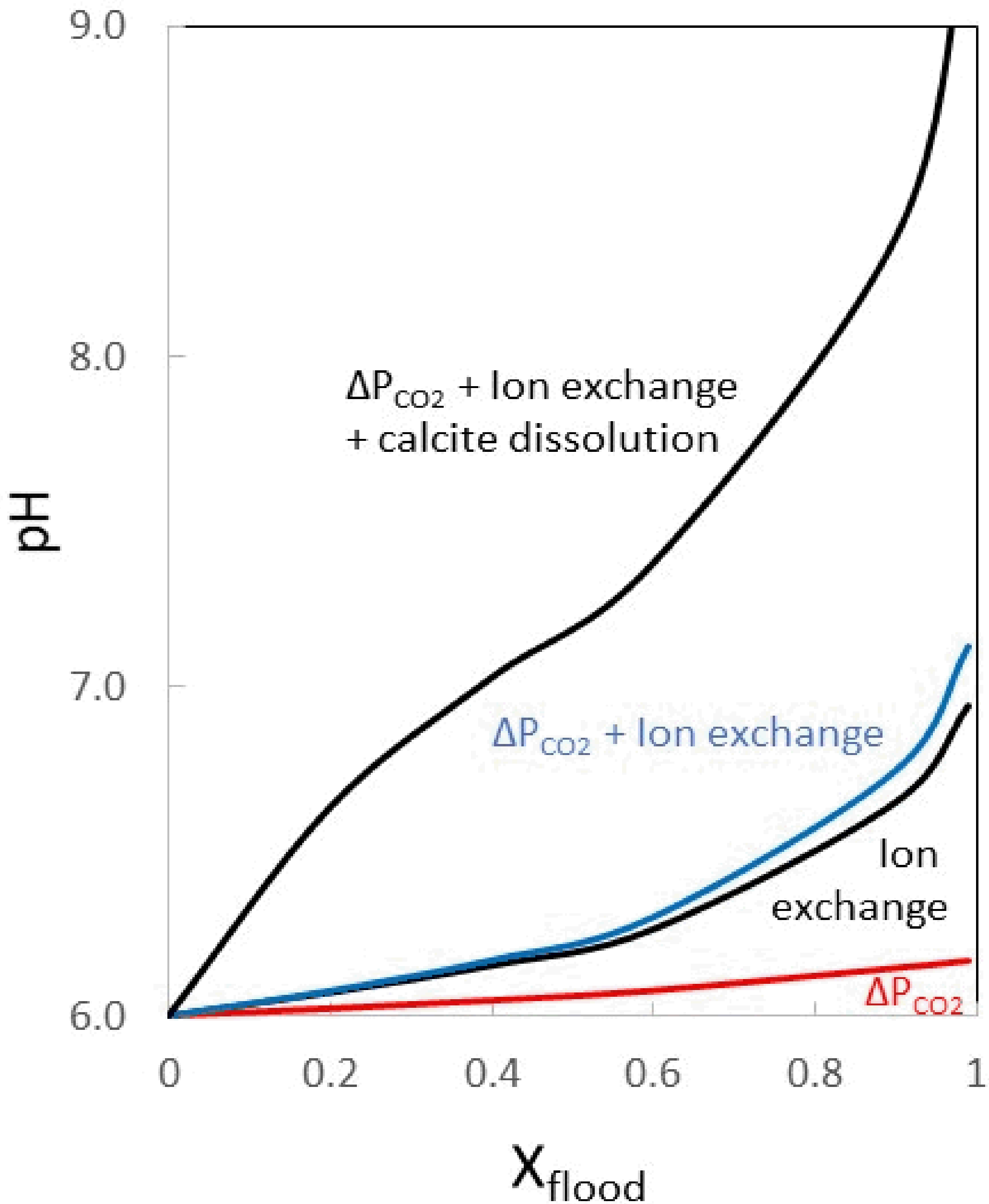


Salinity and pH: Water

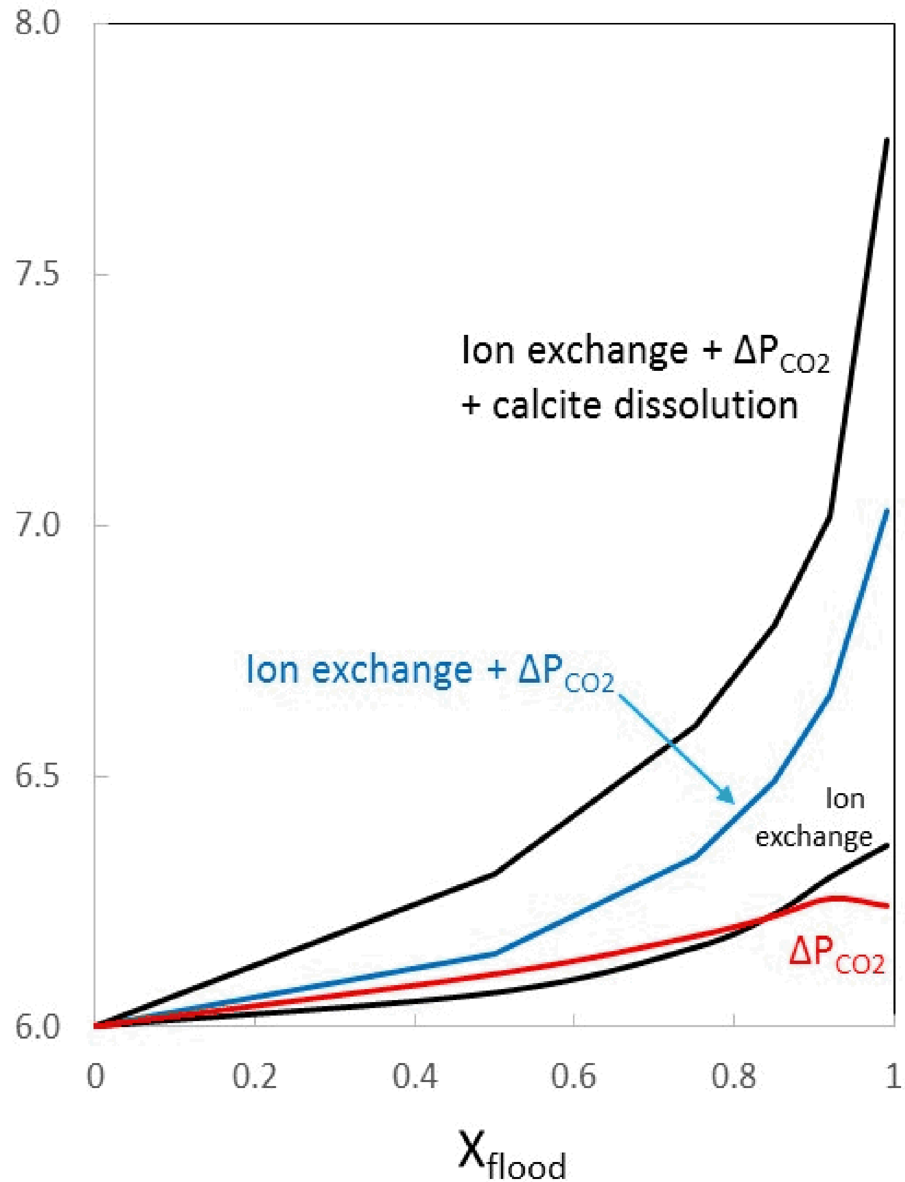
Temperature and pH: Water and Calcite



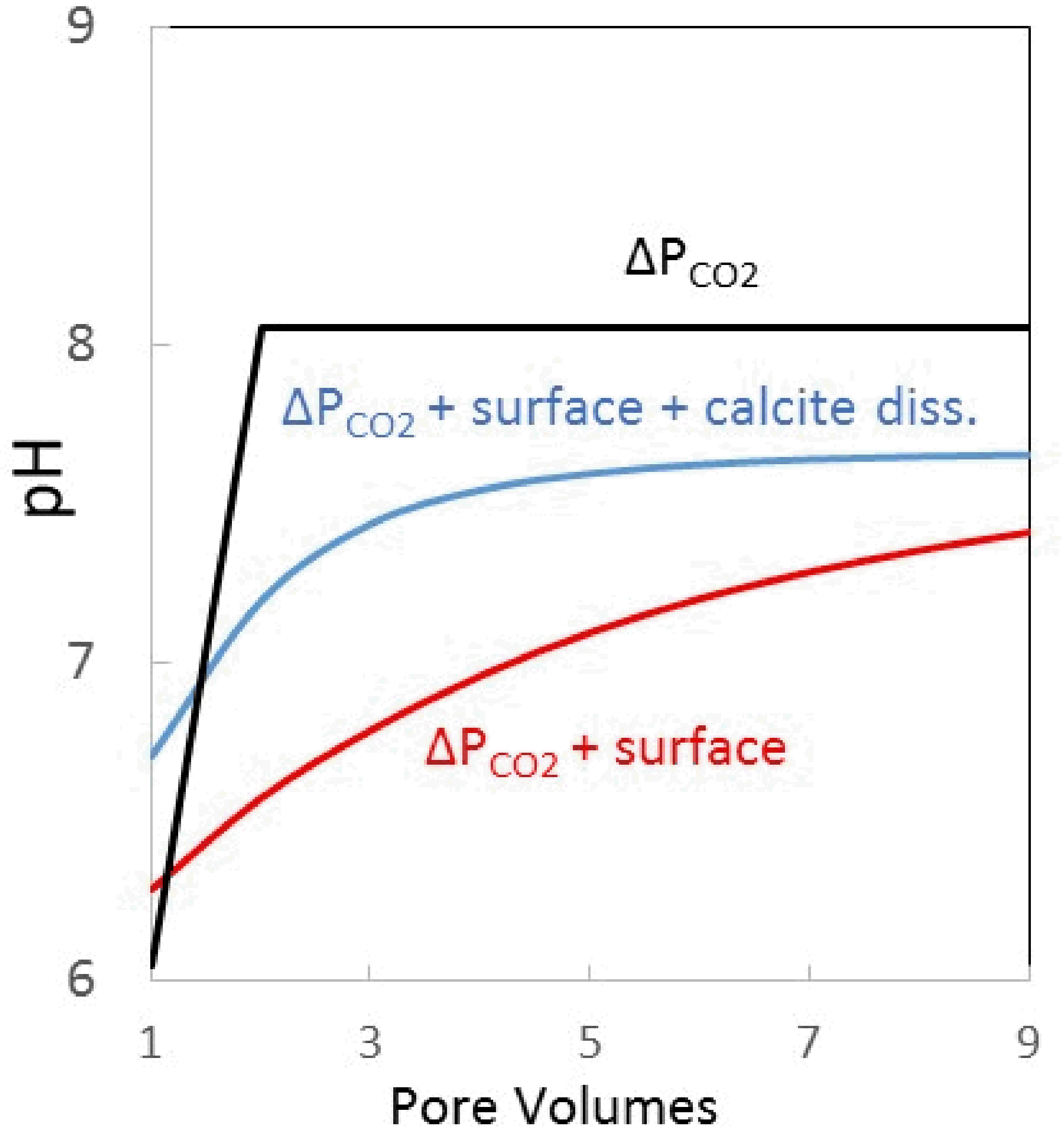
Sandstone + Kaolinite + Calcite Cement at 60ºC



