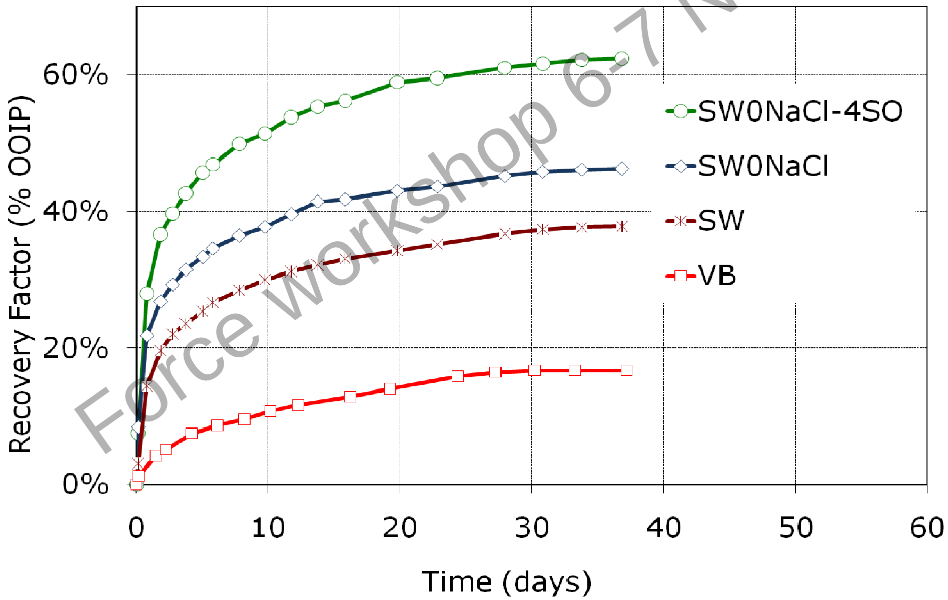
"Smart Water" Flooding in Carbonates and Sandstones: A New Chemical Understanding of the EOR-potential

Tor Austad
(tor.austad@uis.no)
University of Stavanger, Norway

Presented at the FORCE Education Seminar, NPD, Nov. 6-7., 2013.

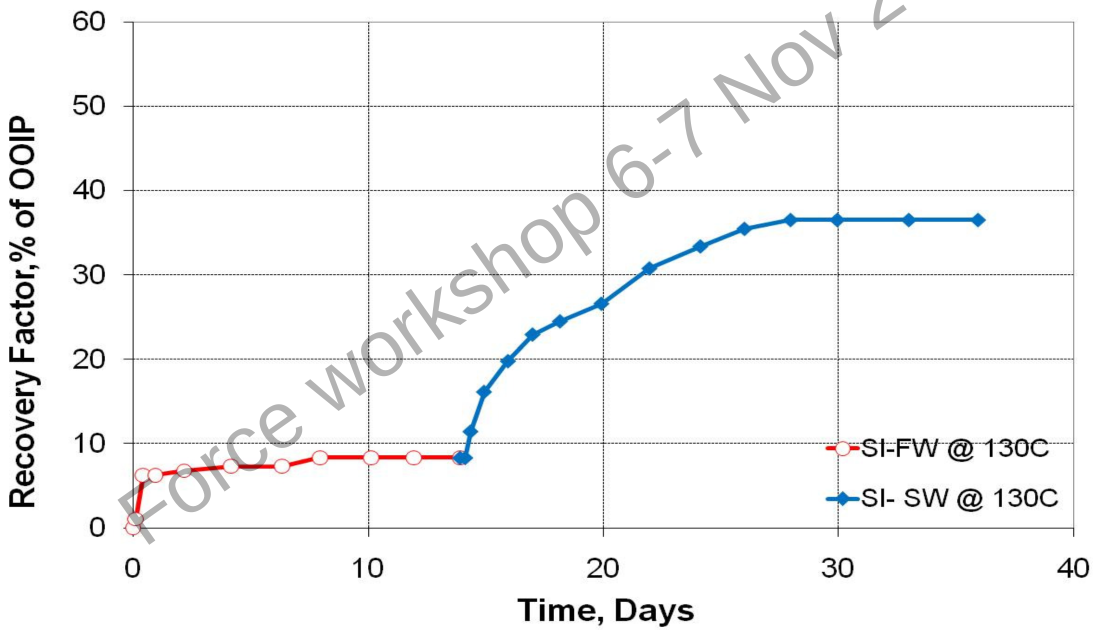
Example: "Smart Water" in Chalk

Spontaneous imbibition: T_{res}=90 °C; Crude oil AN=0.5; S_{wi}=10%
Chalk: 1-2 mD



- Formation water: VB
- Seawater: SW
- Seawater depleted in NaCl
- Seawater depleted in NaCl and spiked with 4x sulfate

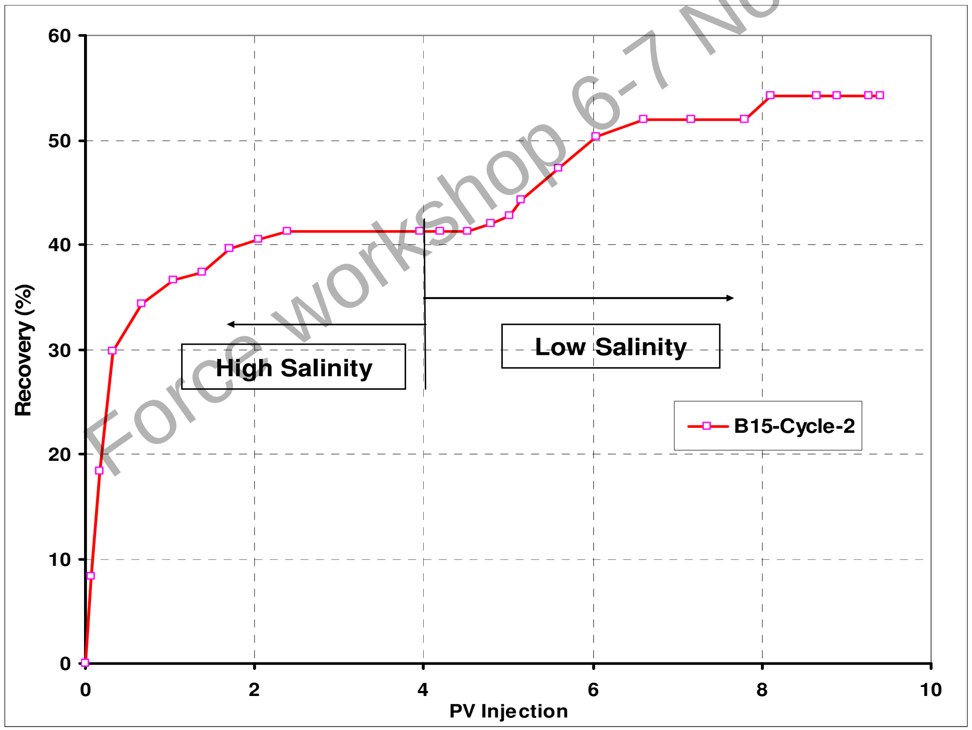
Example: ”Smart Water” in Limestone



Spontaneous imbibition at 130℃ of FW and SW into Res# 4-12 using crude oil with AN=0.50 mgKOH/g. Low perm. 0.1-1 mD.

Example: “Smart Water” in Sandstone

Low Salinity EOR-effect under forced displacement



HS: 100 000 ppm; **LS: 750 ppm**

What is "Smart Water"?

- "Smart water" can improve wetting properties of oil reservoirs and optimize fluid flow/oil recovery in porous medium during production.
- "Smart water" can be made by modifying the ion composition.
  - No expensive chemicals are added.
  - Environmental friendly.
- Wetting condition dictates:
  - Capillary pressure curve; $P_c=f(S_w)$
  - Relative permeability; k_{ro} and k_{rw} = f(Sw)

Water flooding

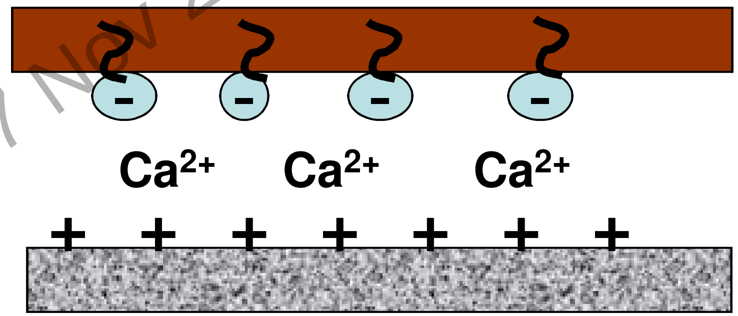
- Water flooding of oil reservoirs has been performed for a century with the purpose of:
  - Pressure support
  - Oil displacement
- Question:
  - Do we know the secret of water flooding of oil reservoirs??
  - If **YES**, then we must be able to explain why a "Smart Water" sometimes increases oil recovery and sometimes not.
- If we know the chemical mechanism, then the injected water can be optimized for oil recovery.
- Injection of the "Smartest" water should be done as early as possible.

