Viruses, Oil Recovery, and Potholes

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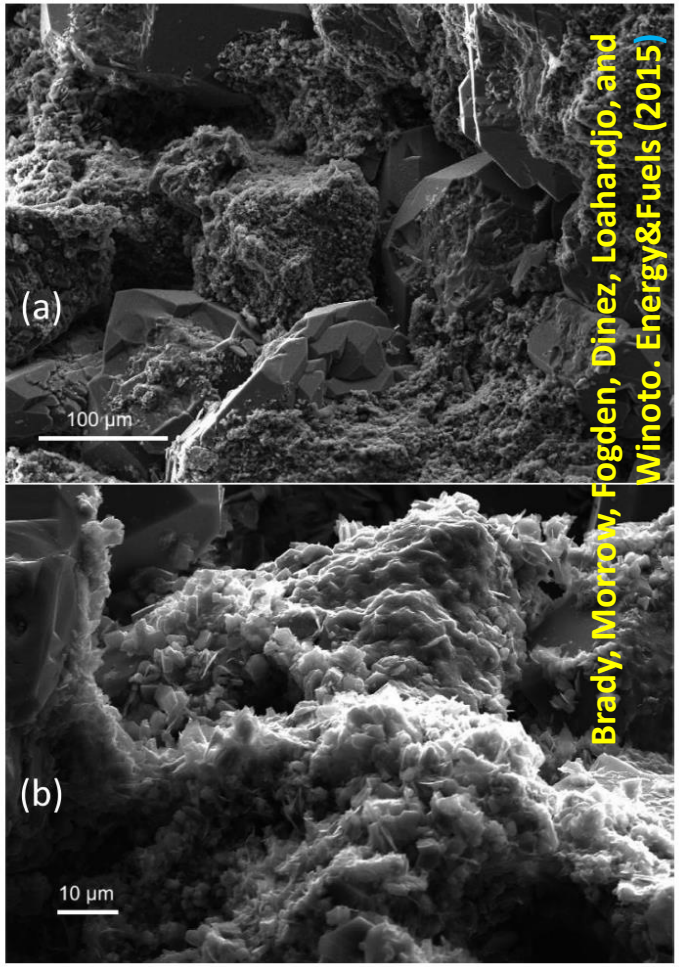
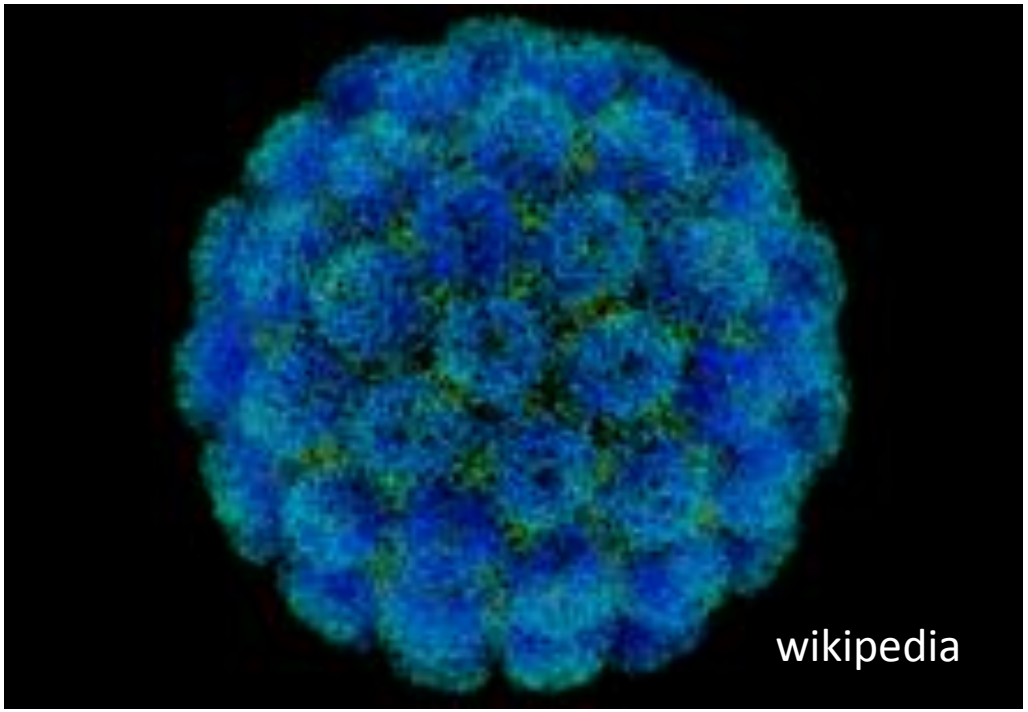
Sandia National Laboratories

SAND2016-7621PE





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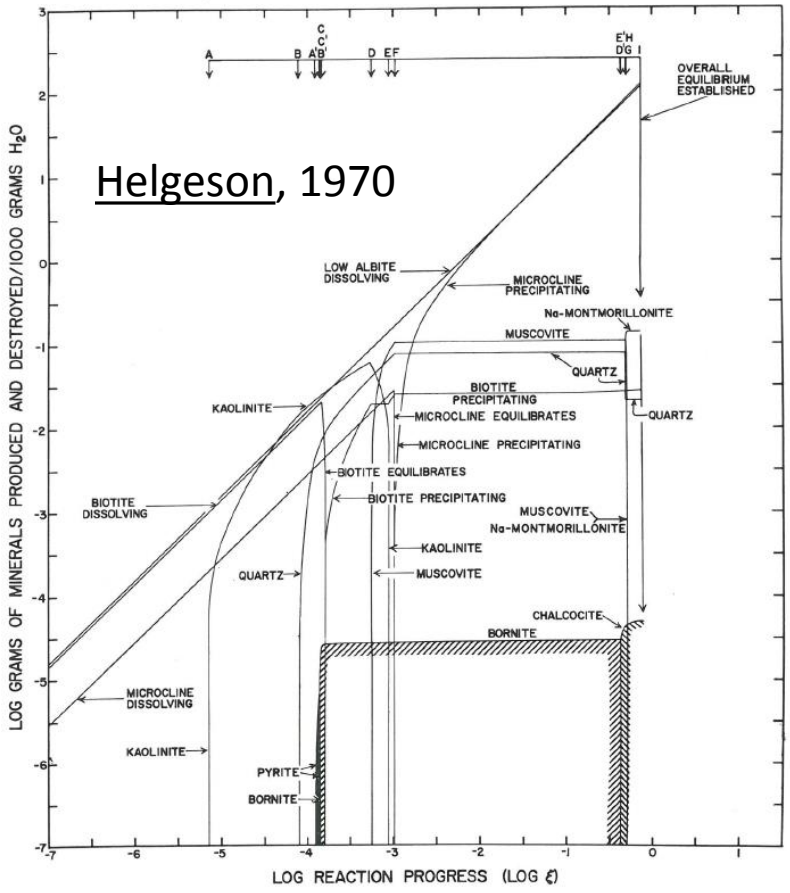
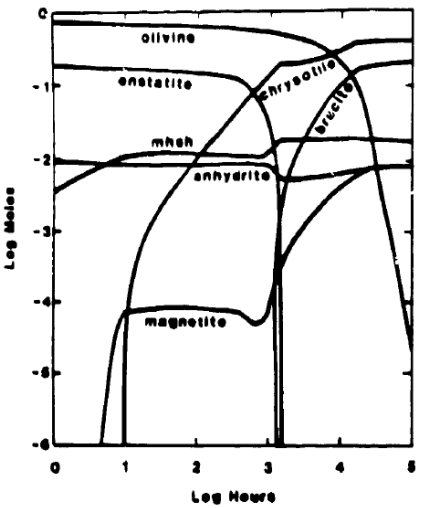
Geochemical Models of the Paleolithic