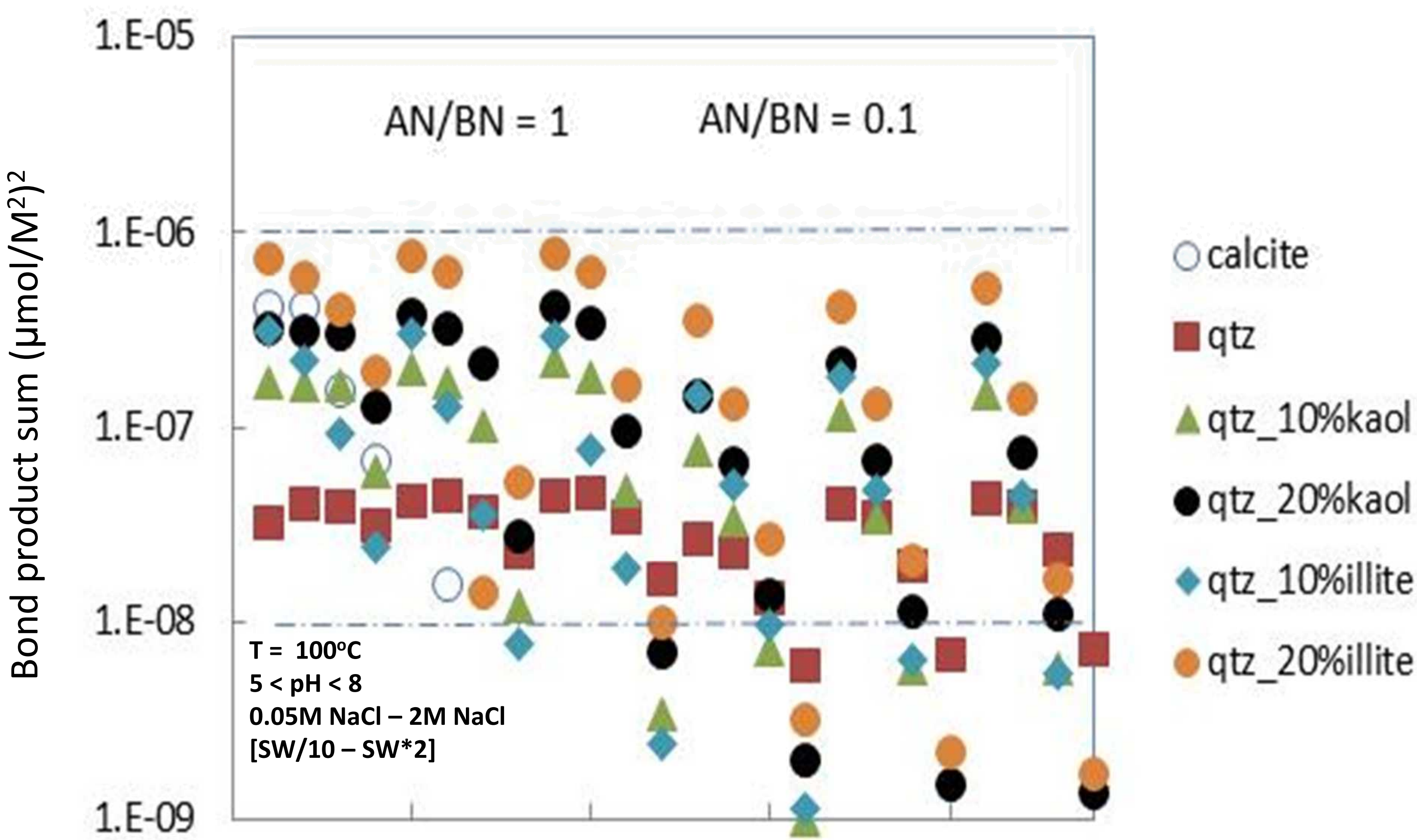
Sandstone + Illite + Calcite Cement at 60°C



Calcite at 25°C



Initial Wettability and Primary Recovery



Oil Adhesion to the World's Reservoirs

Wettability 2030

Pat Brady, Sandia Labs

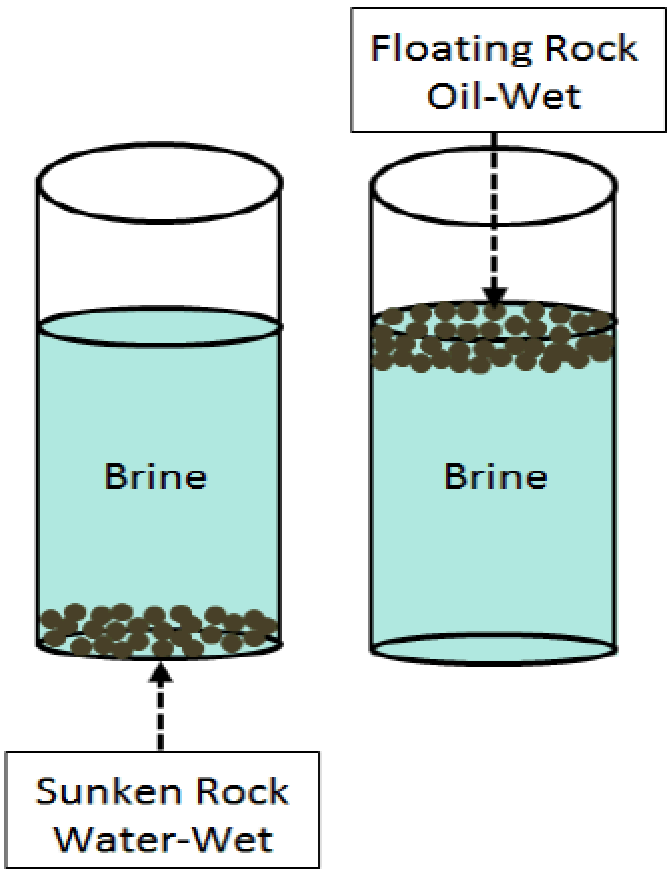
10-30% OOIP was accidental. Could it be greater?
– how to actively manage the reservoir surface chemistry, lots of knobs.

How much can we push the rock?
How much does the rock push back?
Overlaps with other EOR?