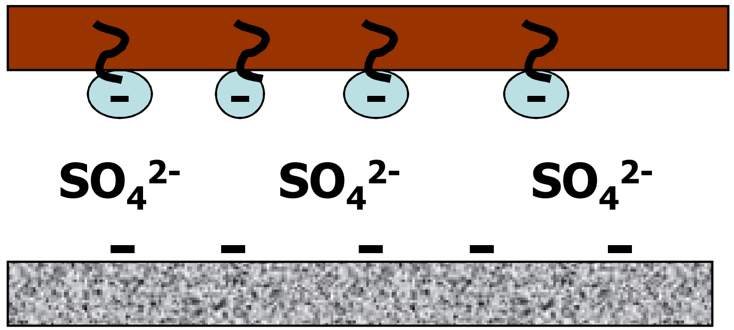
Outline

- Discuss the conditions for observing EOR-effecets by «Smart Water» in:
  - Carbonates
  - Sandstones
- A very simplified chemical explanation

Wetting properties in carbonates

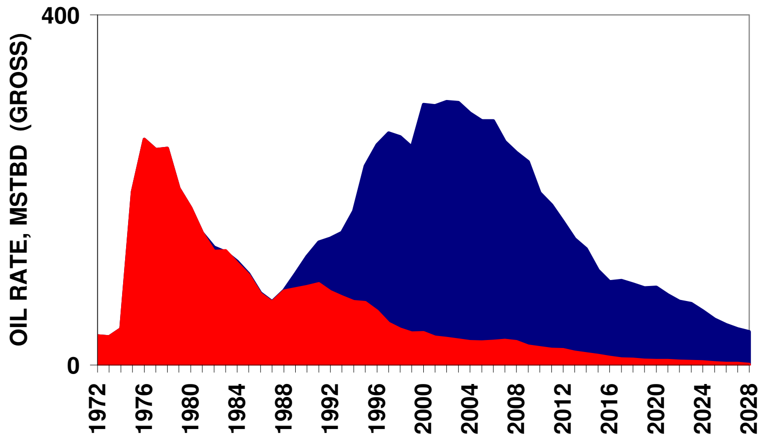
- Carboxylic acids, R-COOH
  - AN (mgKOH/g)
- Bases (minor importance)
  - BN (mgKOH/g)
- Charge on interfaces
  - Oil-Water
    - $R\text{-}COO^-$
  - Water-Rock
    - Potential determining ions
      - **Ca^{2+}, Mg^{2+},**
      - **(SO_4^{2-}, CO_3^{2-}, pH)**





Ekofisk

- **Why is injection of seawater such a tremendous success in the Ekofisk field?**
  - Highly fractured
  - High temperature, 130 °C.
  - Low matrix permeability, 1-2 mD
- **Wettability:**
  - Tor-formation: Preferential water-wet
  - Lower Ekofisk: Low water-wetness
  - Upper Ekofisk: Neutral to oil-wet
- **Estimated recoveries**
  - 1976: 18%
  - 2001: Goal: 46%
  - NPD; 2002: 50%
  - 2007: Goal 55 %



Brine composition

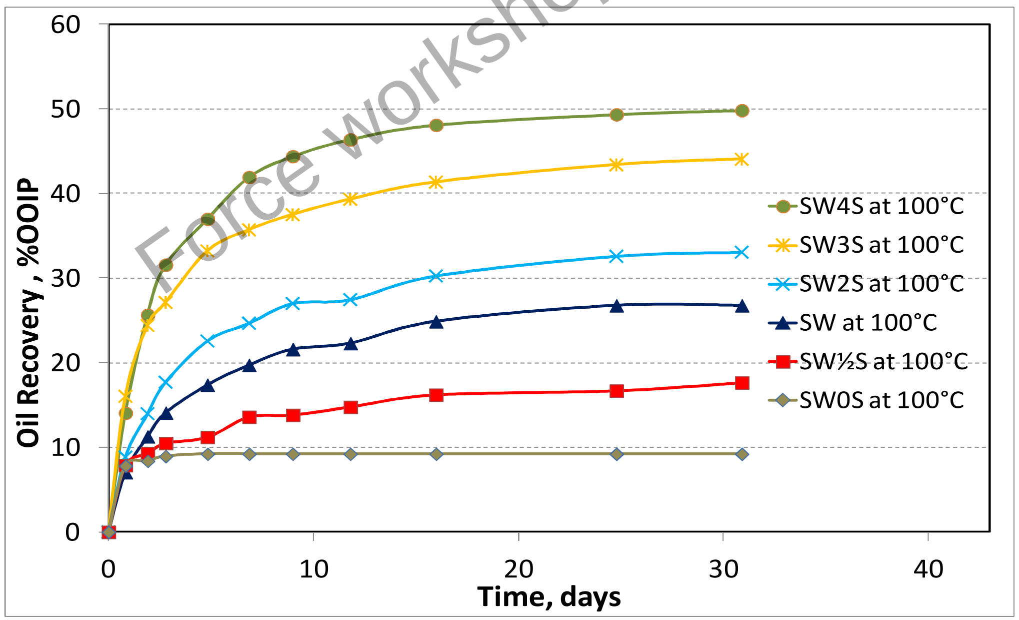
Comp.	Ekofisk (mole/l)	Seawater (mole/l)
Na^+	0.685	0.450
K^+	0	0.010
Mg^{2+}	**0.025**	**0.045**
Ca^{2+}	**0.231**	**0.013**
Cl^-	1.197	0.528
HCO_3^-	0	0.002
SO_4^{2-}	**0**	**0.024**

Seawater: $[SO_4^{2-}]$~2 $[Ca^{2+}]$ and $[Mg^{2+}]$~ 2 $[SO_4^{2-}]$

$[Mg^{2+}]$~4 $[Ca^{2+}]$

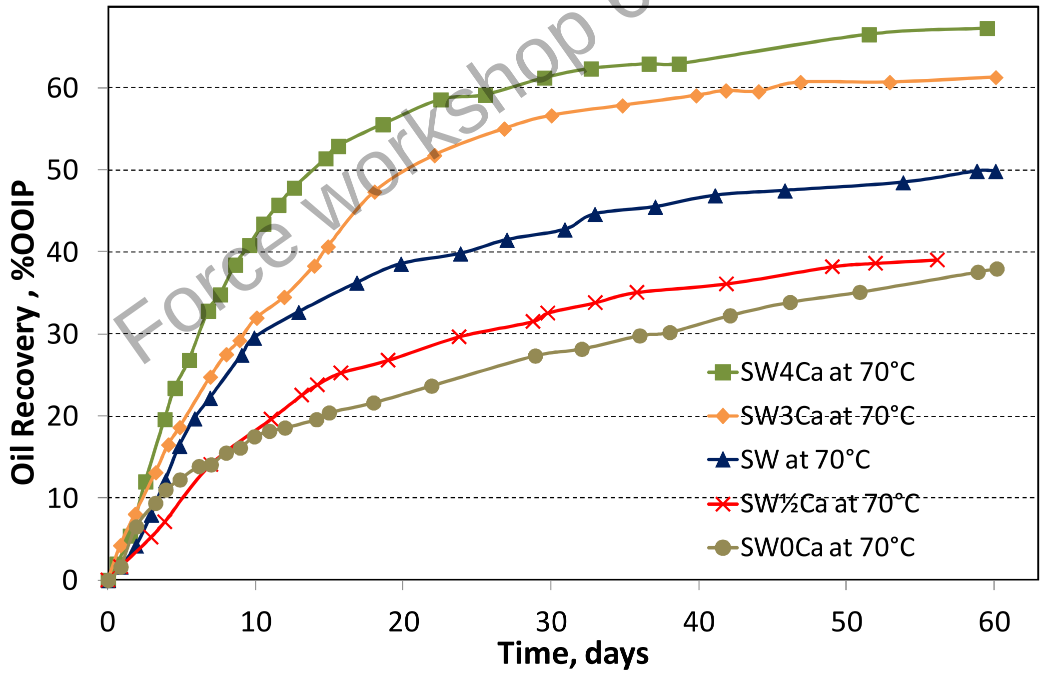
Effect of Sulfate in SW

- Crude oil: AN=2.0 mgKOH/g
- Initial brine: EF-water
- Imbibing fluid: Modified SSW
- Spontaneous imbibition at 100 °C

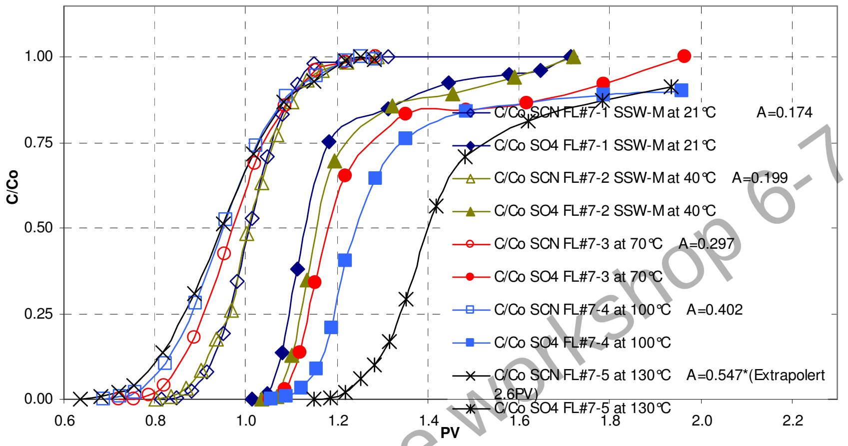


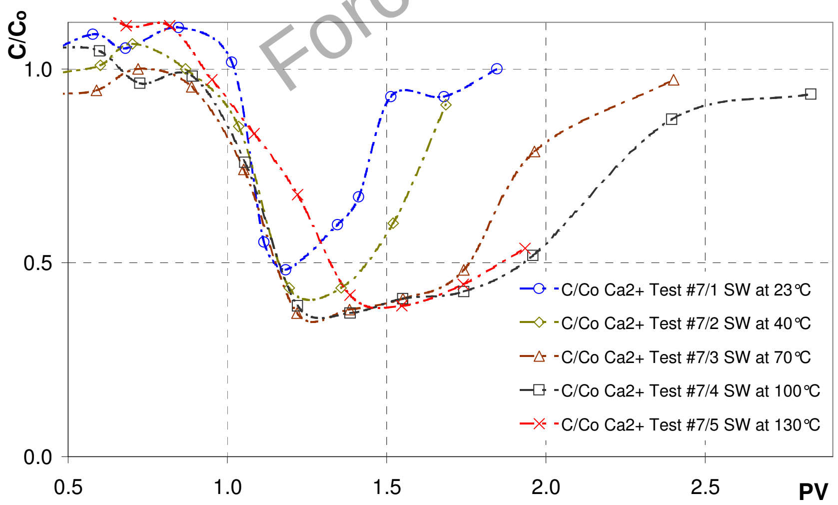
Is Ca^{2+} active in the wettability alteration?