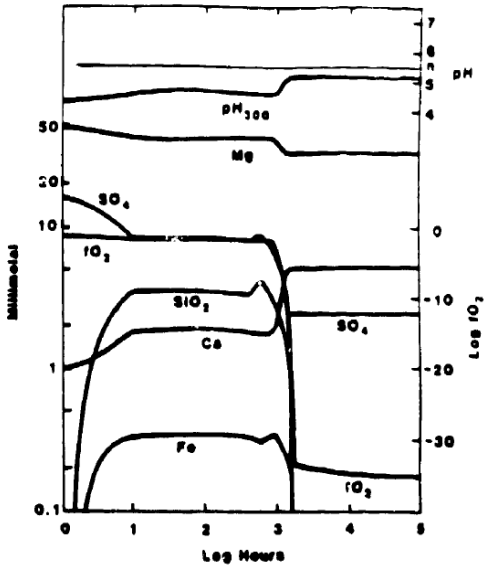
Hydrothermal Ore Deposits



Helgeson, 1970

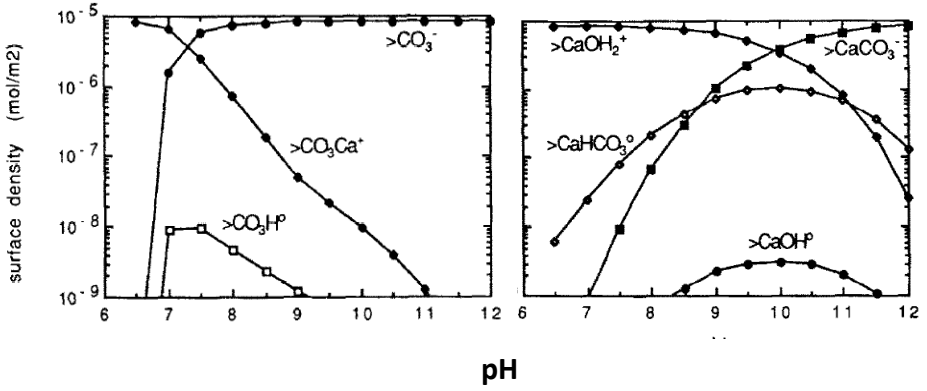
Mid-Ocean Ridge Alteration





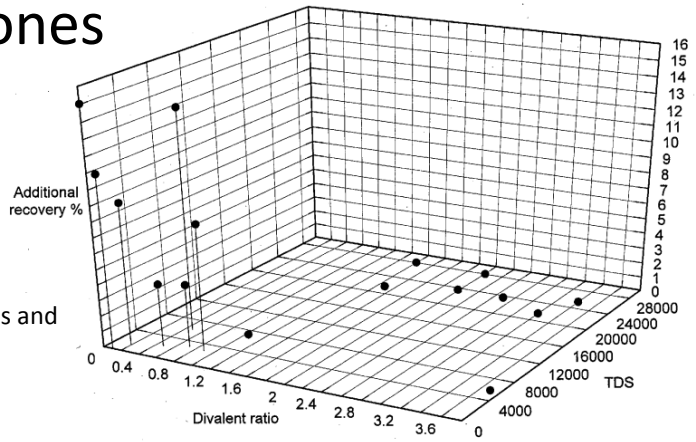
Janecky, 1986

Calcite Surface Speciation

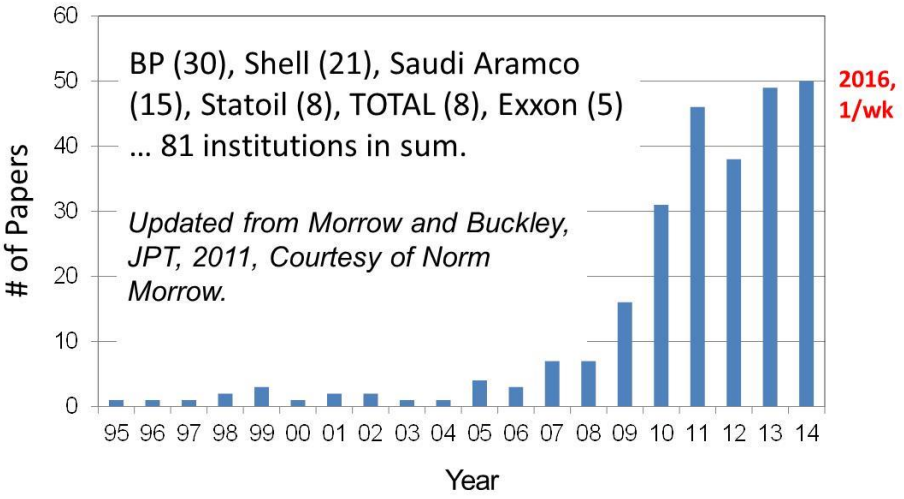


Van Cappellen, Charlet, Stumm, & Wersin 1993

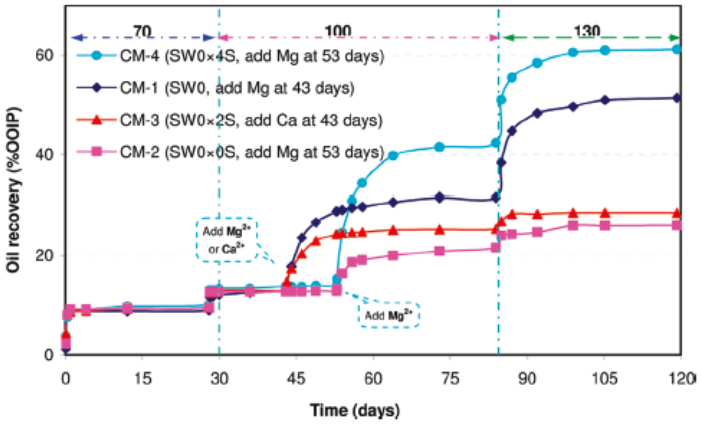
Sandstones



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



Limestones



From Rezaei Doust, A., T. Puntervold, et al. (2009). Energy & Fuels 23: 4479-4485.

Which one of the following statements from an SPE Insider are true?

1. "I think the mechanism is relatively well understood.

2. What isn't so well understood is the range of oil properties, rock composition and water composition where you'll get the benefit.