Dolomite Surface Chemistry
Kerogen/Shale Surface Chemistry

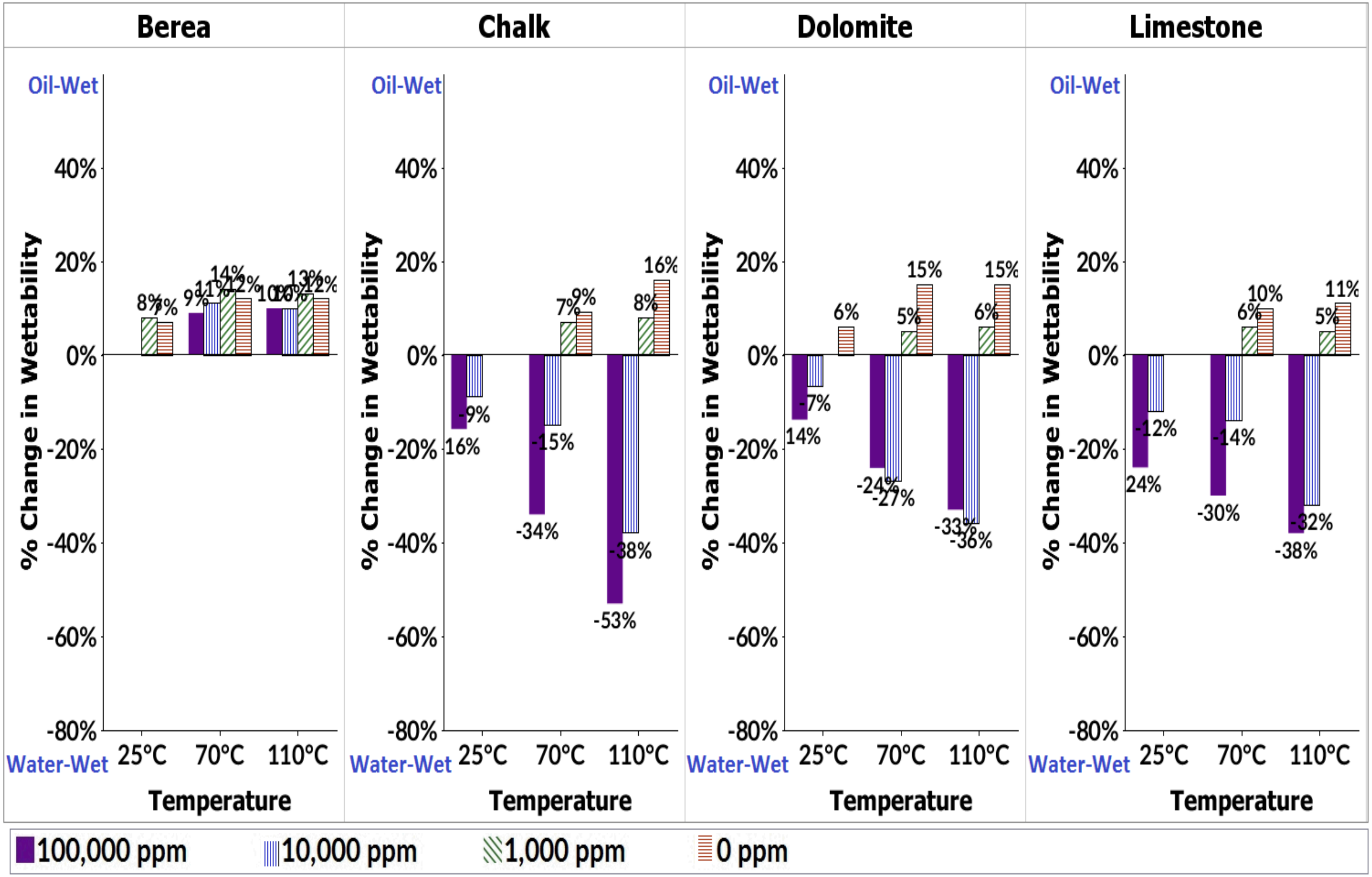
Direct Measurement of Wettability by Flotation

Mwangi and Thyne, Sohal and Thyne, Fjelde et al.



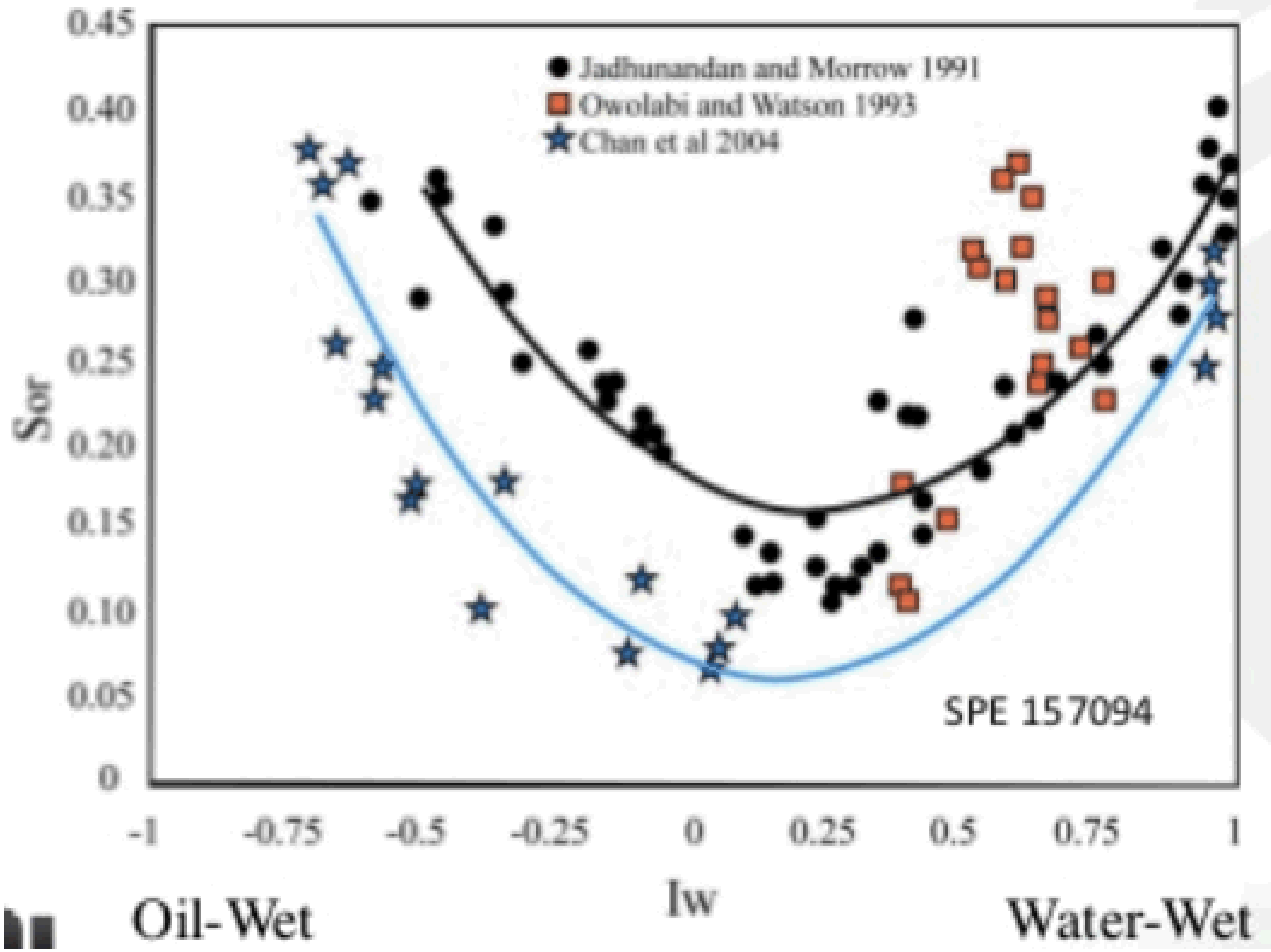
Flotation Test Procedure

- Age 0.2 grams of rock in 10 ml of brine for 48 hours.
- Separate brine from rock, measure pH, and save it for later reuse.
- Age rock in 3ml of oil for 48 hours and stir the mixture every 12 hours.
- Add the saved brine in oil-rock mixture.
- Vigorously stir and allow to settle for 24 hours.
- Decant, dry and weight



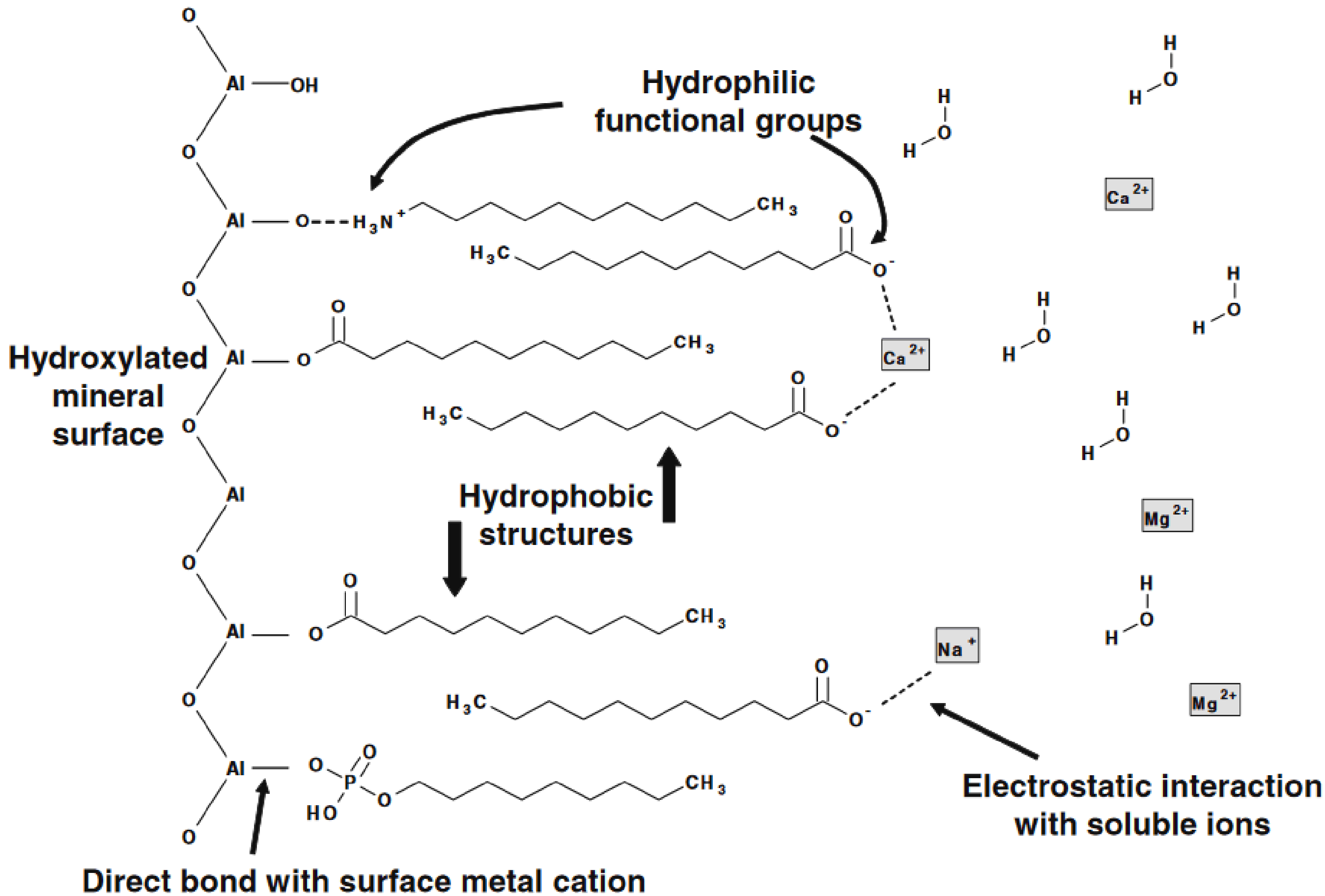
Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when adding 2000 ppm myristic acid (O2) to decane. Values below 5% are not displayed.