- Crude oil: AN=0.55 mgKOH/g
- S_{wi} = 0; Imbibing fluid: Modified SSW
- Spontaneous imbibition at 70 °C



Co-Adsorption of SO_4^{2-} and Ca^{2+} vs. Temperature





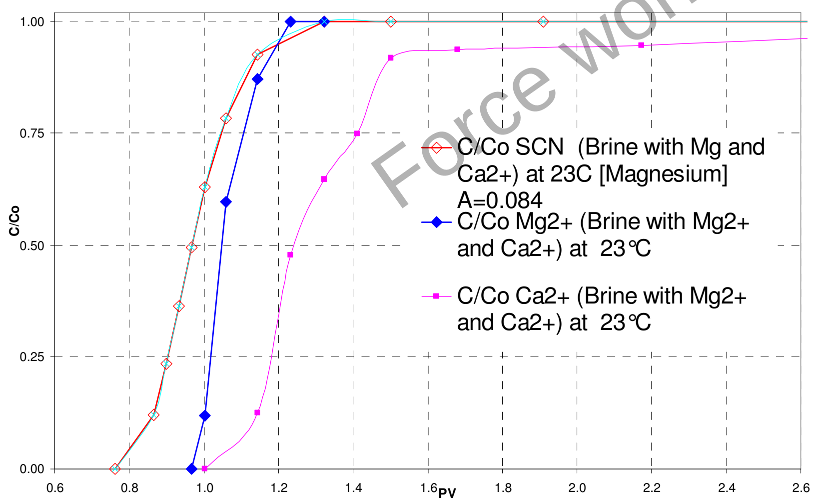
Method:

1. Core saturated with SW without SO_4^{2-}
2. Core flooded with SW spiked with SCN^- (Chromatographic separation of SCN^- and SO_4^{2-})

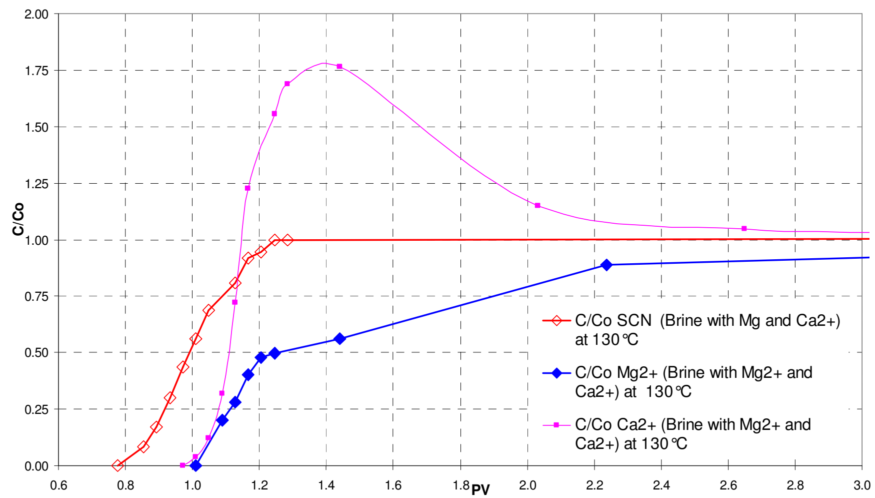
Affinities of Ca^{2+} and Mg^{2+} towards the chalk surface