3. To assess this accurately requires a very strong reservoir engineering capability"

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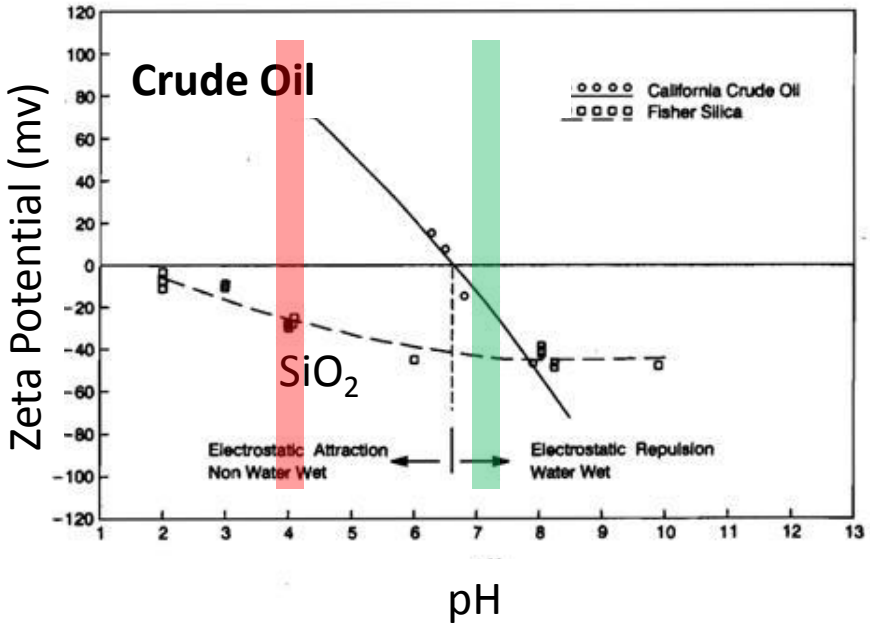
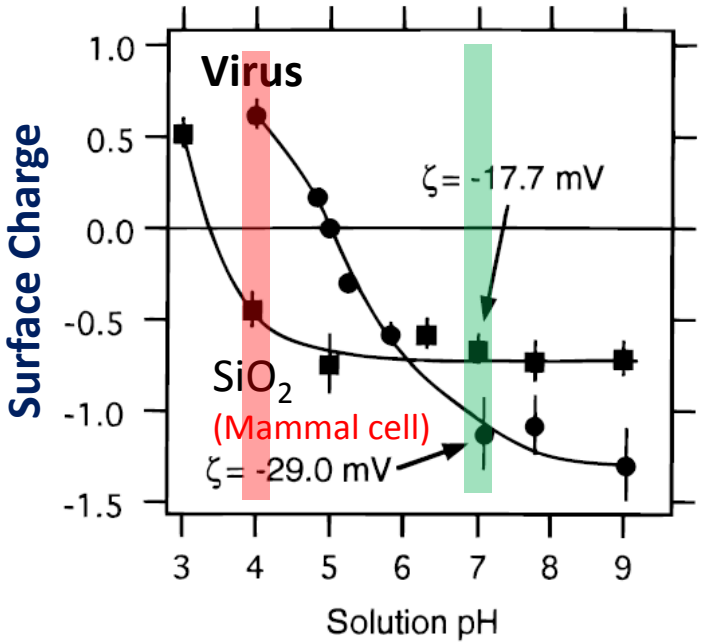
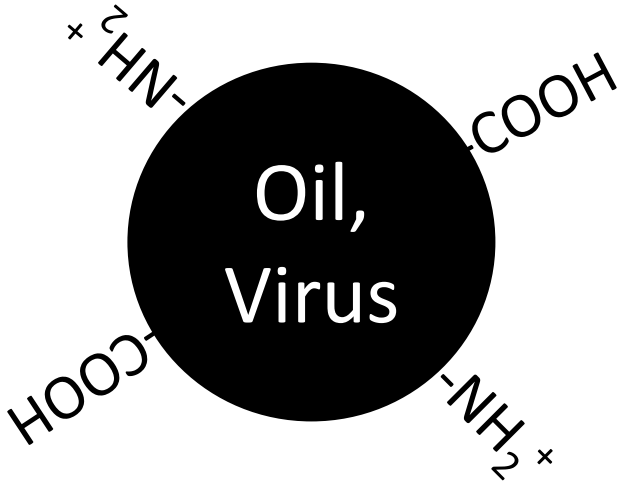
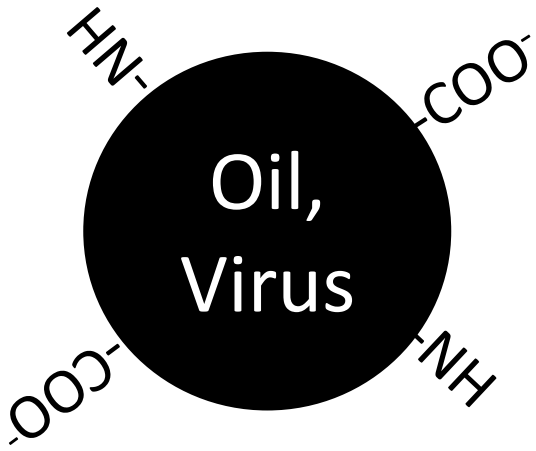


from Dubey and Doe (1993) *Base number and wetting properties of crude oil*. SPE Reservoir Engineering, 8 (195-200).