From: Mwangi, Thyne, et al. 2017



Courtesy of: Geoffrey Thyne

Organic Coatings on Silicates, Carbonates?



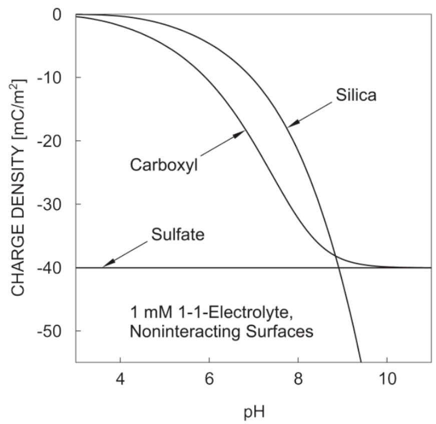
From: Kleber, M., P. Sollins, and R. Sutton. "A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces." *Biogeochemistry* 85, no. 1 (2007): 9-24.

After: Matthiesen, J., Bovet, N., Hilner, E., Andersson, M.P., Schmidt, D.A., Webb, K.J., Dalby, K.N., Hassenkam, T., Crouch, J., Collins, I.R. and Stipp, S.L.S., 2014. How naturally adsorbed material on minerals affects low salinity enhanced oil recovery. *Energy & Fuels*, *28*(8), pp.4849-4858.

EXERCISES

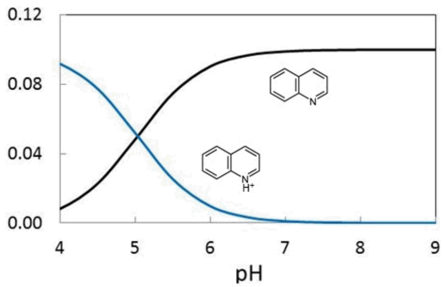
Exercise 1. Using the graphs below write a balanced reaction for sorption of quinoline to quartz as a function of pH. Sketch what the graph should look like if all quinoline-quartz binding is electrostatic. Do the same thing for carboxylate.

http://physics.nyu.edu/grierlab/charge6c/http://physics.nyu.edu/grierlab/charge6c/

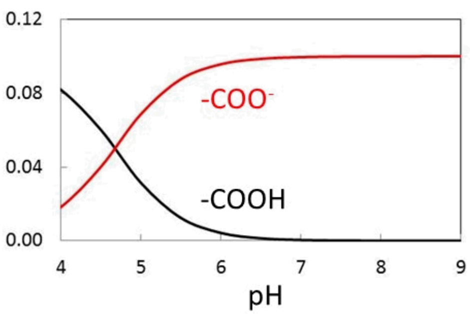


Quartz

Concentration (mol/L)



Quinoline



Carboxyate

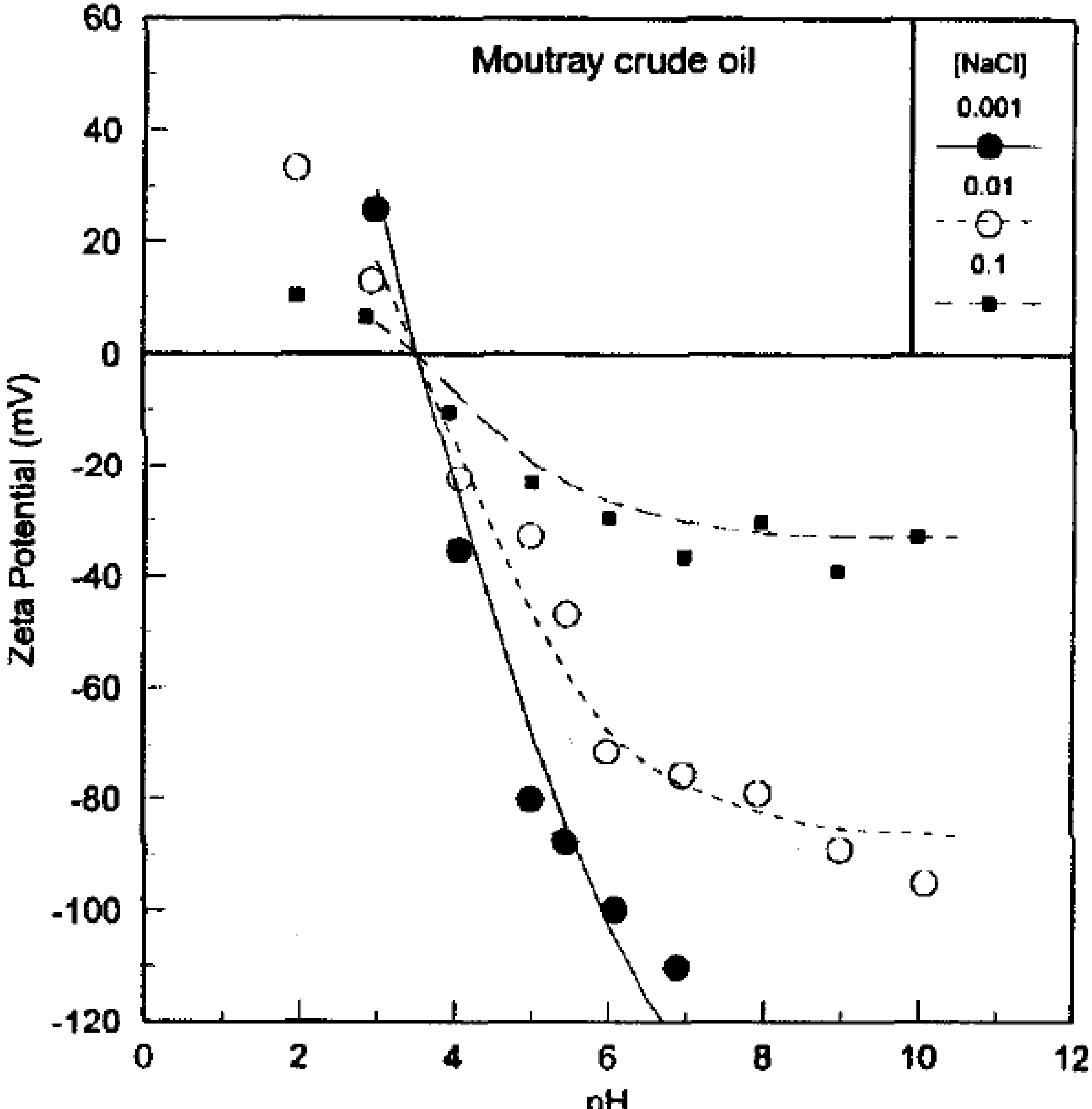
Exercise 2. How will NaCl, $CaCl_2$ affect each of your sorption curves? Make an overlay sketch.

Exercise 3. How much will pH change, if at all, when a low salinity fluid is introduced into a sandstone? a limestone? What will the pH shift depend on? Give as much detail as possible.