NaCl-brine; $[SCN^-] = [Ca^{2+}] = [Mg^{2+}] = 0.013$ mole/l

T=23 °C

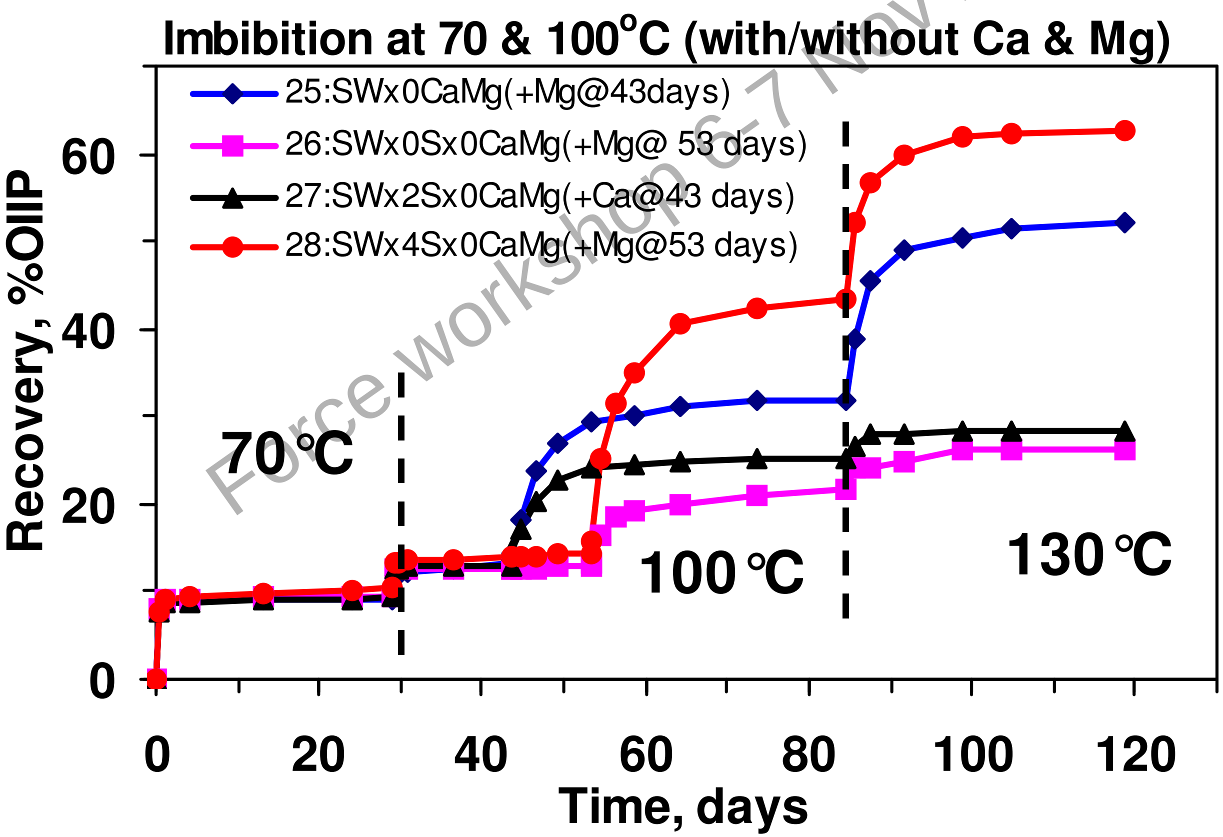


T=130 °C

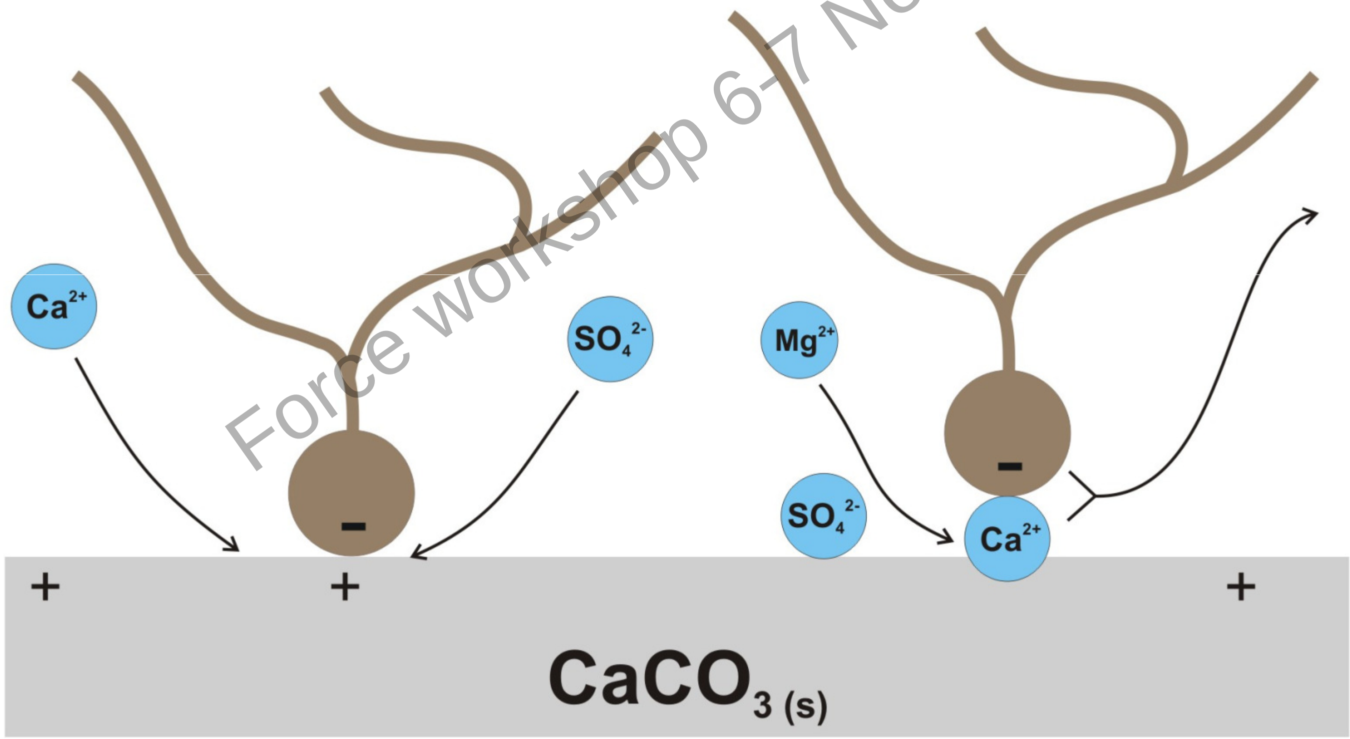


$$CaCO_3(s) + Mg^{2+} = MgCO_3(s) + Ca^{2+}$$

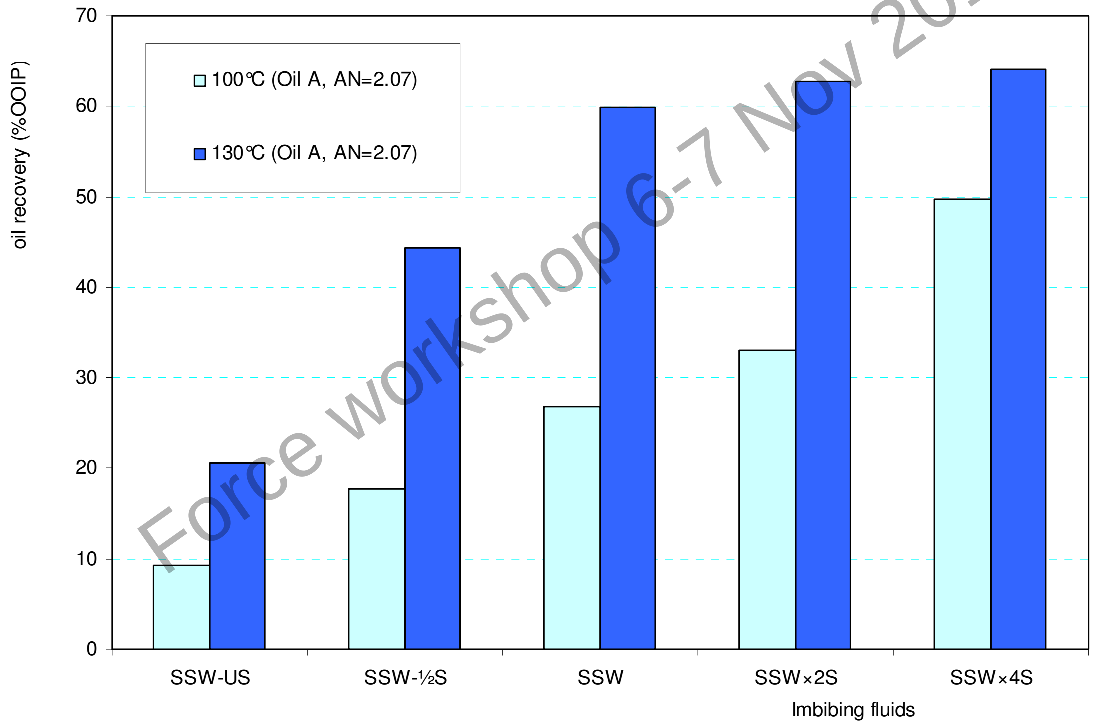
Effects of potential determining ions and temperature on spontaneous imbibition



Suggested wettability mechanism



Can SO_4^{2-} compensate for low T_{res} ?



Maximum oil recovery from chalk cores when different imbibing fluids were used (SW with varying SO_4^{2-} conc.). Oil: AN=2.07 mgKOH/g).

Ion composition in PW from Ekofisk

PW contained 73.6 vol% SW and 26.4 vol%FW

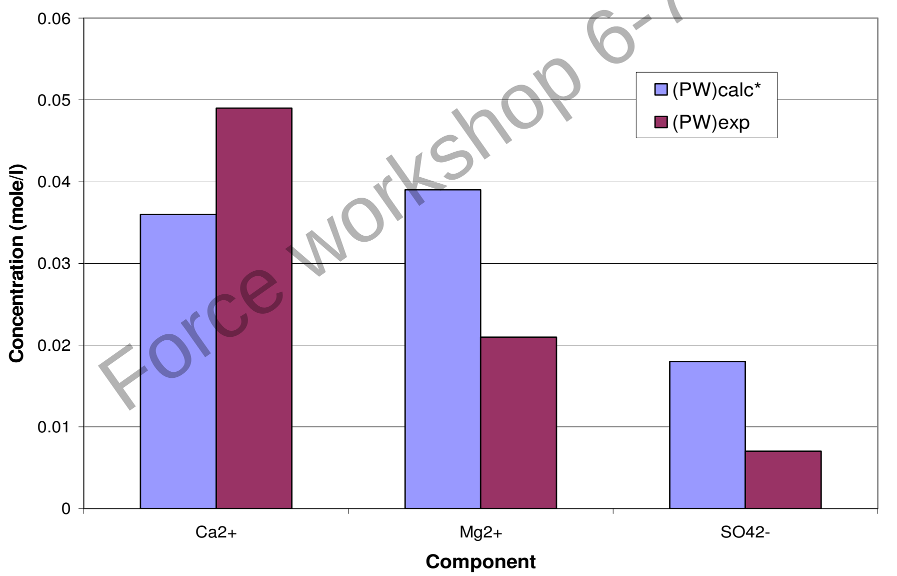
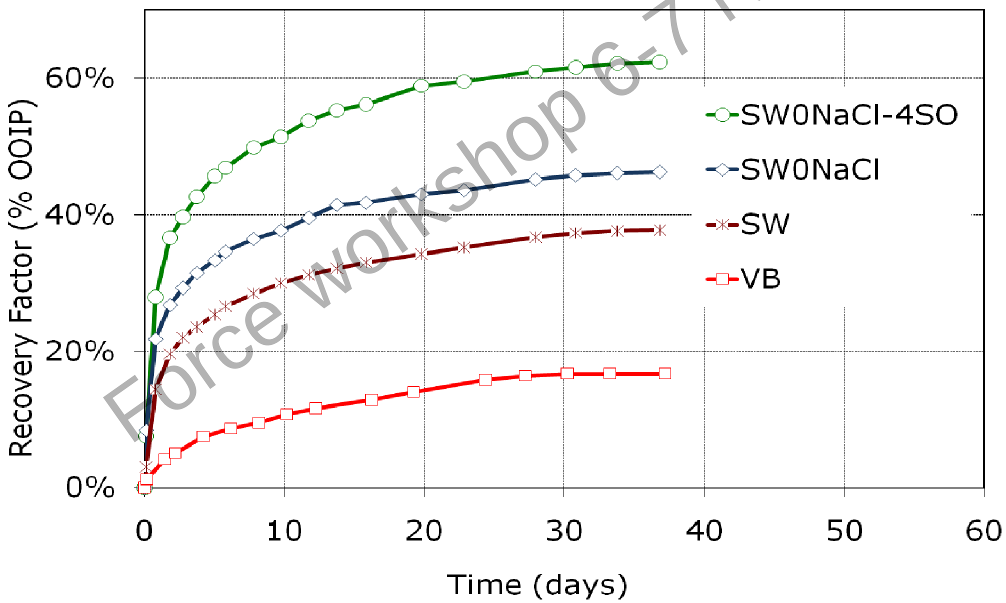


Fig. 3 Calculated and measured component concentration in PW linked to substitution of Ca^{2+} by Mg^{2+} at the rock surface, adsorption of SO_4^{2-} onto the rock and precipitation of $CaSO_4$.