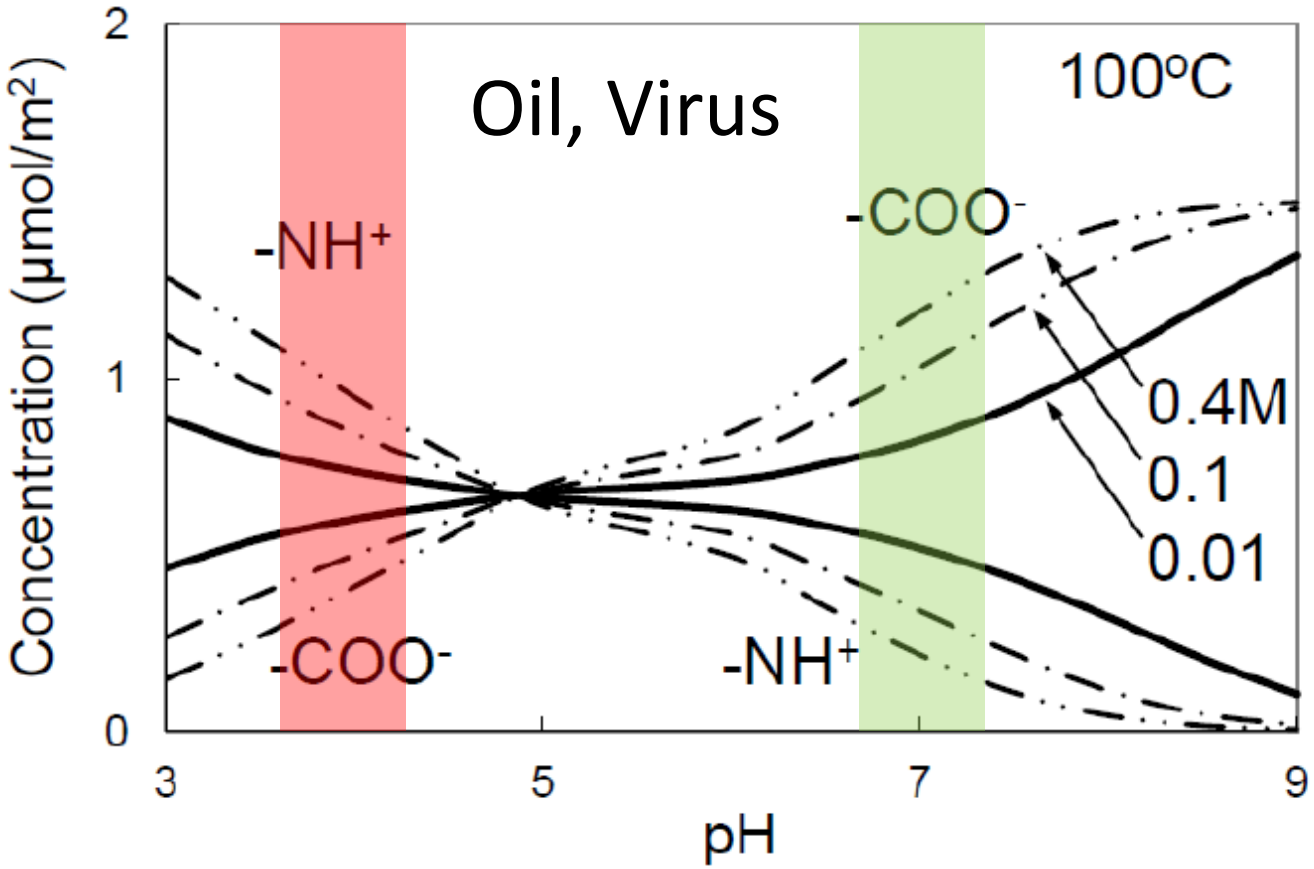


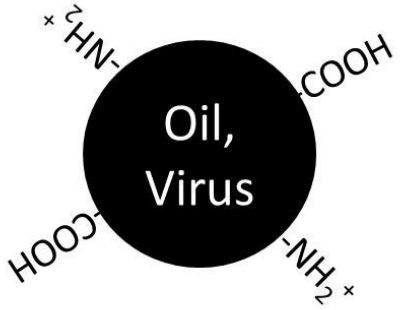


pH 4

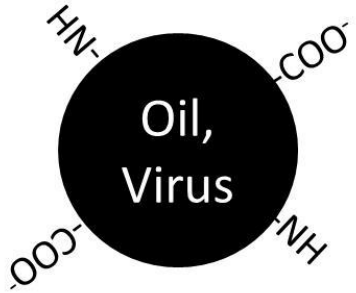


pH 7


Oil, Virus
100°C
Concentration (µmol/m²)
2
1
0
-NH⁺
-COO⁻
-COO⁻
-NH⁺
0.4M
0.1
0.01
3
5
7
9
pH


Oil,
Virus
-NH₂⁺
-COOH
-COOH
-NH₂⁺

pH 4


Oil,
Virus
HN-
-COO⁻
-COO⁻
-NH

pH 7

Oil/Virus

$$-NH + H^+ \leftrightarrow -NH_2^+$$
$$-COOH \leftrightarrow -COO^- + H^+$$
$$COOH + Ca^{+2} \leftrightarrow -COOCa^+ + H^+$$

Kaolinite Edges

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

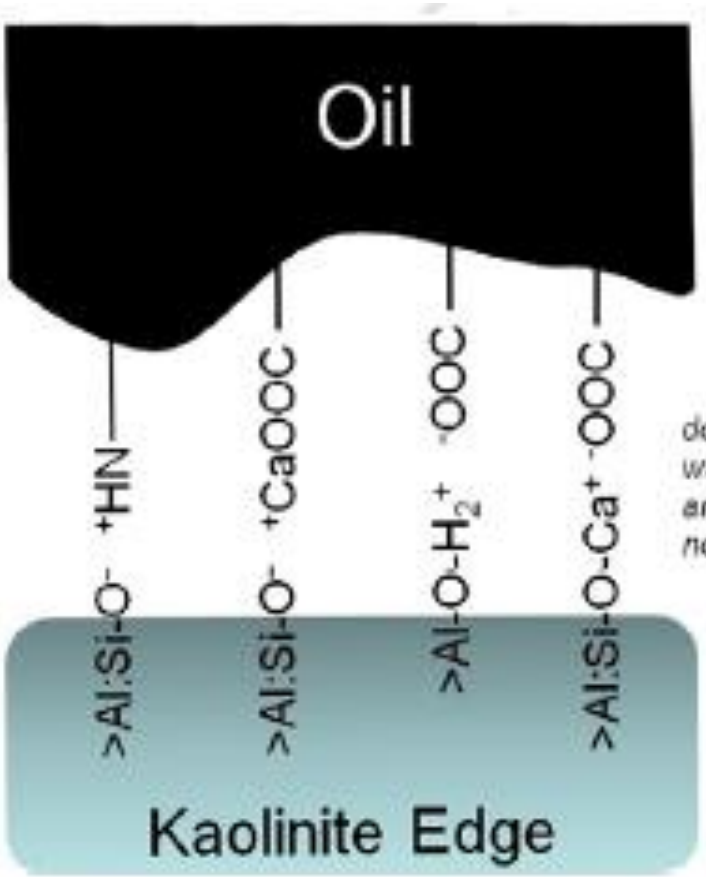
Illite, Smectite Basal Planes

$$Na + H^+ \leftrightarrow >H + Na^+$$
$$>Na + -NH^+ \leftrightarrow >\text{-}NH + Na^+$$
$$>Na + -COOCa^+ \leftrightarrow >\text{-}COOCa + Na^+$$
$$2>Na + Ca^{+2} \leftrightarrow >Ca + 2Na^+$$

