Oil Reservoirs as Ion Exchange Columns

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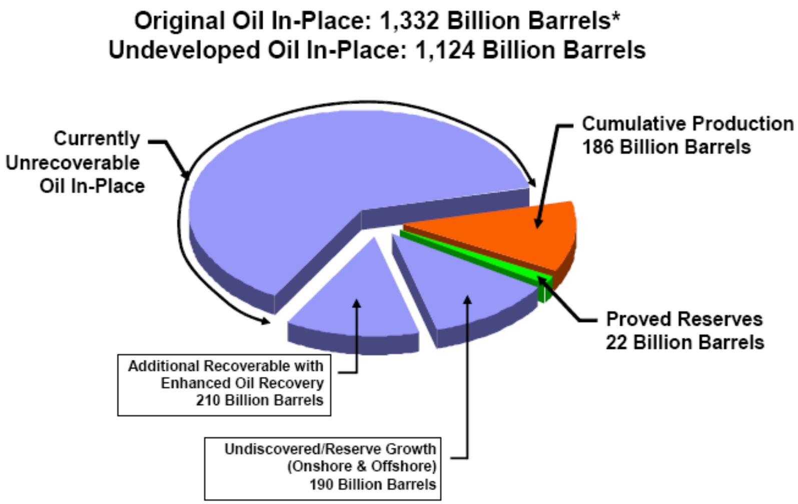
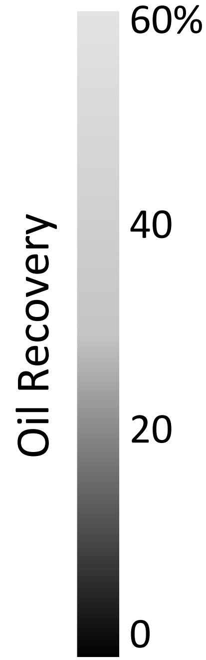


*From DOE, 2006. UNDEVELOPED DOMESTIC OIL RESOURCES: THE FOUNDATION FOR INCREASED OIL PRODUCTION AND A VIABLE DOMESTIC OIL INDUSTRY



Tertiary – Injection of steam, surfactants, polymers, etc.

Secondary – Waterflooding to restore pressure.

Primary – Reservoir "pumps itself".

Department of Earth and Environmental Engineering,
Columbia University,
October 25, 2013

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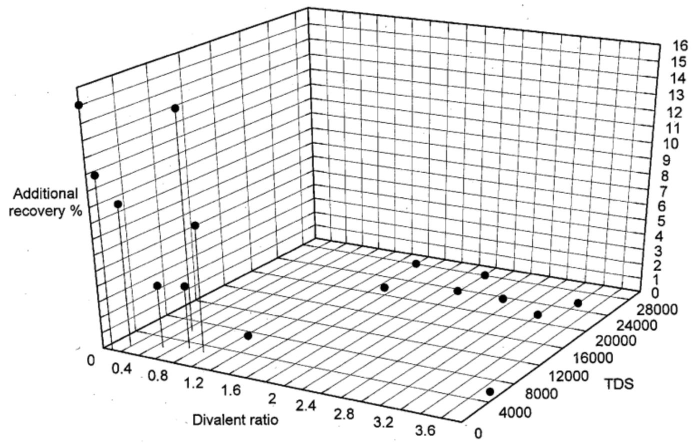
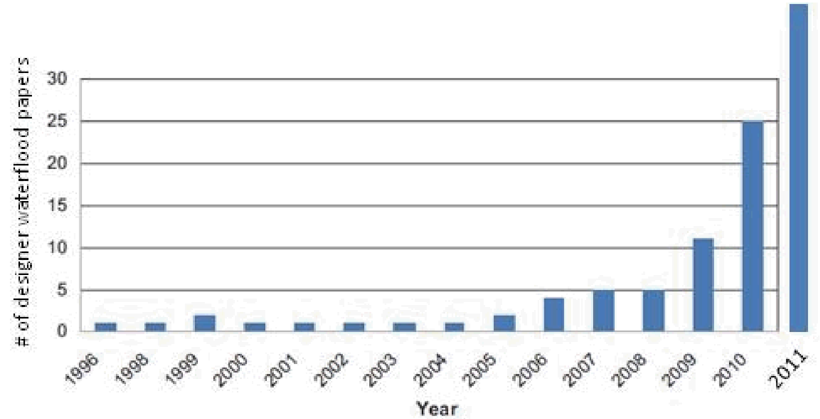
Sandstones