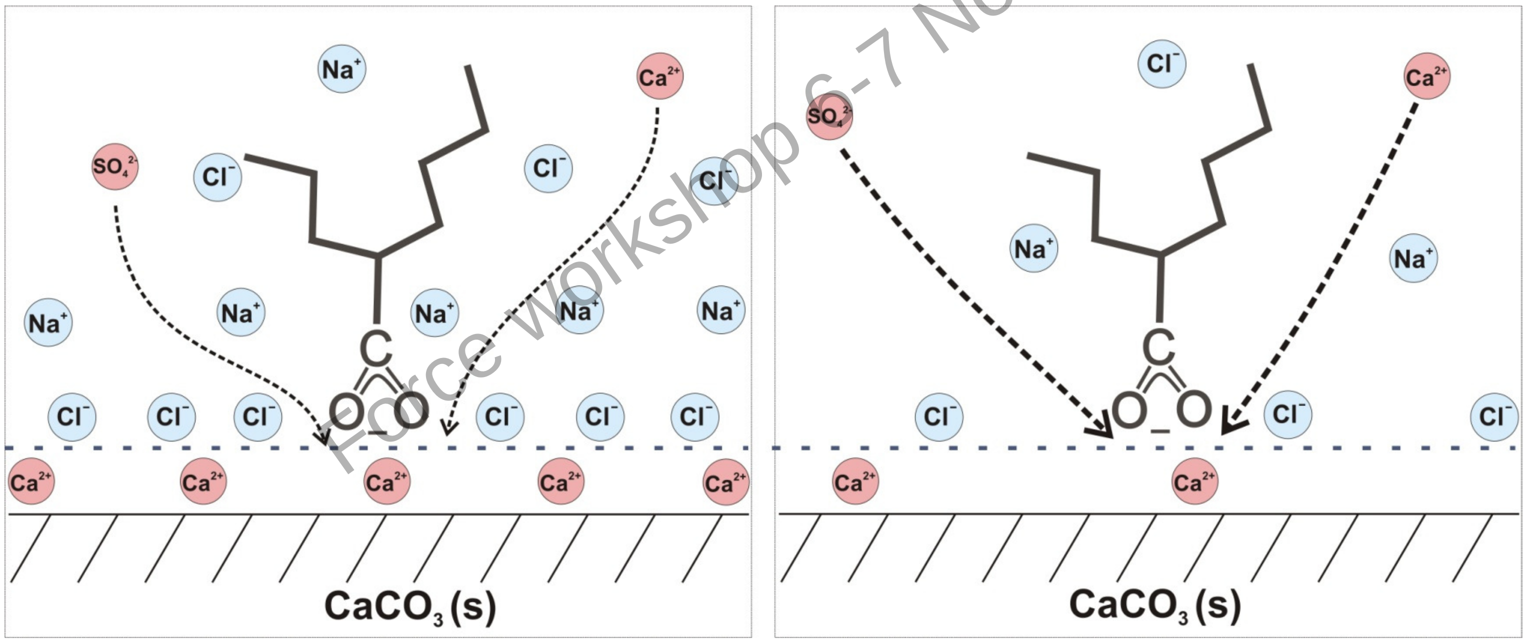
Can modified SW be an even "Smarter" EOR-fluid

Spontaneous imbibition: T_{res}=90 °C; Crude oil AN=0.5; S_{wi}=10%



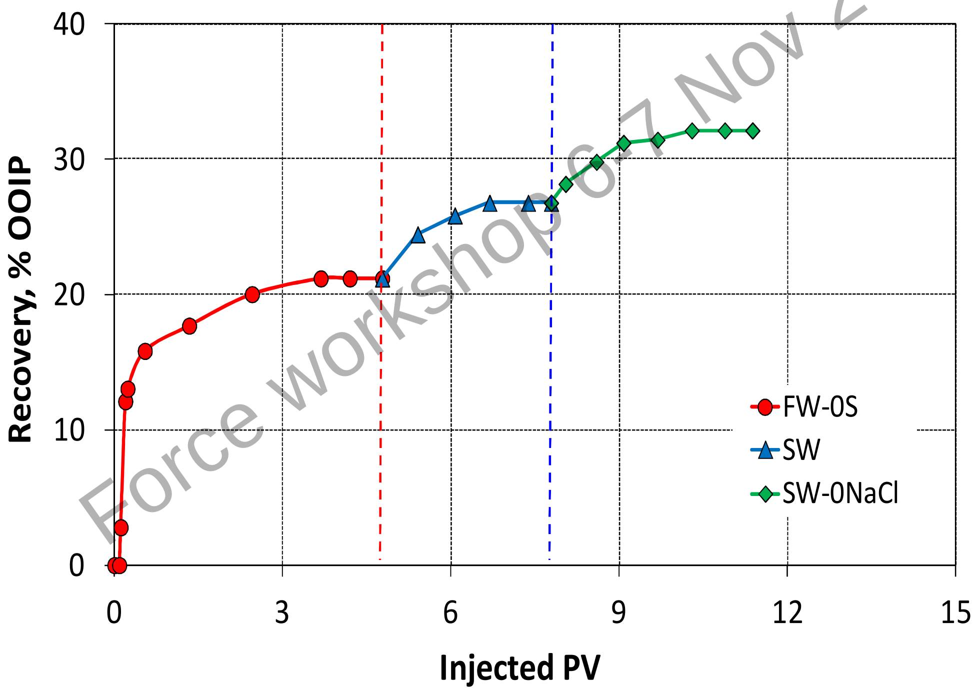
- Formation water: VB
- Seawater: SW
- Seawater depleted in NaCl
- Seawater depleted in NaCl and spiked with 4x sulfate

Effect of Salinity and Ion concentration



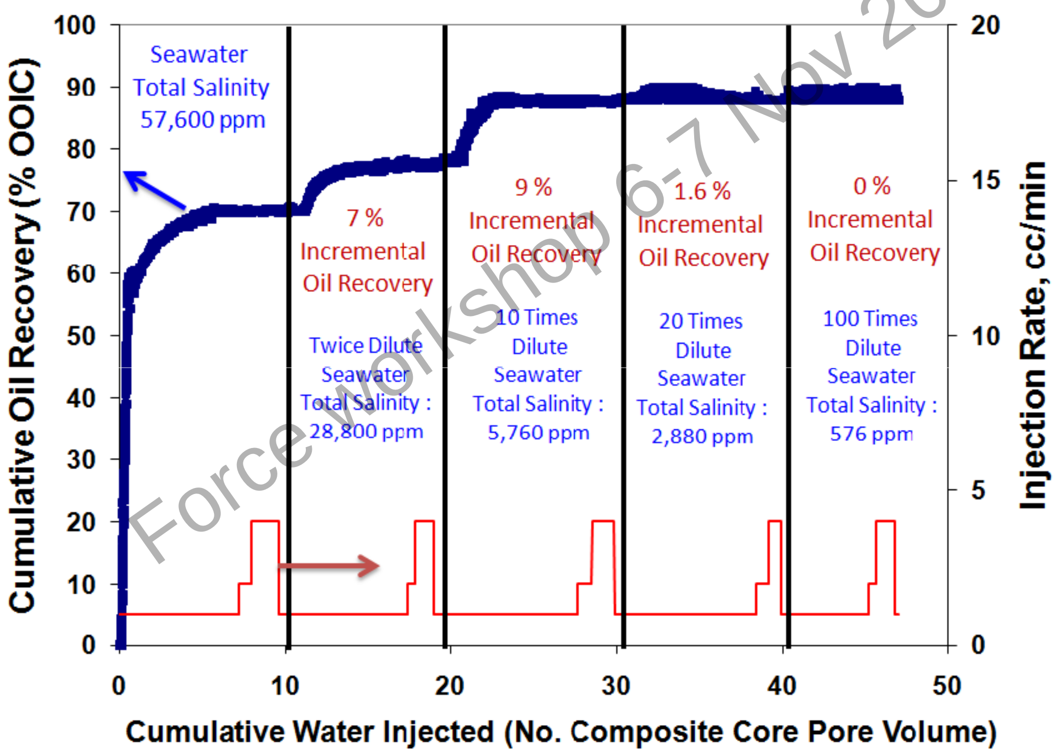
The access of potential determining ions to the calcite surface
is affected by the concentration of non active ions in the double layer

Forced displacement using «Smart SW Water»



Oil recovery by forced displacement from the composite limestone reservoir core. Successive injection of FW, SW and SW-0NaCl. T_{test}: 100°C. Injection rate: 0.01 ml/min (≈0.6 PV/D).

Low salinity EOR-effects in carbonates



SPE 137634 Ali A. Yousef et al. (Saudi Aramco)

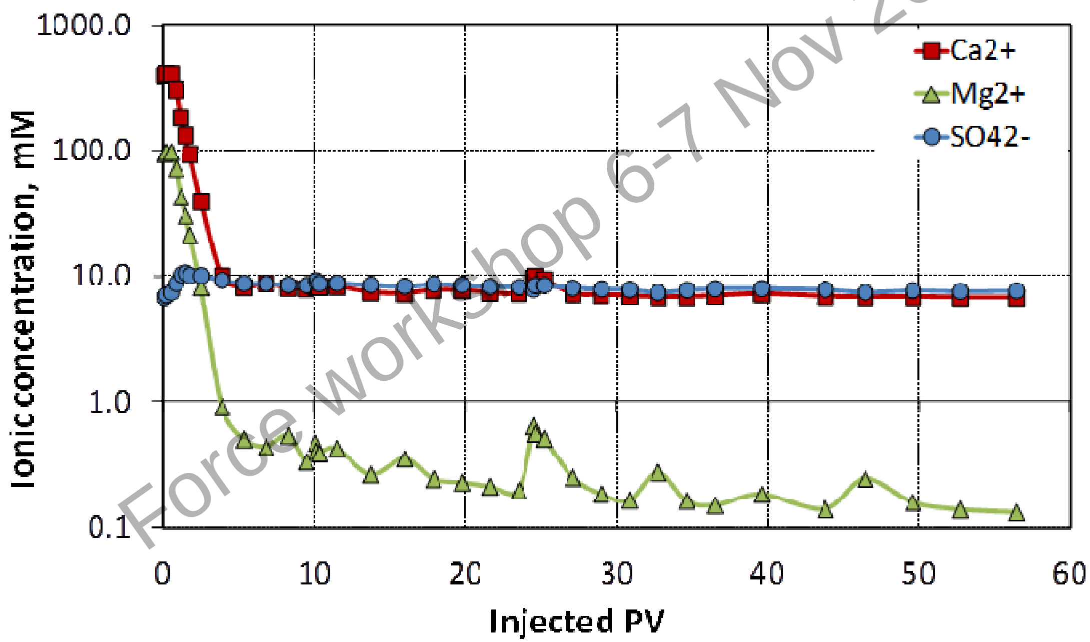
Codition for observing low salinity EOR-effects in carbonates