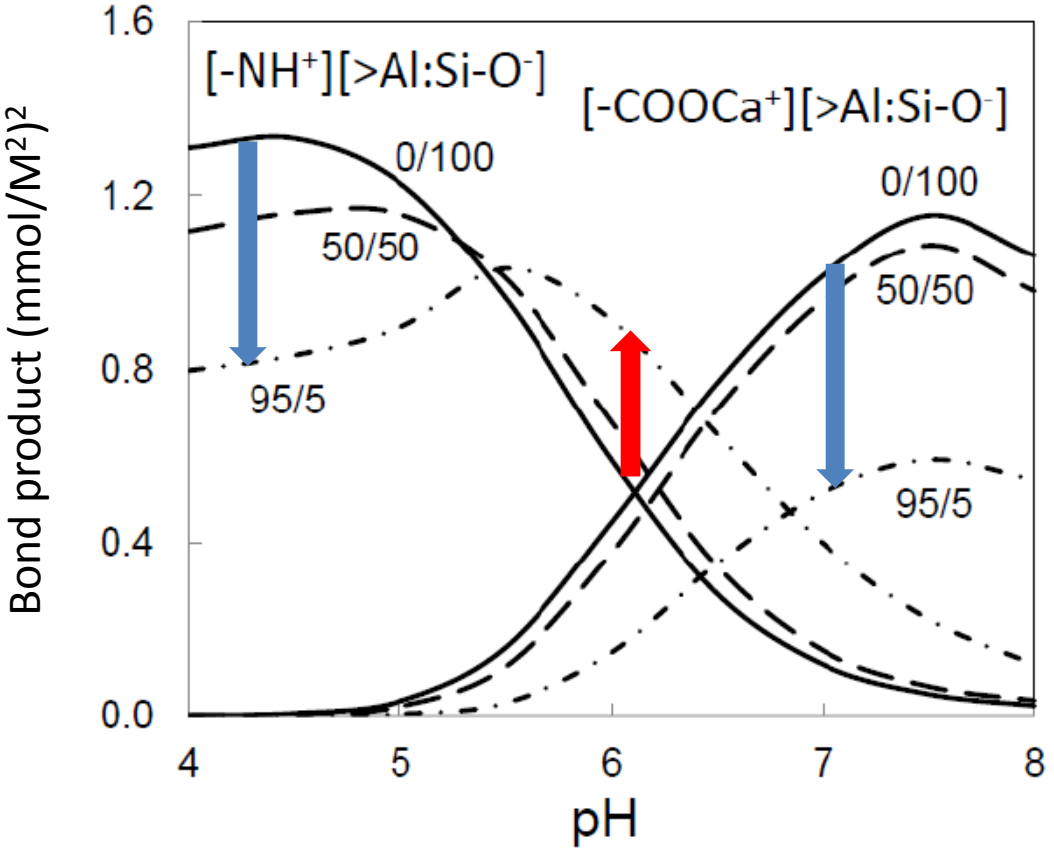
Calcite

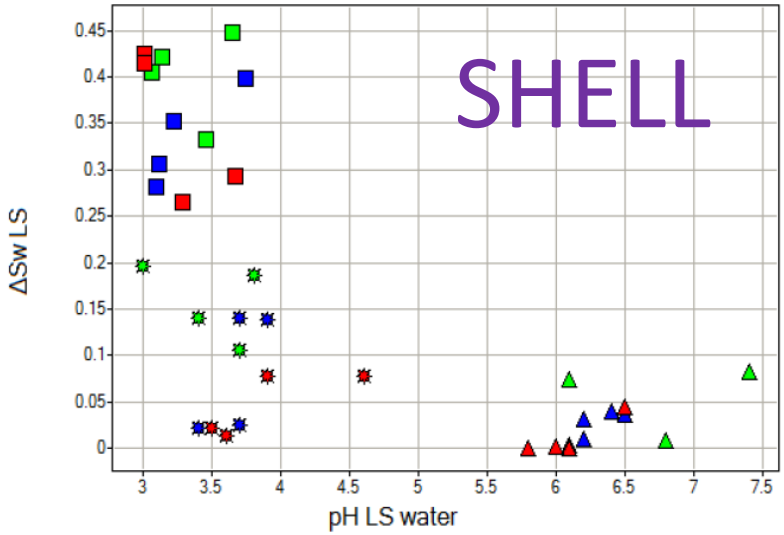
$$>CaOH + H^+ \leftrightarrow >CaOH_2^+$$
$$>CaOH + HCO_3^- \leftrightarrow >CaCO_3^- + H_2O$$
$$>CaOH_2^+ + SO_4^{-2} \leftrightarrow >CaSO_4^- + H_2O$$
$$>CO_3H \leftrightarrow >CO_3^- + H^+$$
$$>CO_3H + Ca^{+2} \leftrightarrow >CO_3Ca^+ + H^+$$
$$>CO_3H + Mg^{+2} \leftrightarrow >CO_3Mg^+ + H^+$$

Oil Adhesion to Sandstones



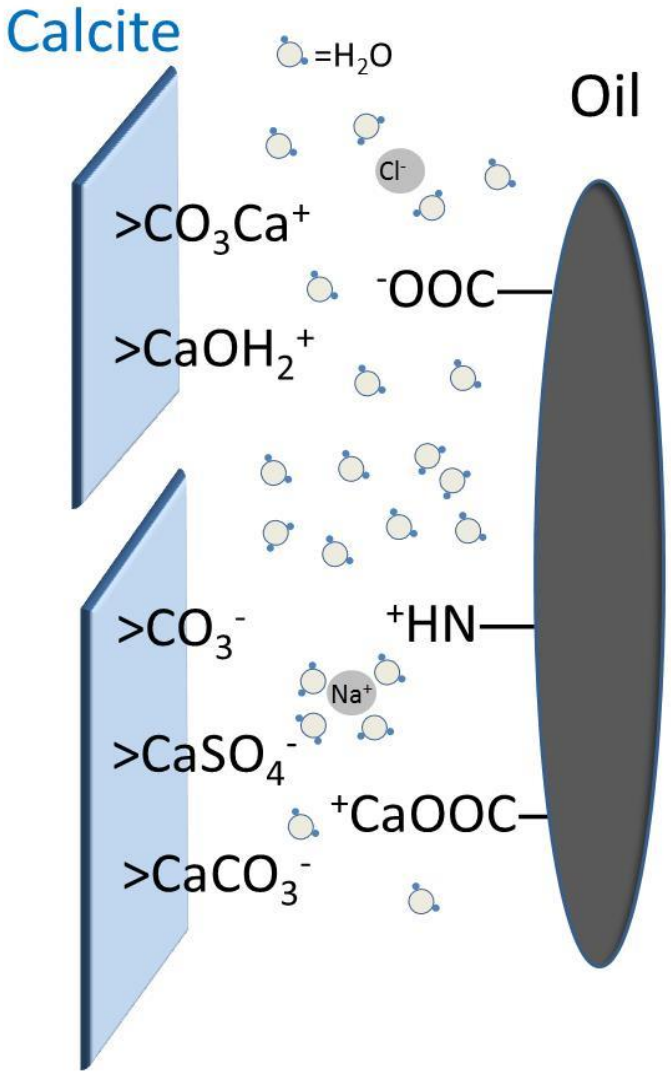
double layer water molecules and counterions not shown