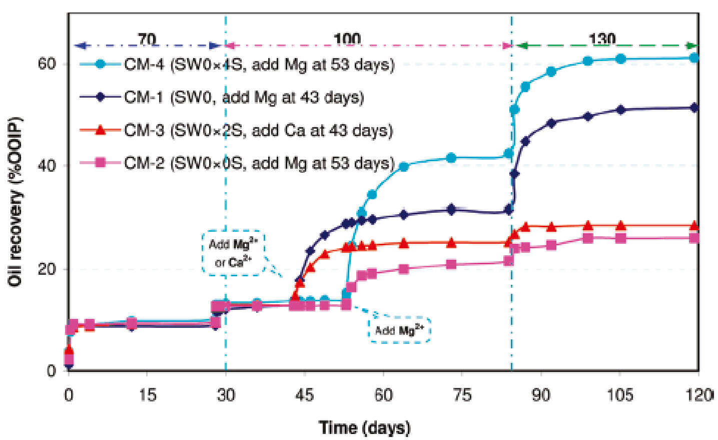


From US patent 7,987,907; Collins and Jerauld (2011)



from *Improved Oil Recovery from Low Salinity Waterflooding*; Norm Morrow and Jill Buckley, JPT, 2011

Limestones



From Rezaei Doust, A., T. Puntervold, et al. (2009). "Smart water as wettability modifier in carbonate and sandstone: A discussion of similarities/differences in the chemical mechanisms." Energy & Fuels 23: 4479-4485.

"I think the mechanism is relatively well understood. What isn't so well understood is the range of oil properties, rock composition and water composition where you'll get the benefit. To assess this accurately requires a very strong reservoir engineering capability" from Henthorne and Walsh, 2013, OTC-24199.

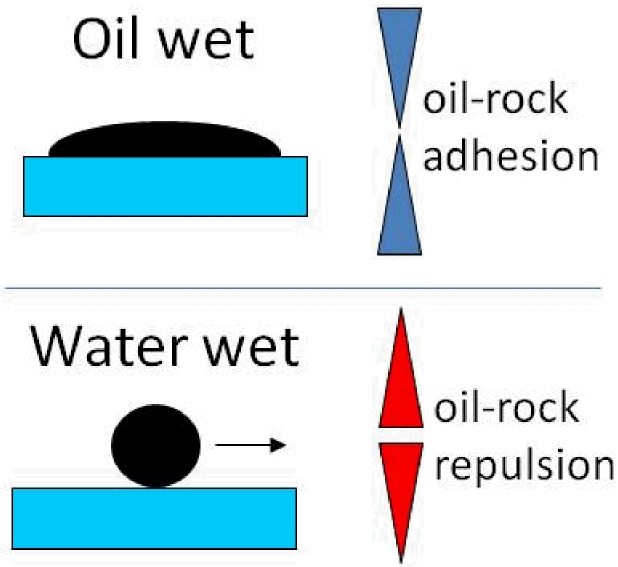
Hypothesis: Electrostatic attraction between oil and reservoir surfaces controls secondary recovery.