- The carbonate rock must contain anhydrite, $CaSO_4(s)$
- Chemical equilibrium:

$$CaSO_4(s) \leftrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) \leftrightarrow Ca^{2+}(ad) + SO_4^{2-}(ad)$$

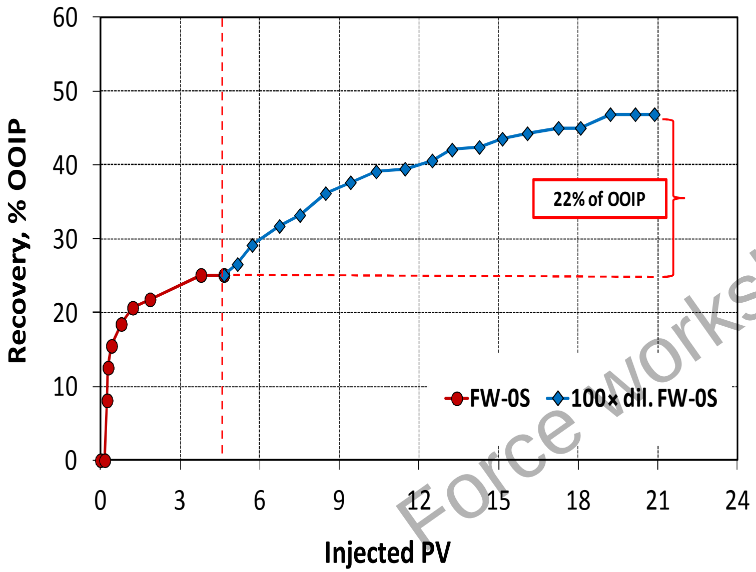
- The concentration of $SO_4^{2-}(aq)$ depends on:
  - Temperature (decreases as T increases)
  - Brine salinity (Ca^{2+} concentration)
- Wettability alteration process:
  - Temperature (increases as T increases)
  - Salinity (increases as NaCl conc. decreases)
- Optimal temperature window
  - 90-110 ^{o}C ?

Presence of $CaSO_4$

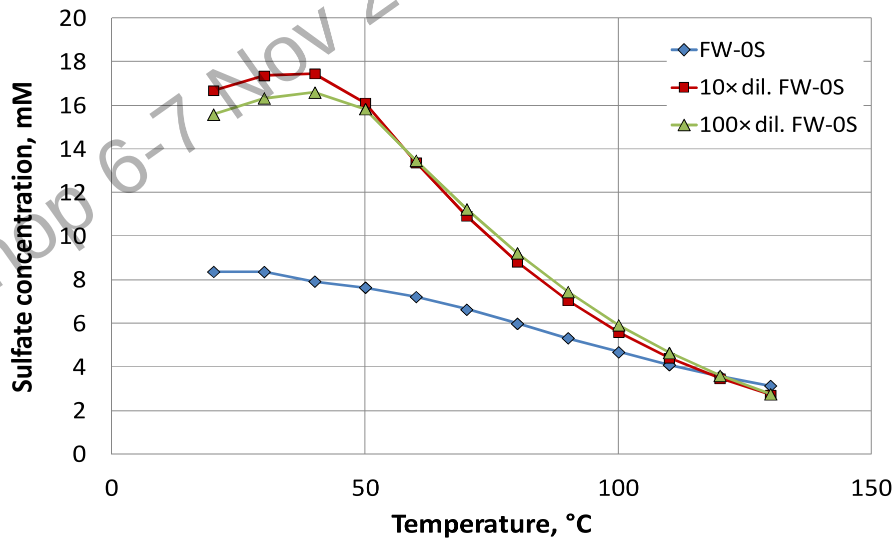


Concentration profiles of Ca^{2+}, Mg^{2+}, and SO_4^{2-} when flooding reservoir limestone core with DI water, after aging with FW. T_{test}: 100°C, Injection rate: 0.1 ml/min.

Low salinity EOR-effect



Oil recovery by forced displacement from a reservoir limestone core containing anhydrite. Successive injection of FW, and 100× diluted FW. T_{test}: 100°C. Injection rate: 0.01 ml/min (≈1 PV/D).

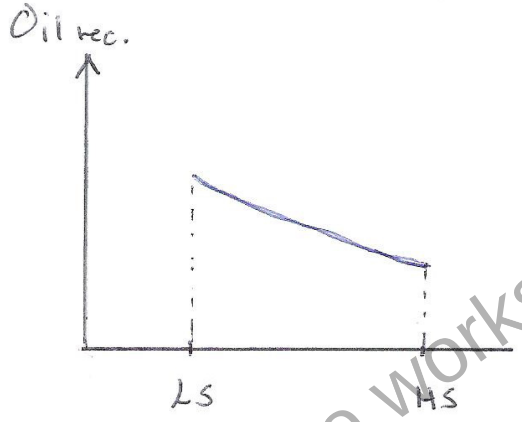


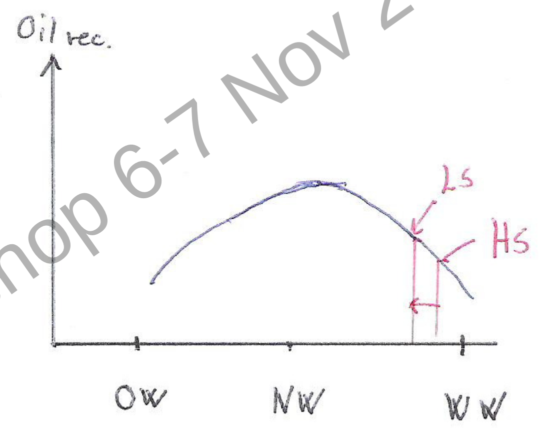
Simulated dissolution of $CaSO_4$(s) when exposed to FW-0S, 10× and 100× diluted FW at different temperatures.

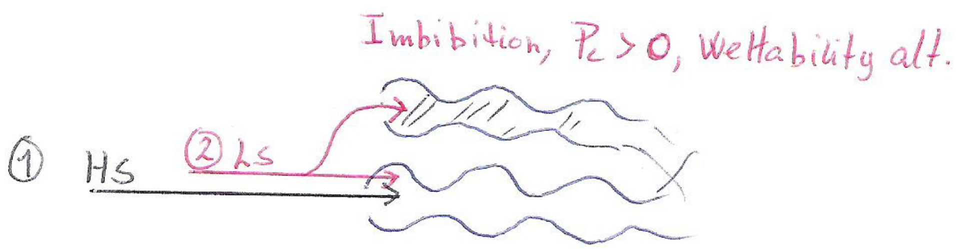
“Smart Water” in Sandstone

- Some experimental facts
  - Porous medium
    - Clay must be present
  - Crude oil
    - Must contain polar components (acids and/or bases)
  - Formation water
    - Must contain active ions towards the clay (Especially divalent ions like Ca^{2+} and Mg^{2+})