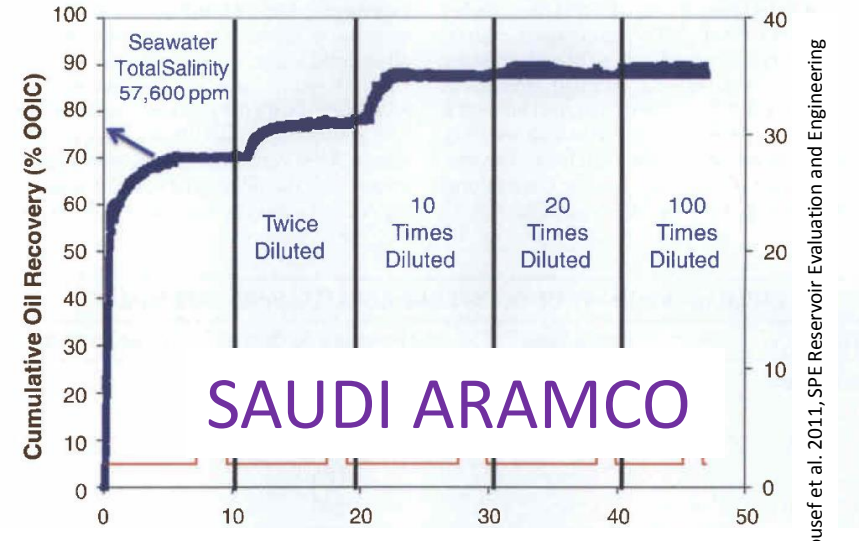




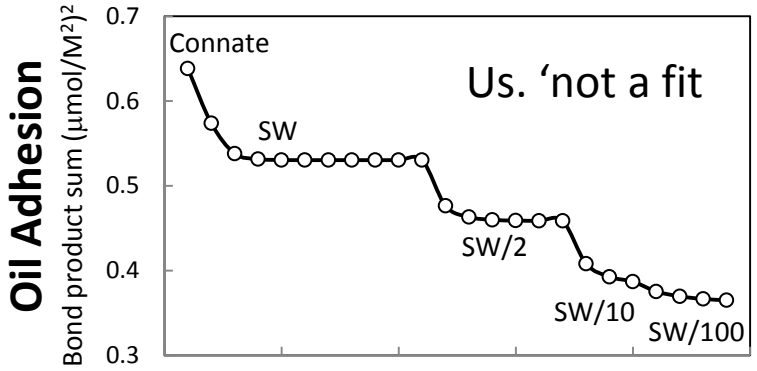
From van Winden et al. (2013)