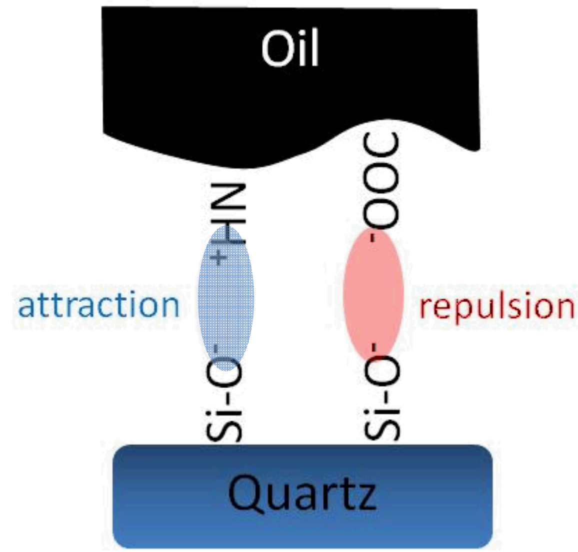
Prediction: Change waterflood chemistry to decrease oil-mineral attraction and more oil will be recovered.

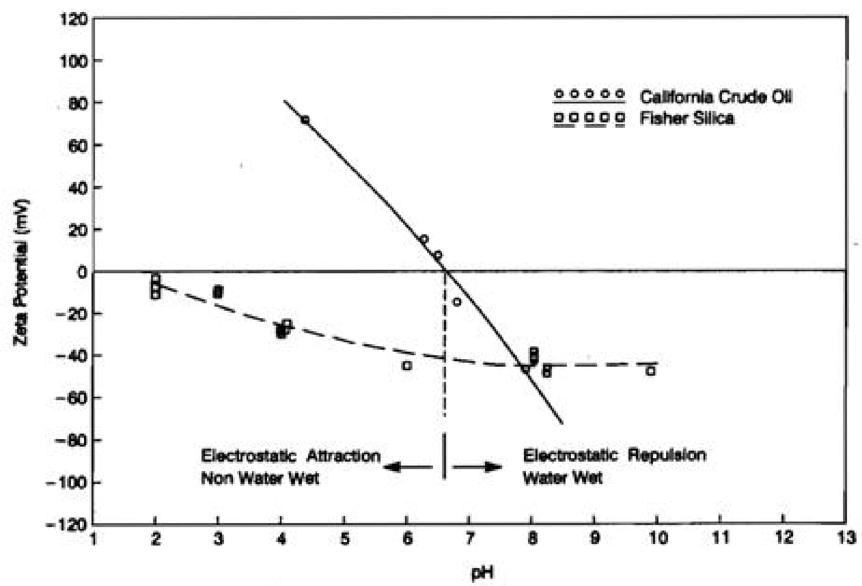
How to test:
1. Build models of oil and mineral surface charge,
2. Overlay the models to calculate attraction,
3. Parameterize attraction as *f*(mineralogy, pH, salinity, Ca^{+2}, etc.),
4. Compare calculated attraction against measured oil recovery.