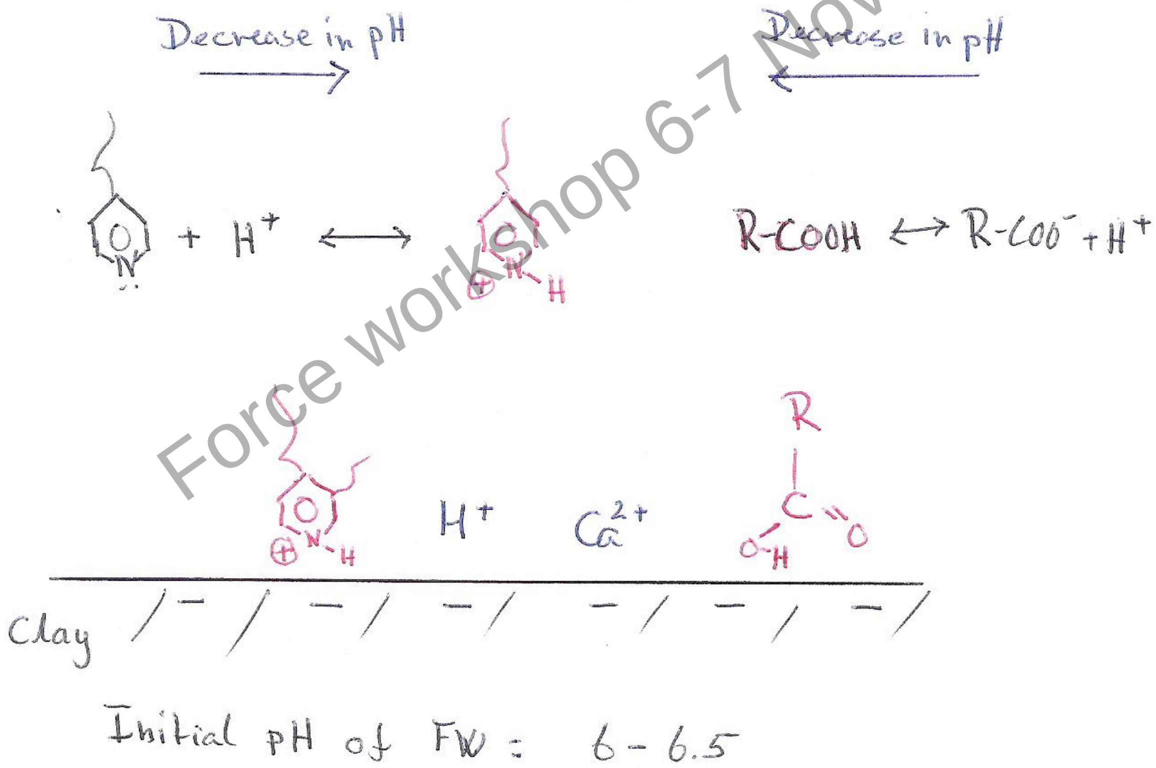
General information





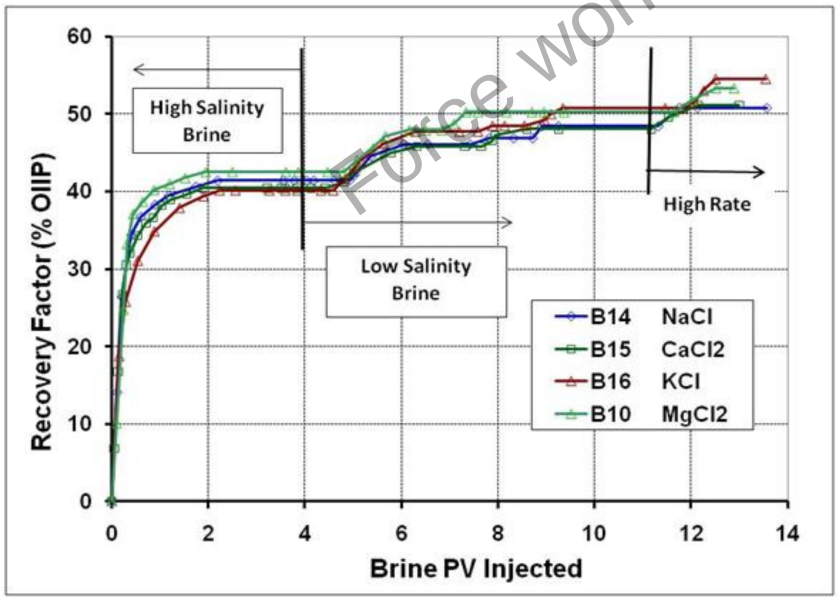


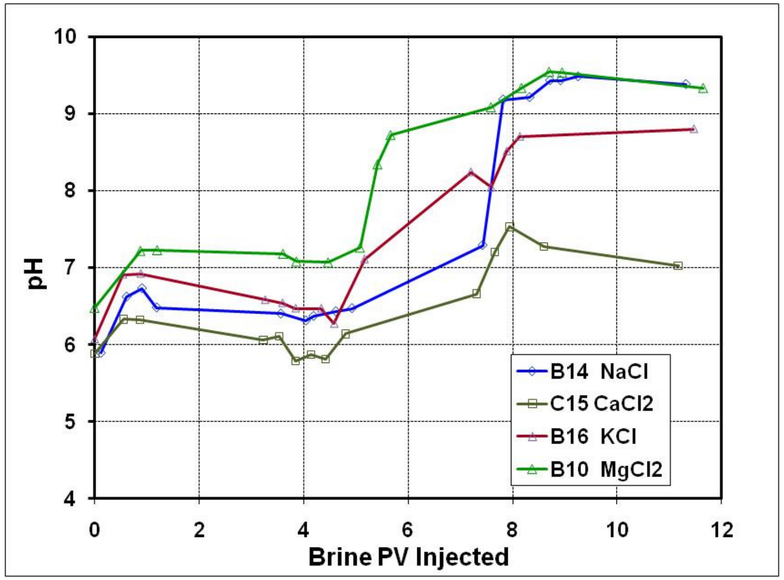
Adsorption onto clay



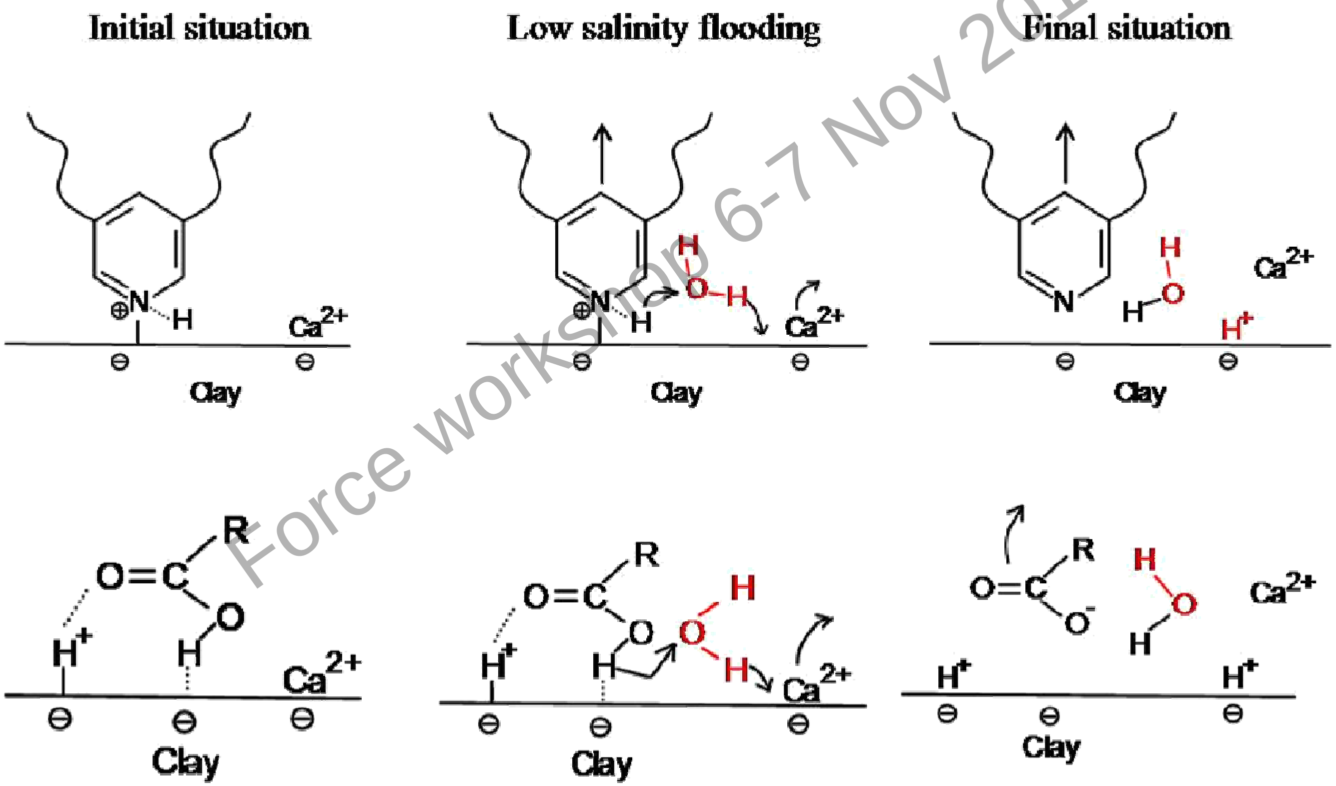
Local increase in pH important

	NaCl (mole/l)	$CaCl_2.2H_2O$ (mole /l)	KCl (mole /l)	$MgCl_2.2H_2O$ (mole /l)
Connate Brine	1.54	0.09	0.0	0.0
Low Salinity Brine-1	0.0171	0.0	0.0	0.0
Low Salinity Brine-2	0.0034	0.0046	0.0	0.0
Low Salinity Brine-3	0.0	0.0	0.0171	0.0
Low Salinity Brine-4	0.0034	0.0	0.0	0.0046





Suggested mechanism



Proposed mechanism for low salinity EOR effects. Upper: Desorption of basic material. Lower: Desorption of acidic material.

The initial pH at reservoir conditions may be in the range of 6

Clay minerals

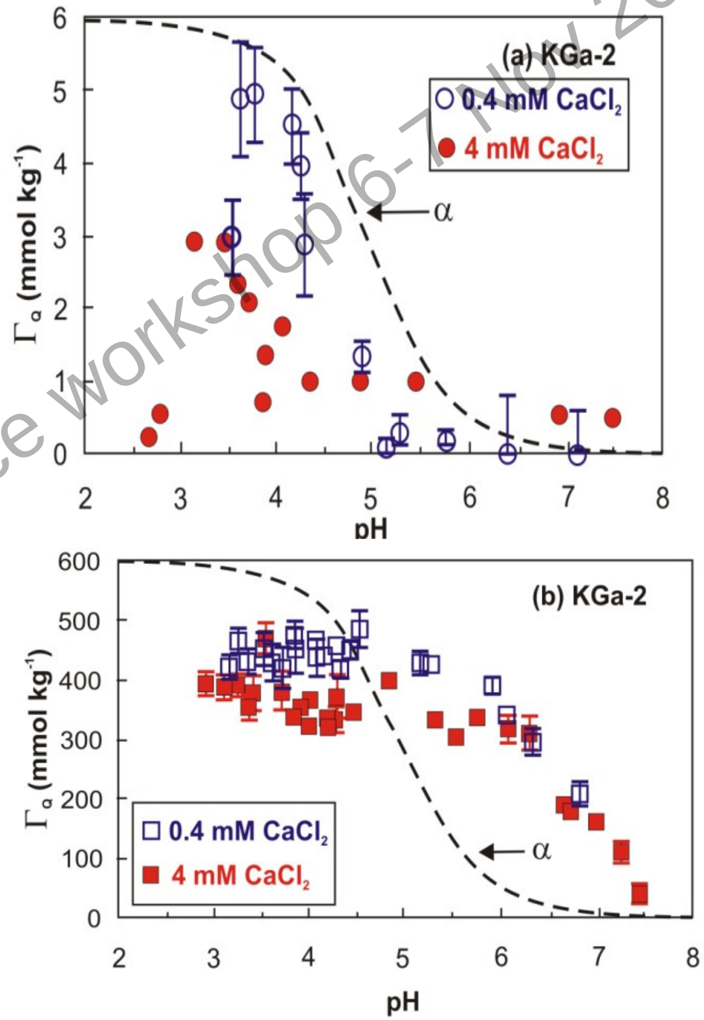
- Clays are chemically unique
  - Permanent localised negative charges
  - Act as cation exchangers
    - General order of affinity:

      $Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} << H^+$

Adsorption of basic material Quinoline

Kaolinite

Nonsweeling(1:1 Clay)



Montmorillonite

Swelling (2:1 clay, similar in structure to illite/mica)

Burgos et al.