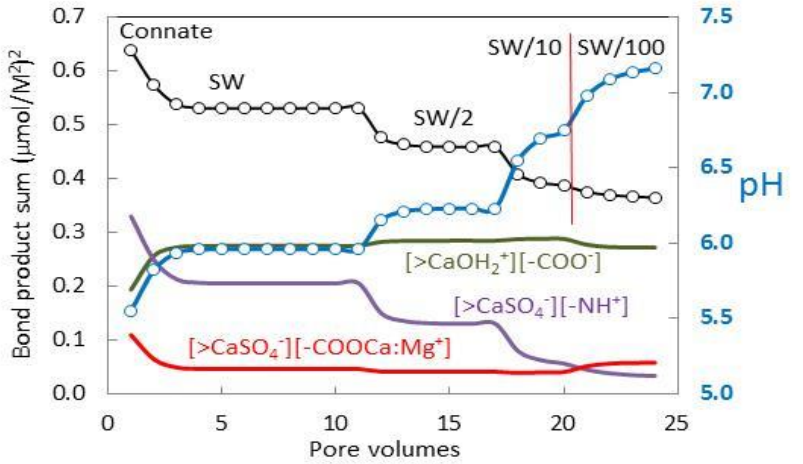
Oil Adhesion to Limestones



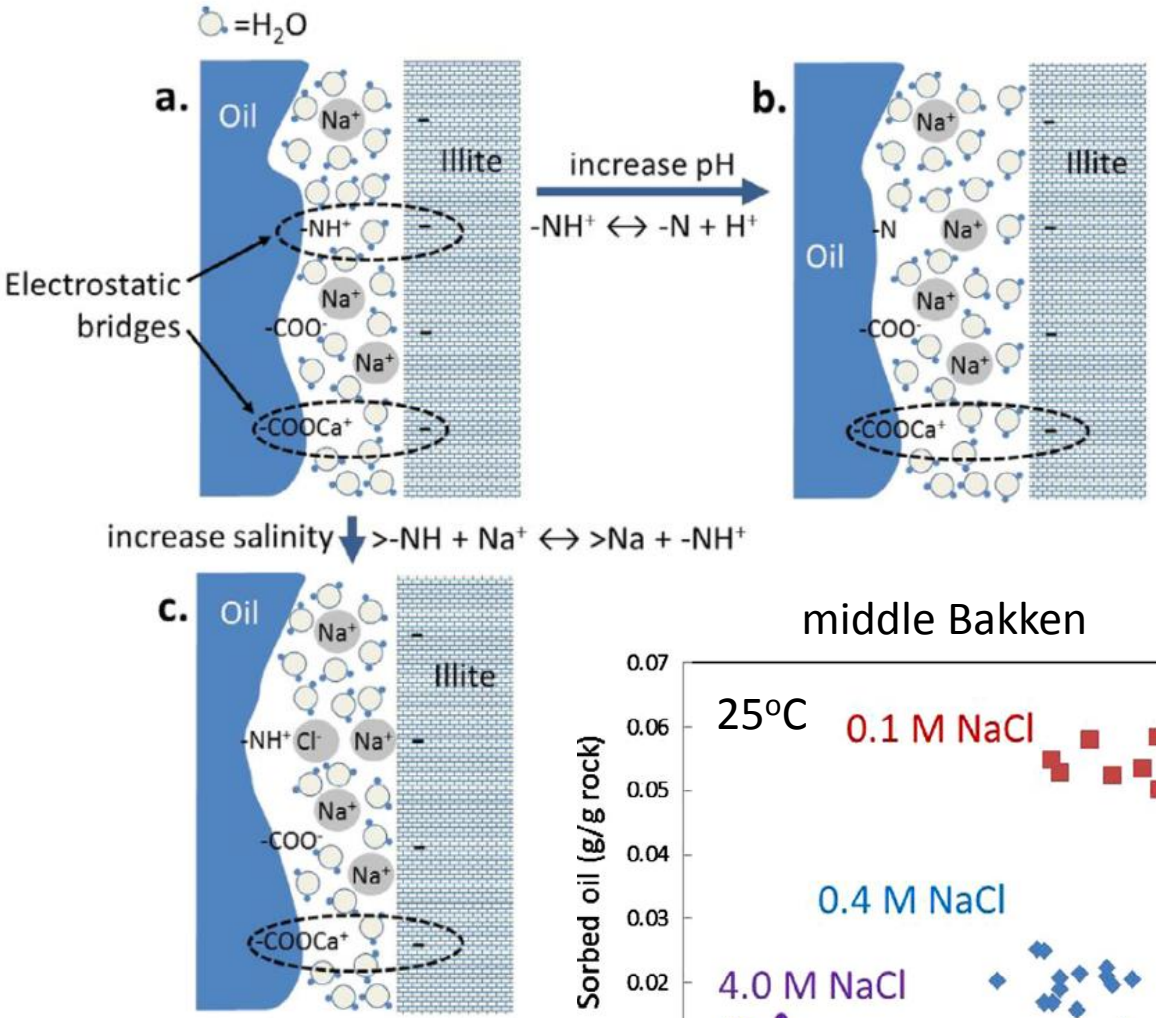


Yousef et al. 2011, SPE Reservoir Evaluation and Engineering

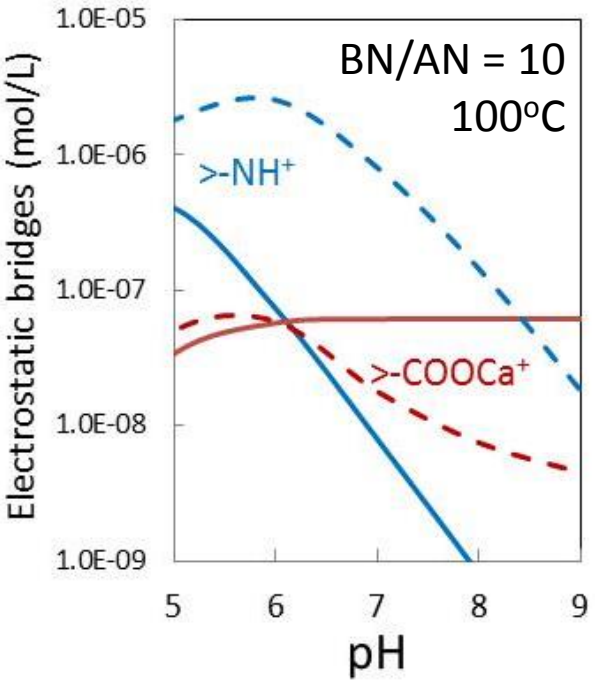




Oil Adhesion to Tight Formations (Illite)



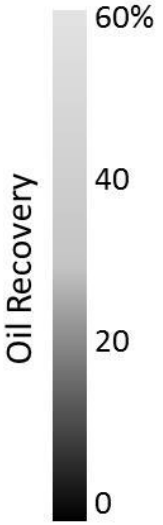
Brady et al., 2016, J. Unconventional Oil and Gas Resources



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.

Primary Migration
Primary Recovery

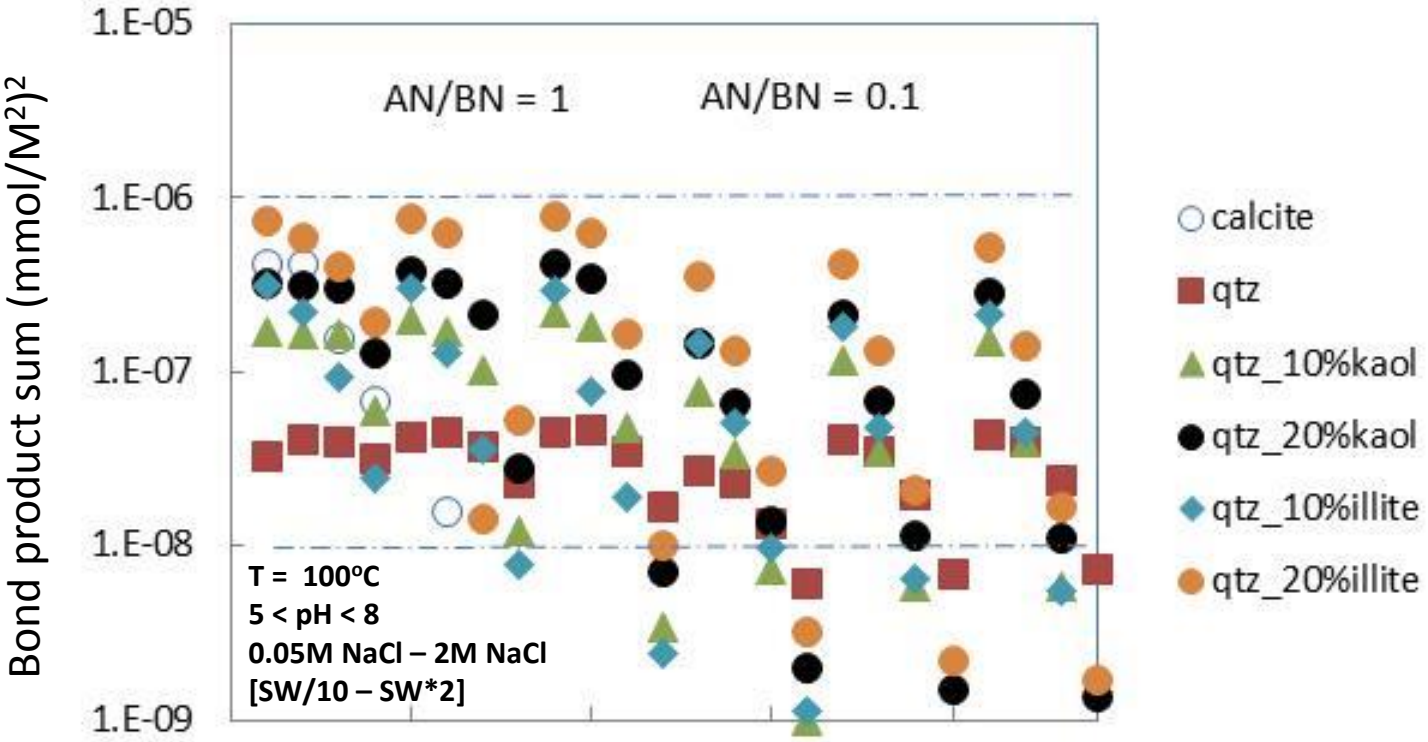


Tertiary – Injection of steam, surfactants, polymers, etc.

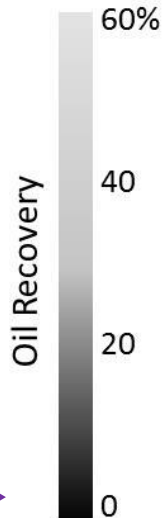
Secondary – Waterflooding to restore pressure.

Primary – Reservoir "pumps itself".

Oil Adhesion in *All* the World's Reservoirs



New Field



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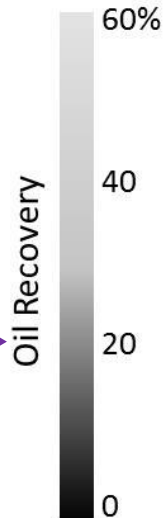
Old Field