What we see

Why it occurs

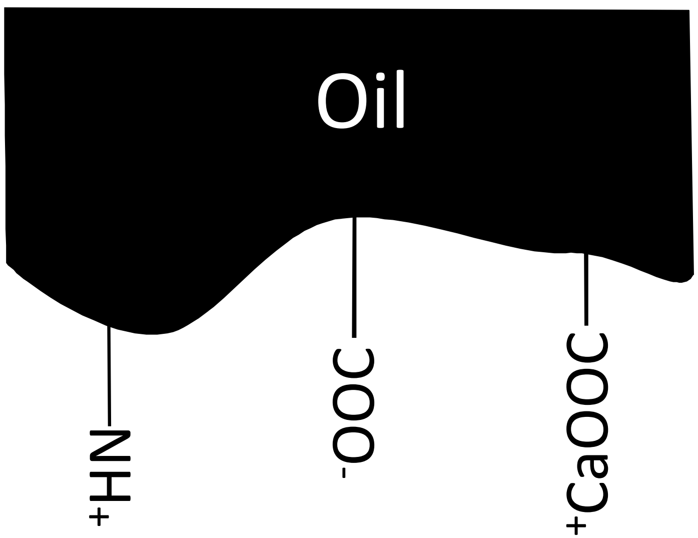




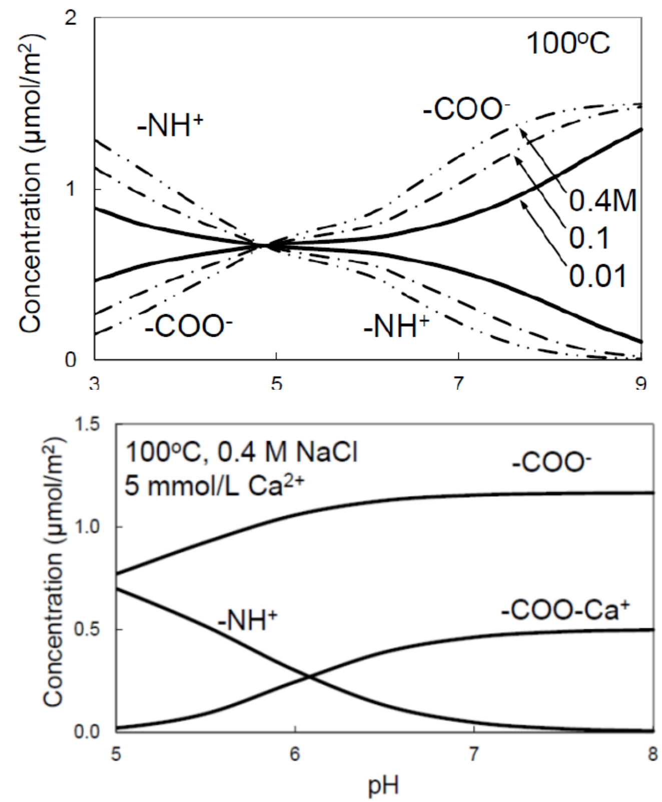


from Dubey and Doe (1993) *Base number and wetting properties of crude oil*. SPE Reservoir Engineering, 8 (195-200).

Oil Surface Charge



double layer water molecules and counterions not shown



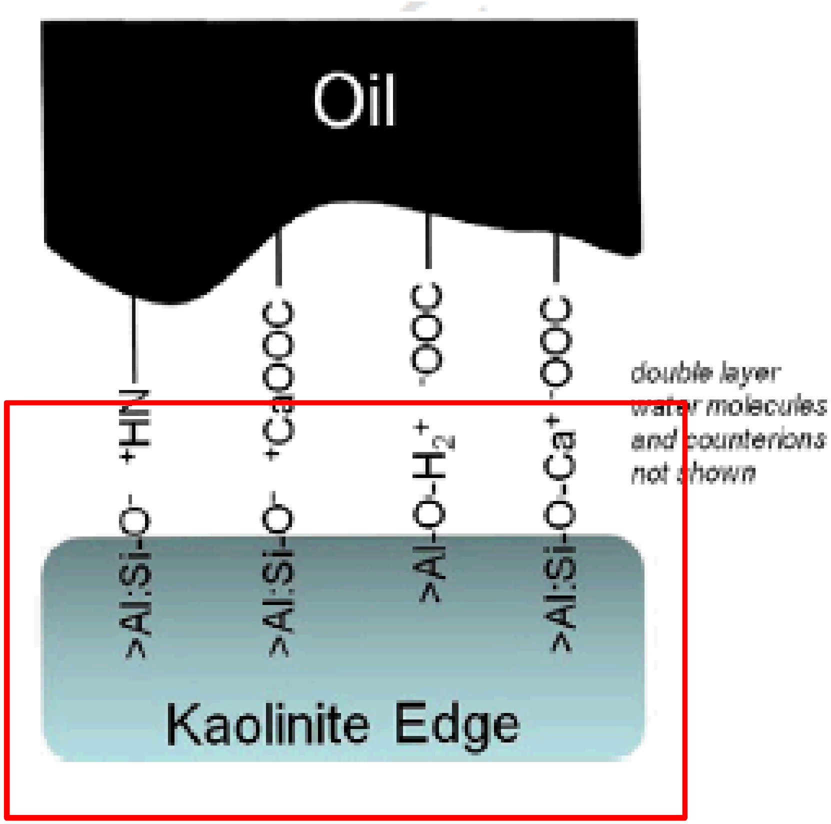
From Brady and Krumhansl (2012) A surface complexation model of oil-brine-sandstone interfaces at100°C: Low Salinity waterflooding. J. Petroleum Science and Engineering (81) 171-176.