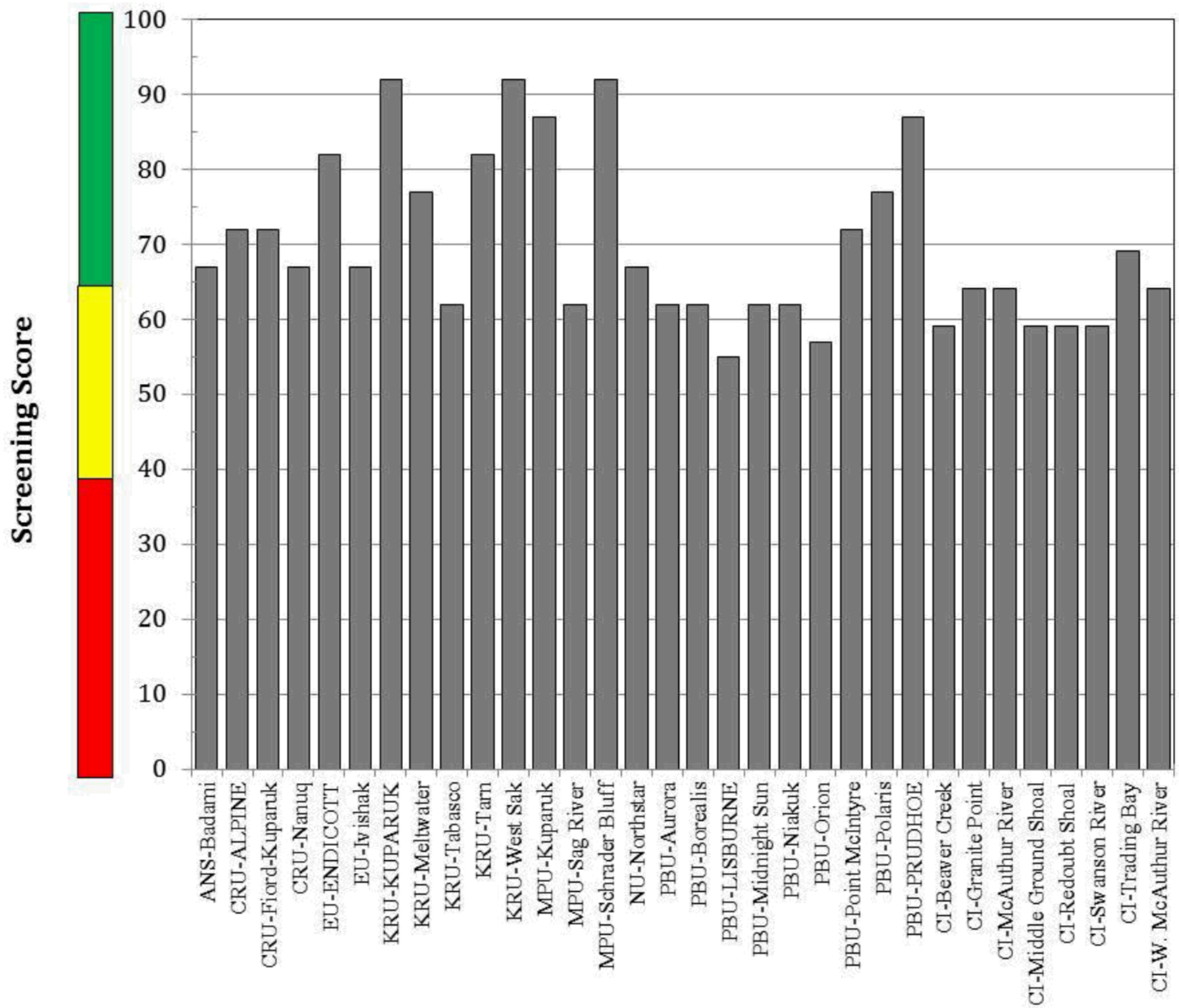
Exercise 4. What does the pH shift calculated in Exercise 3 do to sorption of an AN:BN = 0.1 oil onto a quartz sandstone reservoir?

Exercise 5. Your Boss (from the Dutch word Baas for Master) wants you to say if a SmartWater flood of a particular reservoir could work, and asks what information you'll need to answer the question. What information do you ask for? What calculations do you do?

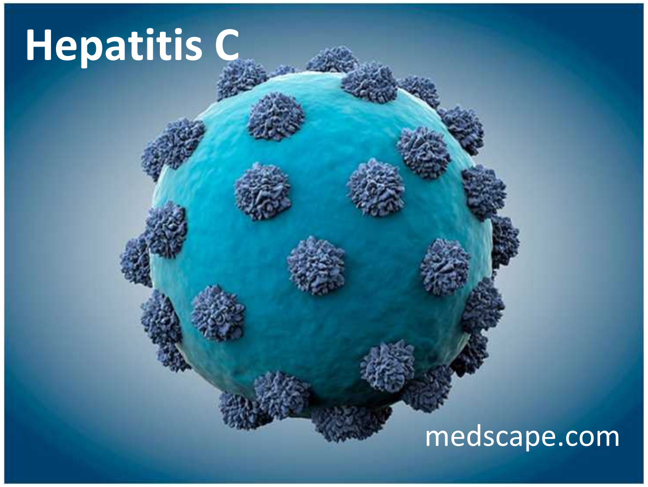
BACKUP SLIDES

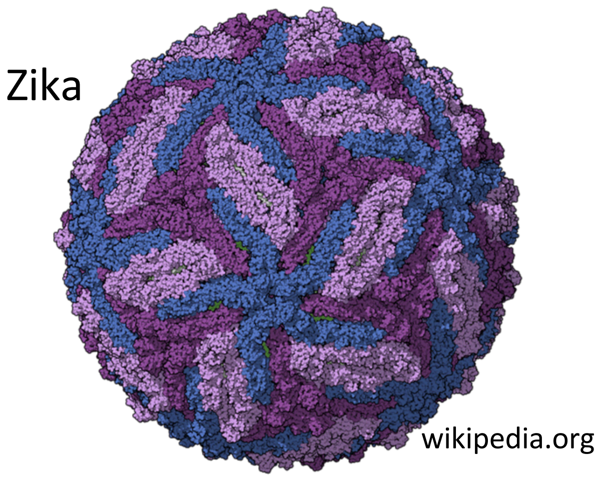


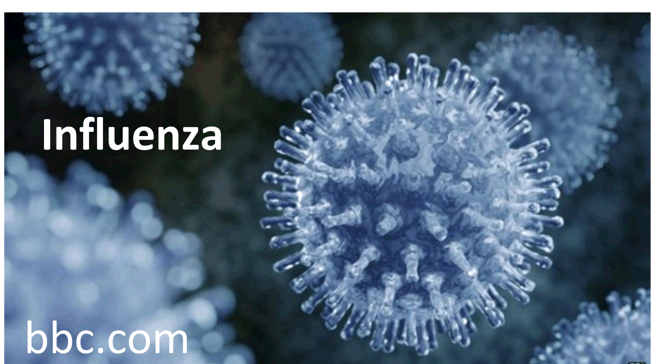
Buckley, Jill S. "Chemistry of the crude oil/brine interface." In *Proc. 3 rd International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery*, pp. 33-38. 1994.

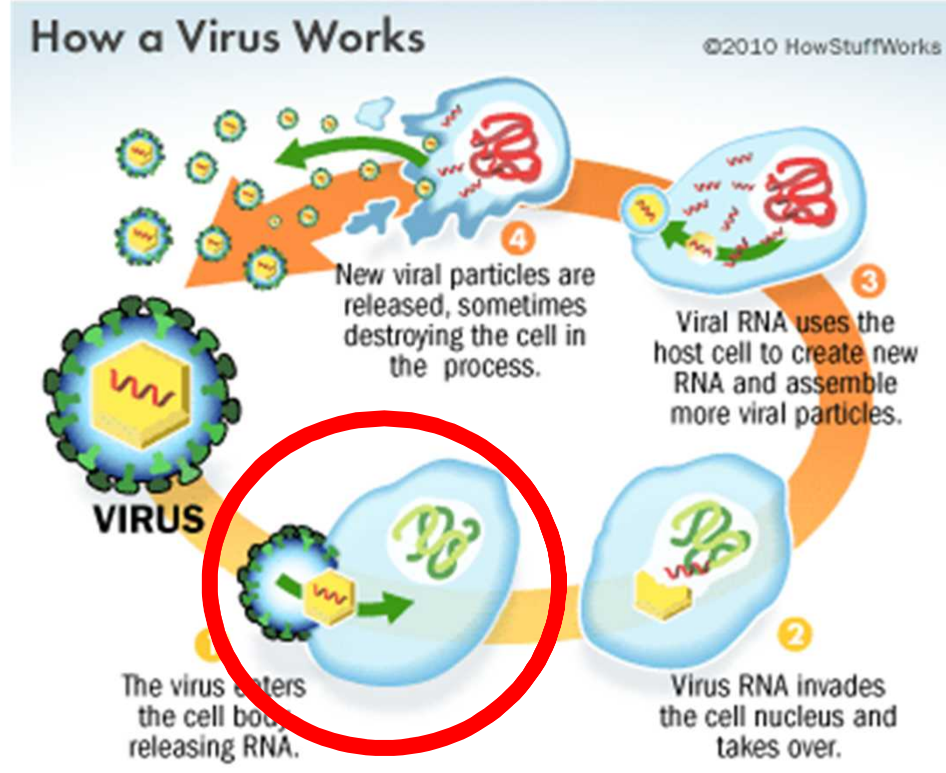


Thyne, Geoffrey. "Wettability Alteration in Reservoirs: How it Applies to Alaskan Oil Production." In *SPE Western Regional Meeting*. Society of Petroleum Engineers, 2016.