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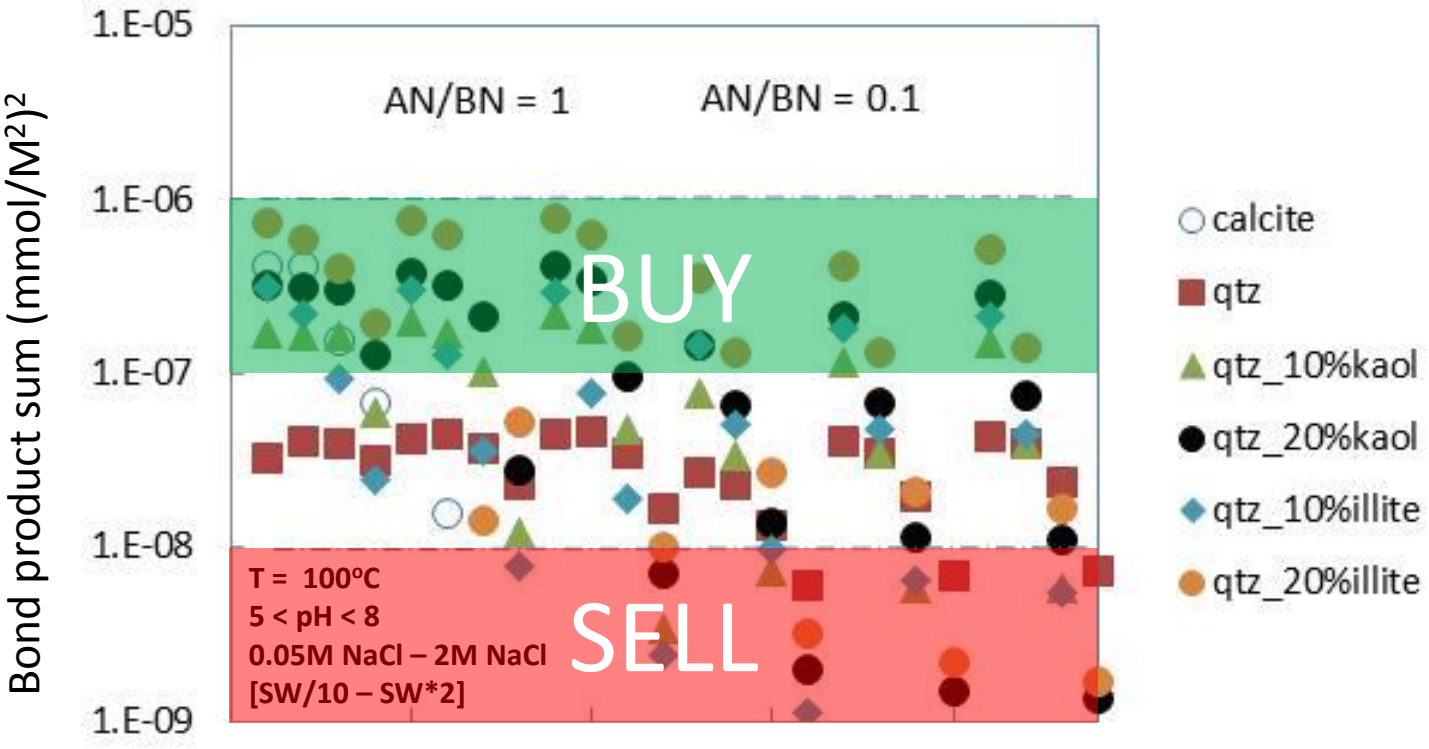
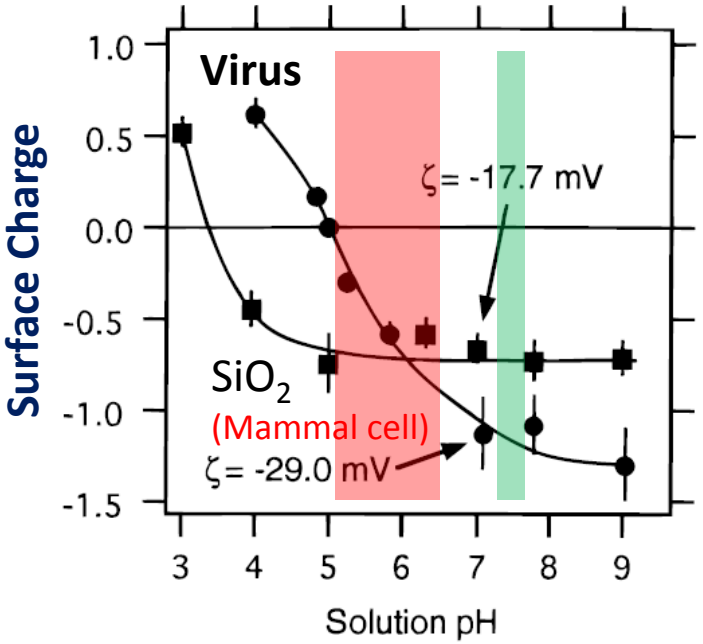


Magic Bullets for Oil Recovery from broad spectrum anti-virals

Endosomal pH 5-6.5 Physiological fluid pH 7.4



What this means for Oil Recovery

Eliminate the oil $–NH^+$ groups by:

1. Raising pH without adding NH_3 polymers,
2. Using anionic nano-particles,
3. Identifying anionic ligands that specifically link to $–NH^+$ groups to lessen their charge.

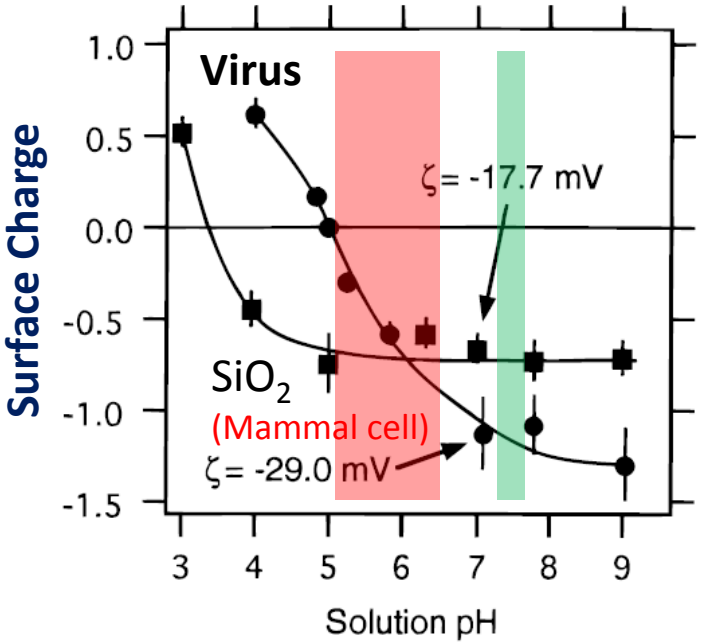
How to make a broad spectrum anti-viral

1. Shift the endosomal pH from 5 to 7.4 so that virus $–NH_2^+$ groups don't dock to cell $–COO^-$ groups, and trigger virus replication,
2. Do the pH jump with a cationic polymer containing lots of NH_2^+ groups (base buffer capacity).
3. Oops!, some of the polymeric NH_2^+ groups will trigger binding to virus $–COO^-$ groups at the higher pH, so.
4. Add more polymeric NH_2^+ groups to make the virus cationic too, so the cell and virus will have the same charge and be repelled from each other.

From Ichiyama et al. (2016) Cooperative orthogonal macromolecular assemblies with broad spectrum antiviral activity, high selectivity, and resistance mitigation. Macromolecules.

Magic Bullets for Broad Spectrum Anti-virals from oil recovery

Endosomal pH 5-6.5 Physiological fluid pH 7.4



1. Use non-cationic base buffers that don't specifically link to virus carboxylate groups – for example, borate and silicate,
2. Use a non-toxic mineral buffer to raise endosomal interface pH,
3. Add sorbate that makes mammalian cell charge positive at pH 6, so the cell won't bind to virus – for example Zn or Al.

What do anti-virals and oil recovery tell us about potholes?

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

Sign up for ENVE 510, Advanced Aquatic Chemistry, ‘meets Tuesday 9:30-11.