$-NH^+ \leftrightarrow -N + H^+$ $K_{NH} = [-N]\exp(F\psi/RT)\, a_{H+}/[-NH^+]$

$-COOH \leftrightarrow -COO^- + H^+$ $K_{COOH} = \exp(F\psi/RT)\,[-COO^-]a_{H+}/[-COOH]$

BN, AN indicate the total number of –N and –COOH groups

Sandstone Surface Charge



Reaction	25°C log K
[a]Oil Surface	
$-NH^+ \leftrightarrow -N + H^+$	-6.0
$-COOH \leftrightarrow -COO^- + H^+$	-5.0
$-COOH + Ca^{2+} \leftrightarrow -COOCa^+ + H^+$	-3.8
$-COOH + Mg^{2+} \leftrightarrow -COOMg^+ + H^+$	-4.0
[a]Kaolinite Edges	
$>Al-O-H_2^+ \leftrightarrow >Al-O-H + H^+$	-3.0
$>Al-O-H \leftrightarrow >Al-O^- + H^+$	-3.8
$>Si-O-H \leftrightarrow >Si-O^- + H^+$	-7.0
$>Al-O-H + Ca^{2+} \leftrightarrow >Al-O-Ca^+ + H^+$	-9.7
$>Si-O-H + Ca^{2+} \leftrightarrow >Si-O-Ca^+ + H^+$	-9.7
$>Al-O-H + CaOH^+ \leftrightarrow >Al-O-CaOH + H^+$	-4.5
$>Si-O-H + CaOH^+ \leftrightarrow >Si-O-CaOH + H^+$	-4.5

Ward and Brady *Clays and Clay Minerals*

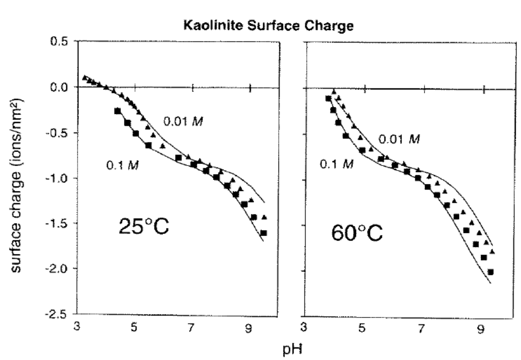
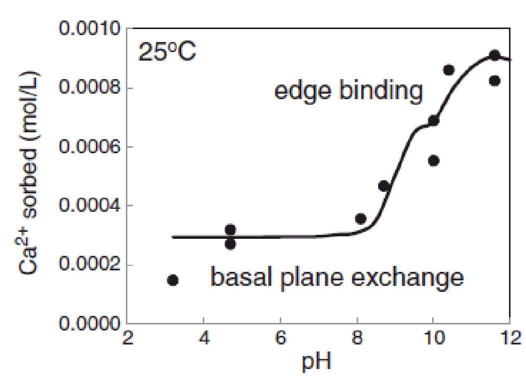
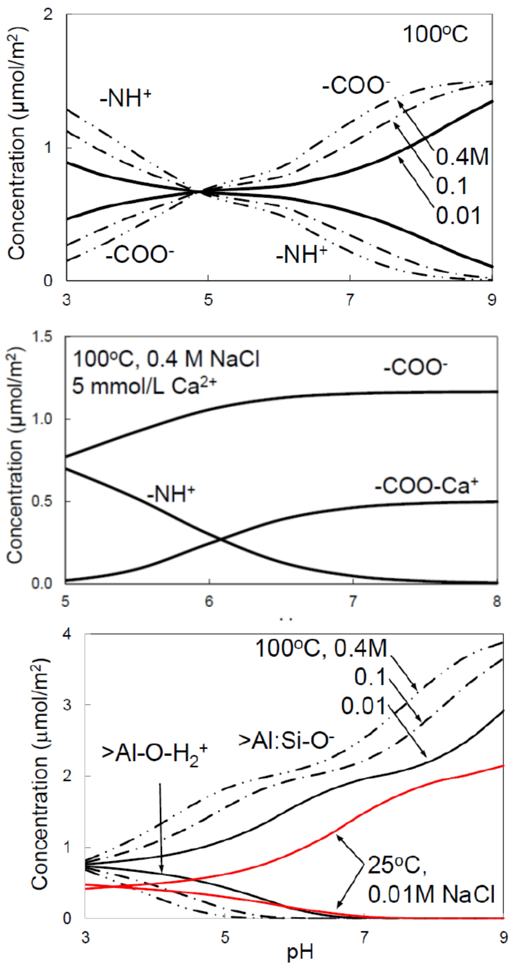