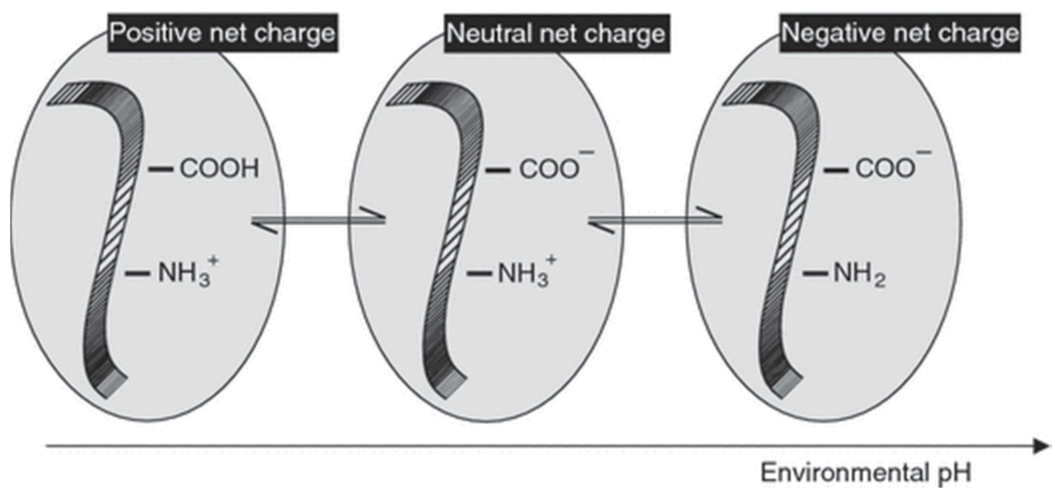




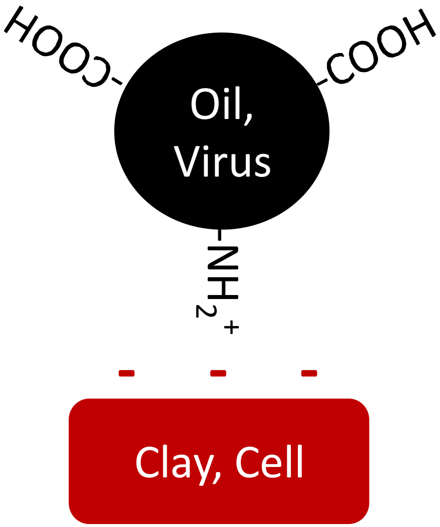


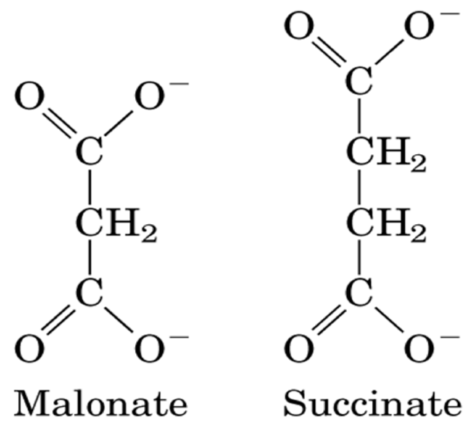


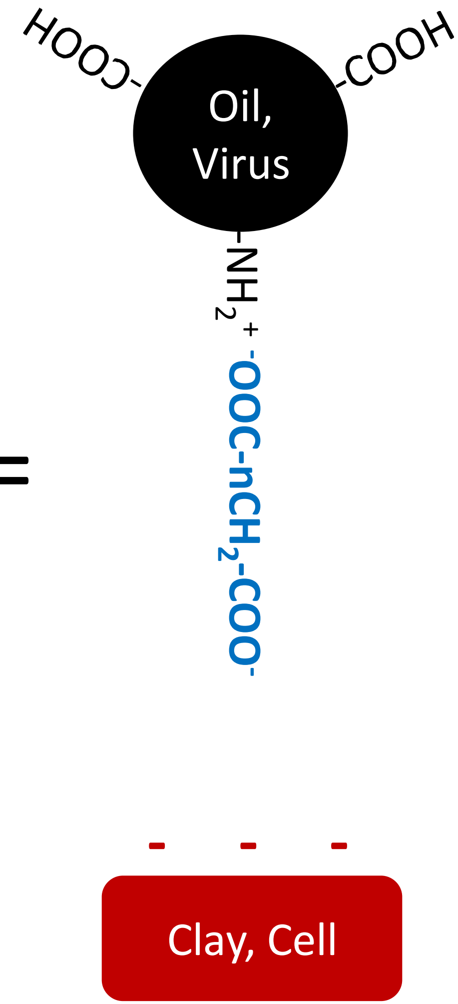
Michen & Graule (2010) J. Applied Microbiology



Better drugs; More oil.







Potential obstacles

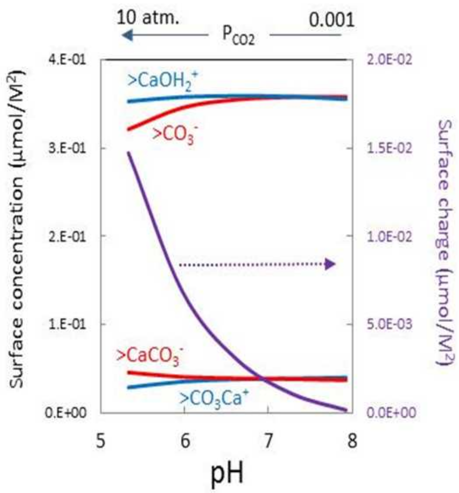
More Oil
Solubility w.r.t Ca/Mg

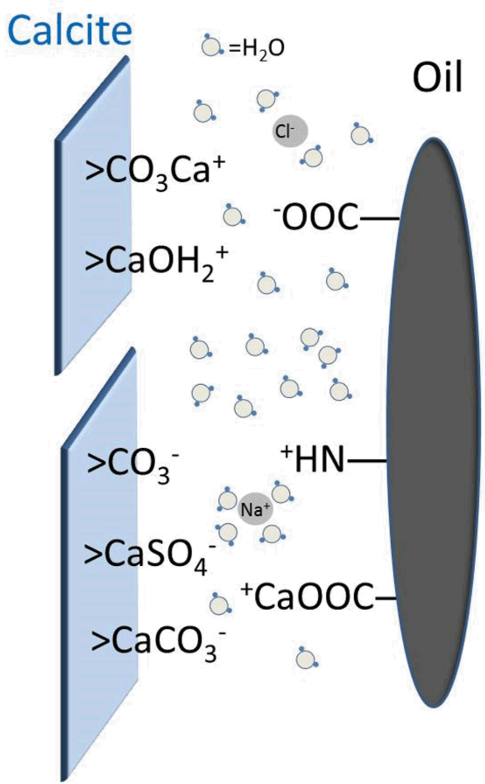
Better Drugs
Speciation in blood plasma,
Linking with proteins,
Toxicity

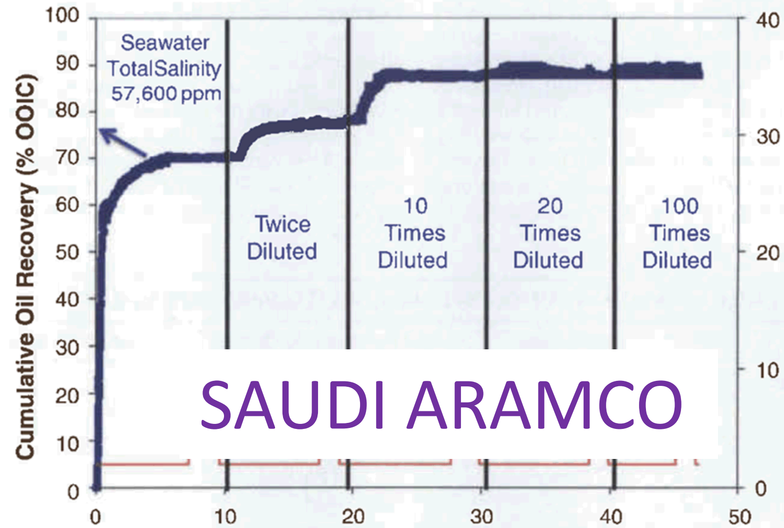
Potholes!

1. Asphalt nitrogen groups are very important,
2. Keeping the in situ pH low is good – so avoid limestone, silica ash, concrete aggregate, rapidly dissolving silicates
3. If limestone, silica ash, concrete aggregate are used, add <u>low</u> doses of nitrogen base polymers.