Figure 4. Potentiometric titrations and TLM for surface charge on kaolinite at 25 and 60 °C.

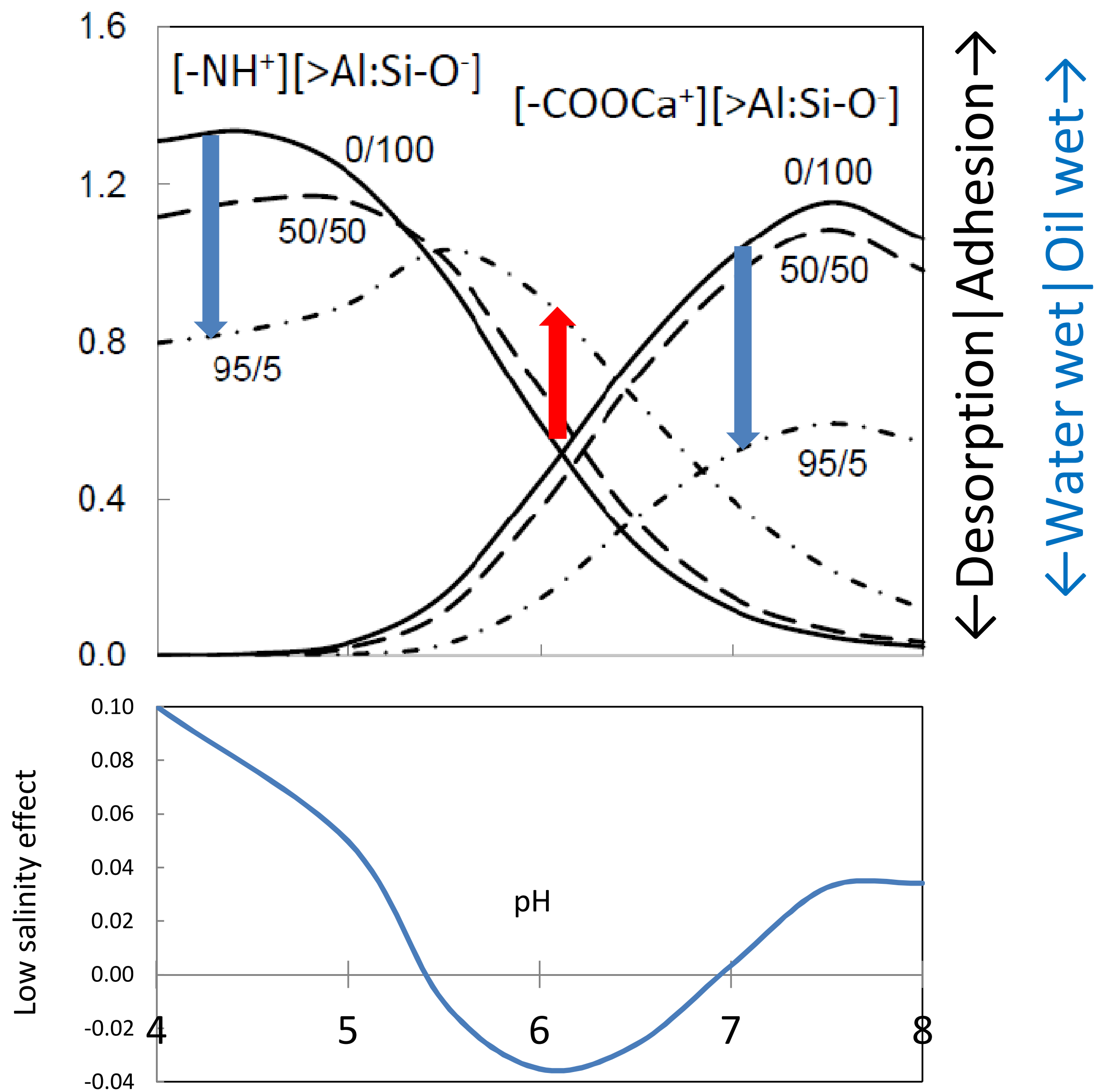


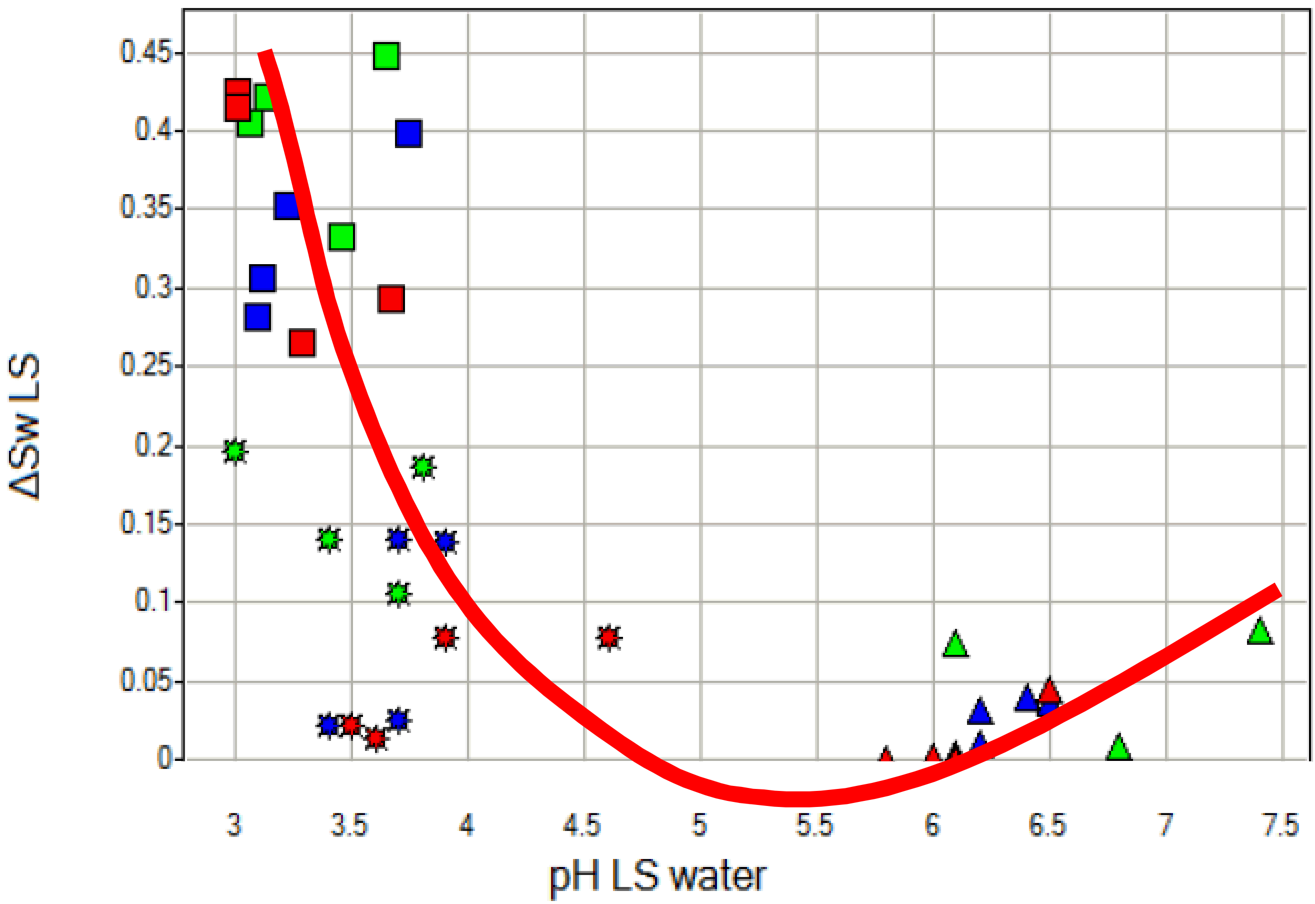
From Brady and Krumhansl (2012) A surface complexation model of oil-brine-sandstone interfaces at 100ºC: Low Salinity waterflooding. J. Petroleum Science and Engineering (81) 171-176.

Sandstone-Oil Adhesion



From Brady and Krumhansl (2013) Surface complexation modeling for waterflooding of sandstones. SPE Journal; April, 214-217.

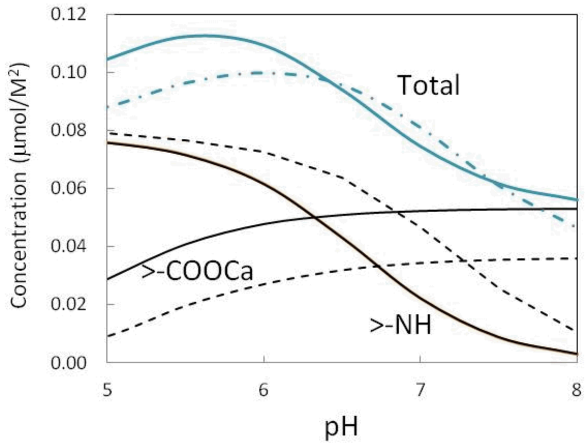




From van Winden et al. (2013) IOR 2013 – 17th European Symposium on Improved Oil Recovery St. Petersburg, Russia, 16-18 April 2013

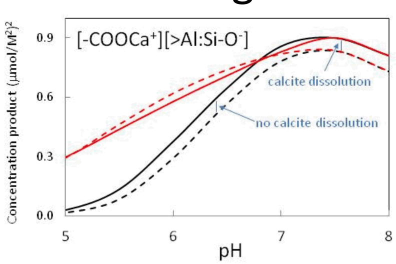
What does knowing the sandstone mechanism tell us that is <u>new</u>?

Basal Planes

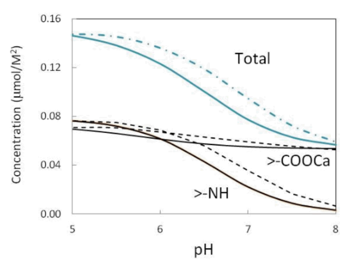


w. calcite

Edge



Basal Planes



Solid lines – Connate
Dashed lines – low TDS, low Ca

1. Calcite cements are bad – but not because they're cements,
2. Swelling clays are bad - but not because they swell,
3. pH matters a great deal,
4. AN/BN too,
5. The waterflood that produces maximal oil is unique to a particular oil-reservoir-connate combination, <u>and it can be predicted</u>.

Why Oil sticks to Calcite and Dolomite