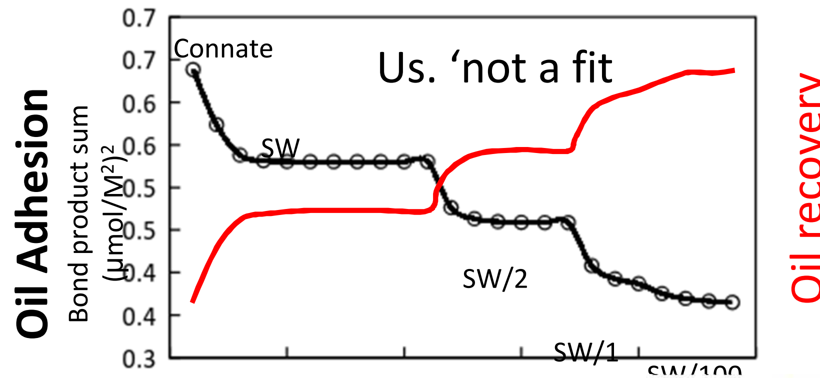
Oil Adhesion to Limestones

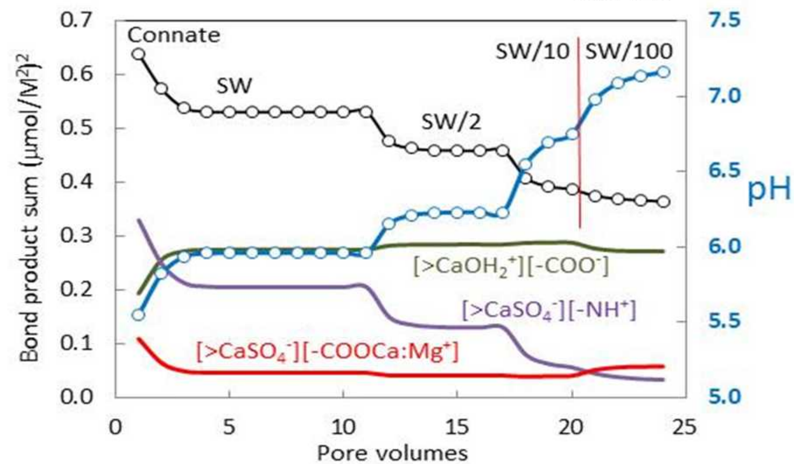






Yousef et al. 2011, SPE Reservoir Evaluation and Engineering



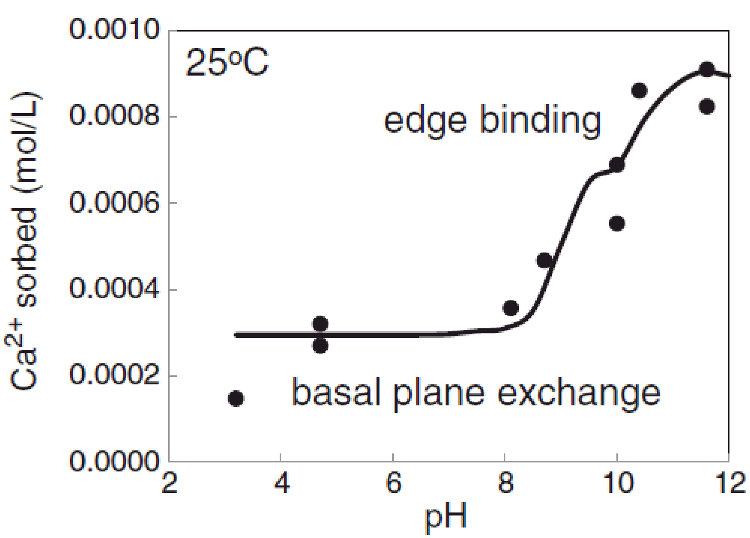


Clay Surface and pH and Ca^{+2}

Basal plane - latttice substitution = permanent negative charge

Edge – broken bonds = pH-dependent charge

Basal plane Clay = Illite, smectite, chlorite



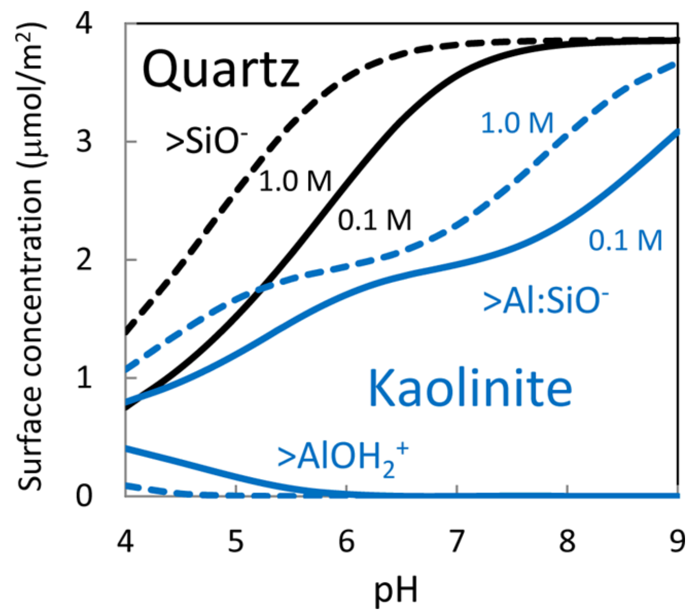
From Brady and Krumhansl (2012). "A surface complexation model of oil–brine–sandstone interfaces at 100° C: Low salinity waterflooding." Journal of Petroleum Science and Engineering 81: 171-176.

$2{>}Na + Ca^{+2} \leftrightarrow {>}Ca + 2Na^{+}$

${>}Na + H^{+} \leftrightarrow {>}H + Na^{+}$

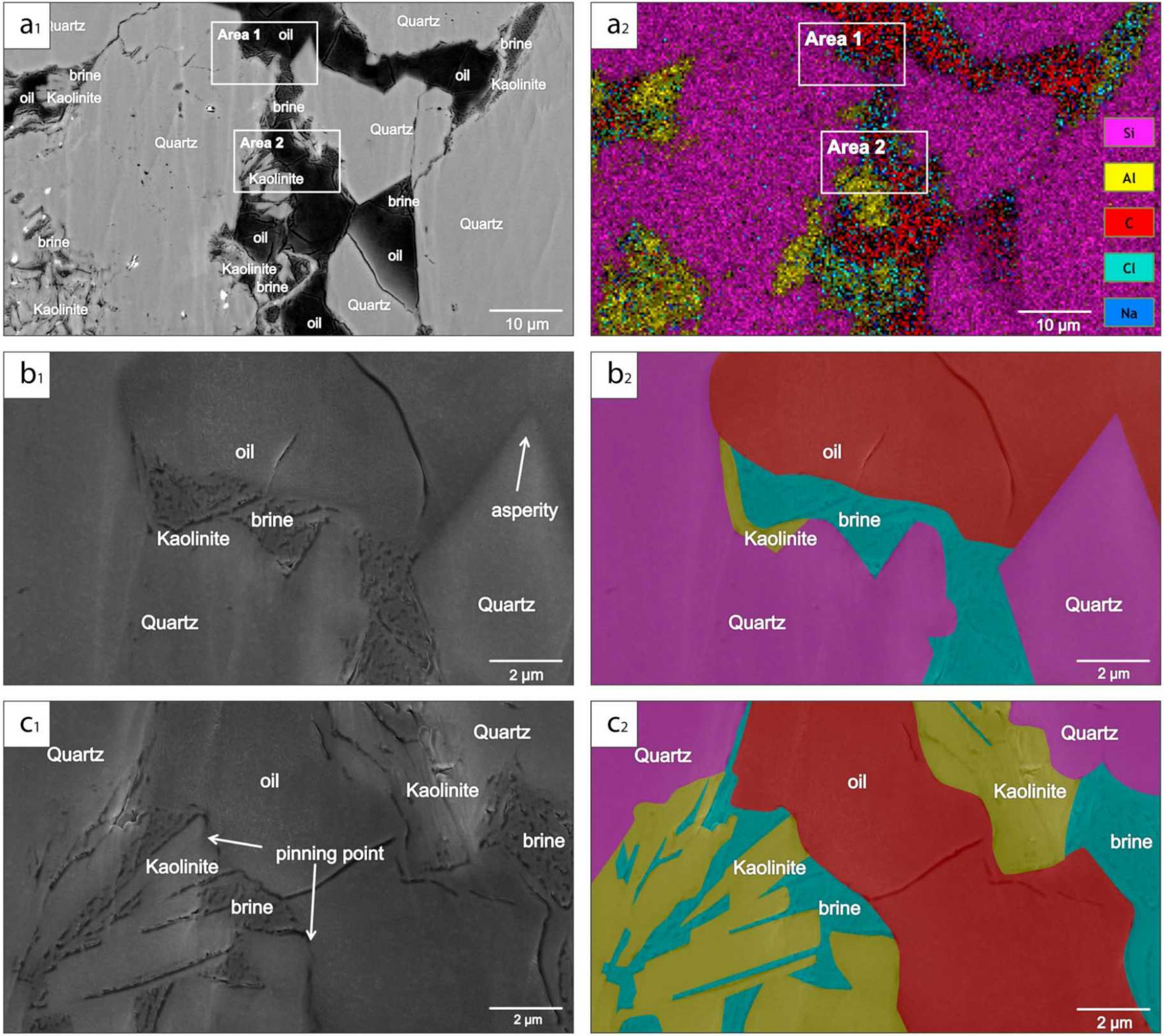
${>}Al{:}SiO^{-} + Ca^{+2} \leftrightarrow {>}Al{:}SiOCa^{+}$

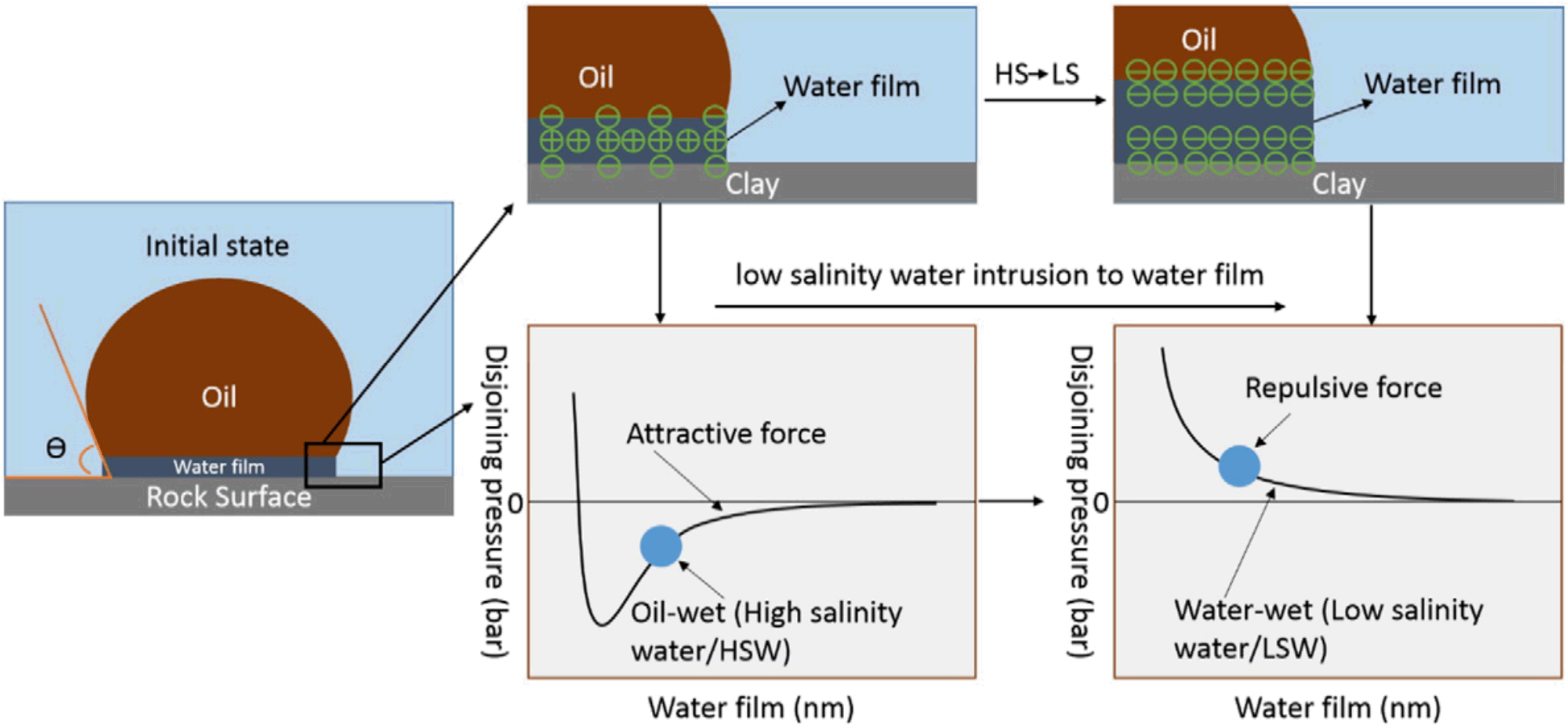
Edge Clay = Kaolinite



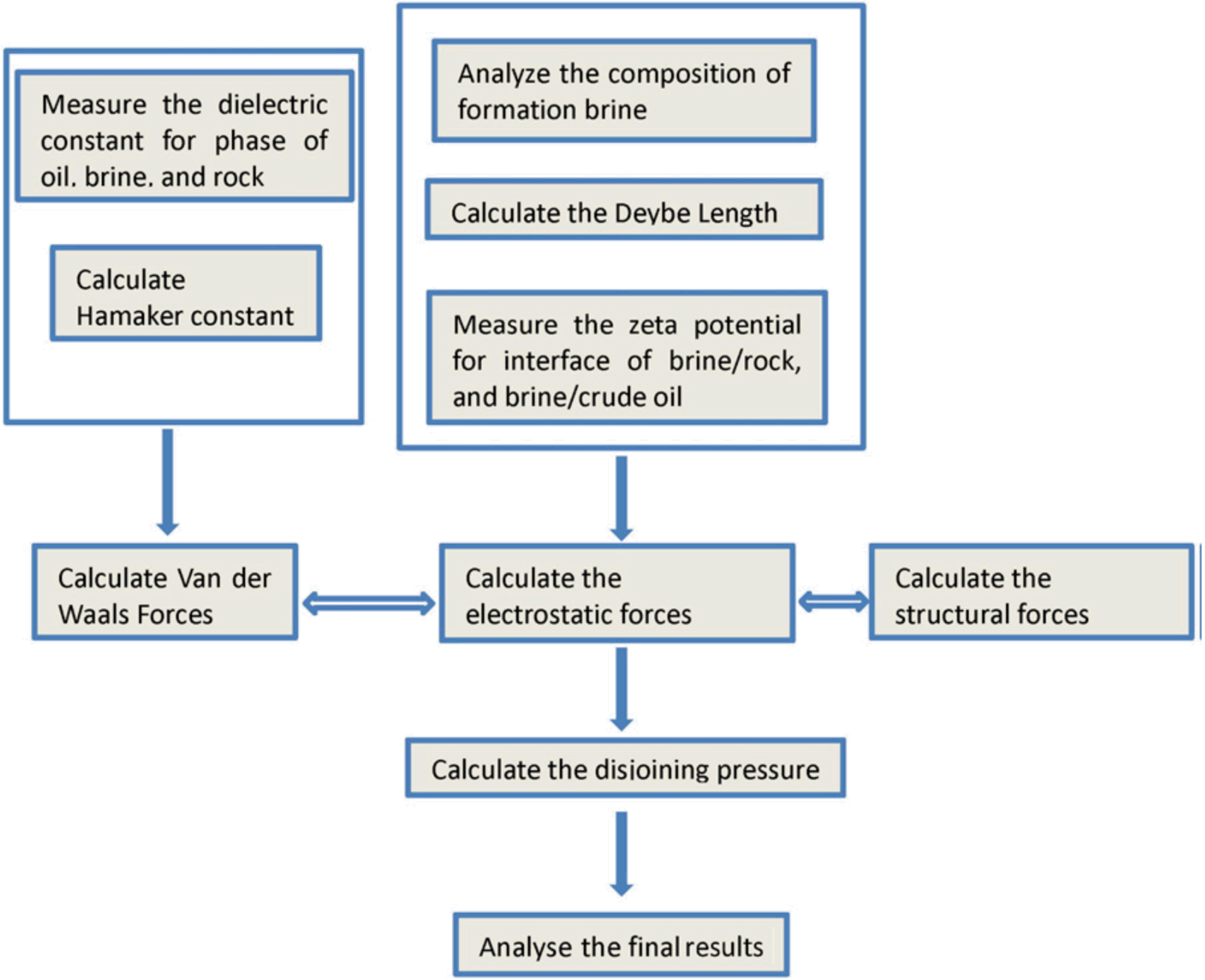
From Brady, P. V., N. R. Morrow, A. Fogden, V. Dinez, N. Loahardjo and Winoto (2015). "Electrostatics and the low salinity effect in sandstones." Energy & Fuels 29(666-667).

Schmatz, Joyce, Janos L. Urai, Steffen Berg, and Holger Ott. "Nanoscale imaging of pore-scale fluid-fluid-solid contacts in sandstone." *Geophysical Research Letters* 42, no. 7 (2015): 2189-2195.





Xie, Quan, Ali Saeedi, Ehsan Pooryousefy, and Yongbing Liu. "Extended DLVO-based estimates of surface force in low salinity water flooding." *Journal of Molecular Liquids* 221 (2016): 658-665.



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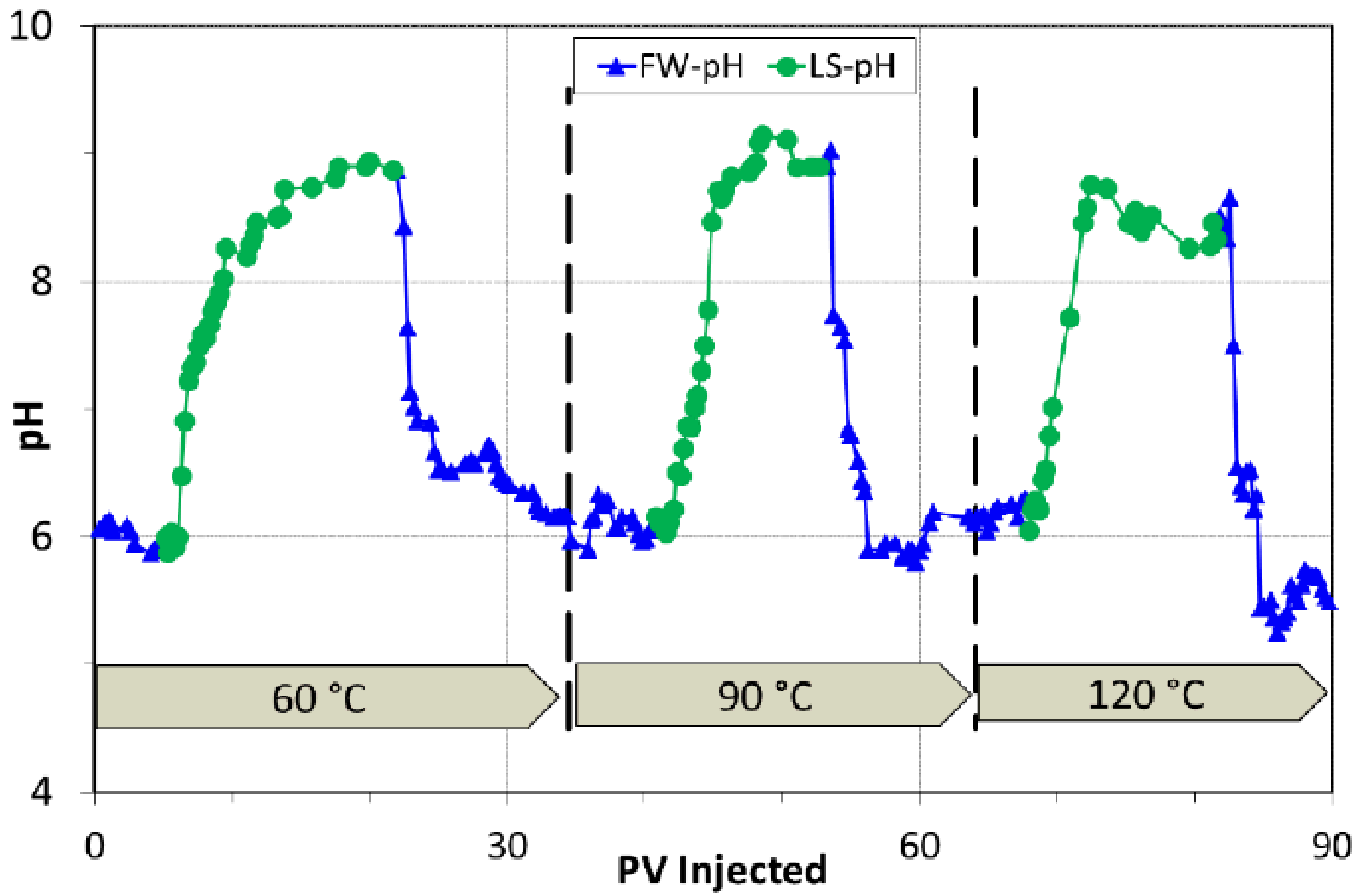

Torrijos et al in press (2017). Journal of Petroleum Science and Engineering, Impact of temperature on the low salinity EOR effect for sandstone cores containing reactive Plagioclase