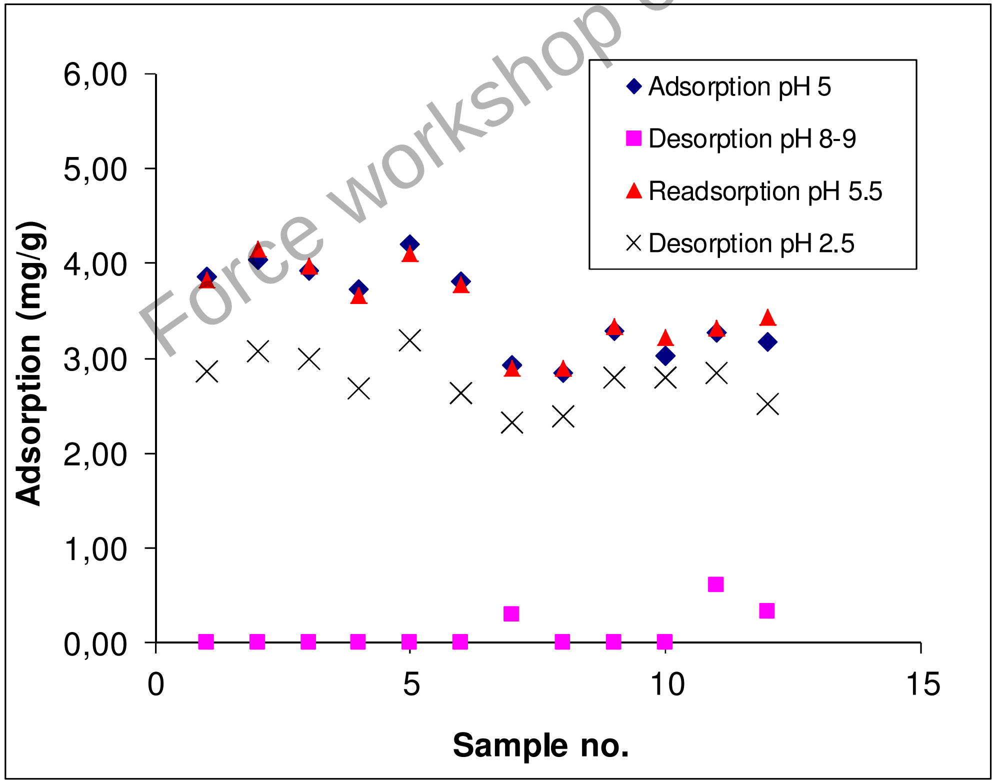
Evir. Eng. Sci.,

19, (2002) 59-68.

Kaolinite: Adsorption reversibility by pH

Quinoline

Samples 1-6: 1000 ppm brine.
Samples 7-12: 25000 ppm brine



Adsorption of acidic components onto Kaolinite

Adsorption of **benzoic acid** onto kaolinite at 32 °C from a NaCl brine
(Madsen and Lind, 1998)

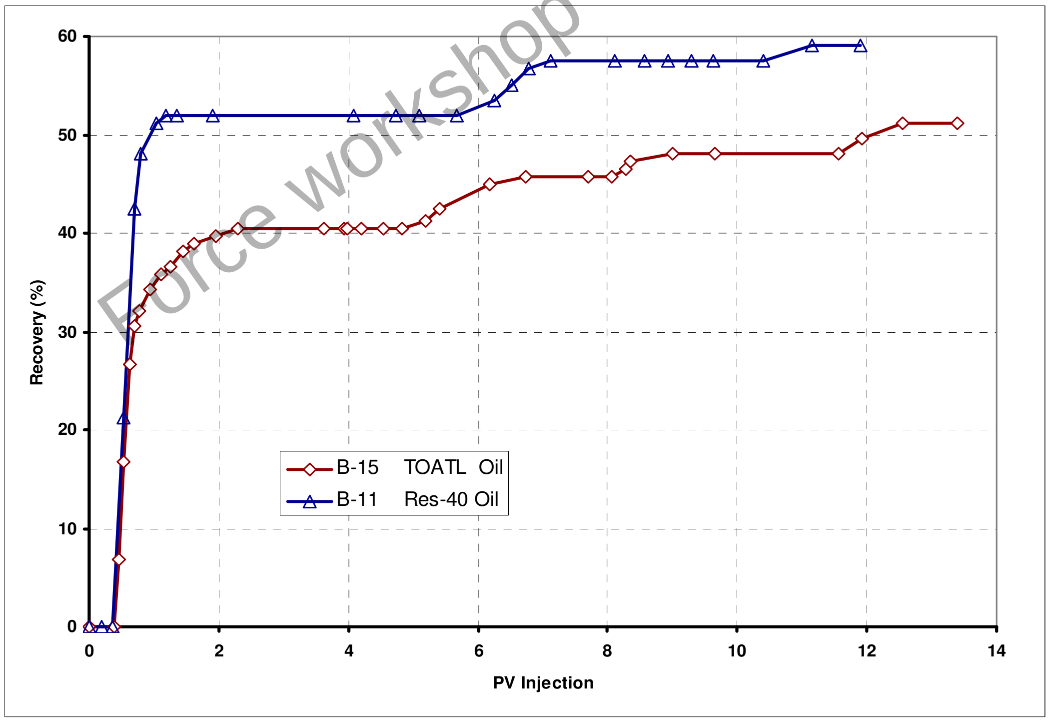
$pH_{initial}$	Γ_{max} µmole/m^2
5.3	3.7
6.0	1.2
8.1	0.1

Increase in pH increases water wetness for an acidic crude oil.

Oil: Acidic or Basic

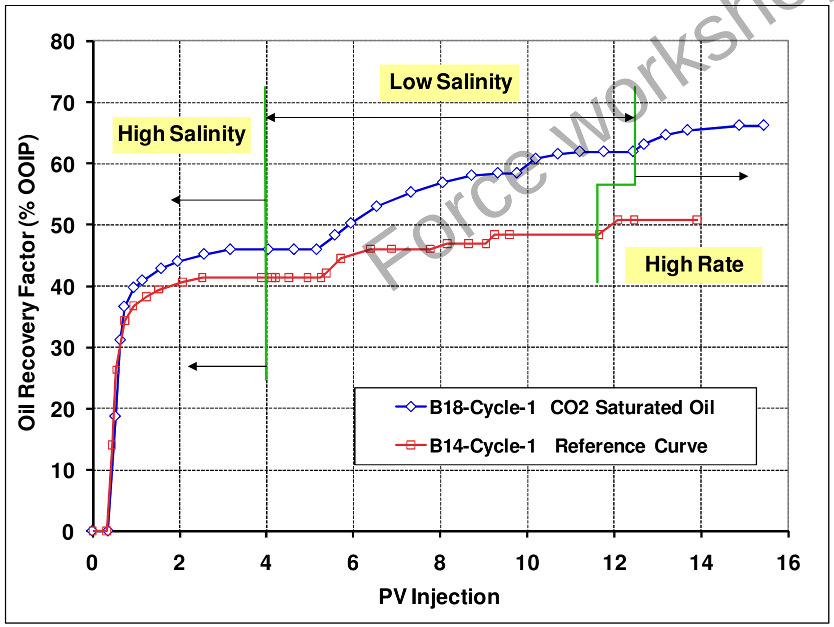
Total oil: **AN=0.1 and BN=1.8 mgKOH/g**

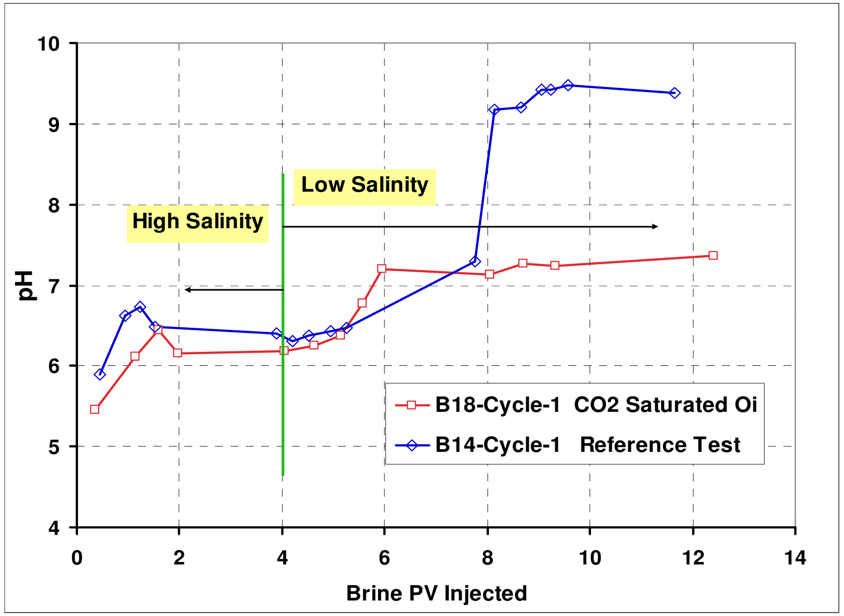
Res 40: **AN=1.9 and BN=0.47 mgKOH/g**



Lower initial pH by CO_2 increses the low salinity effect

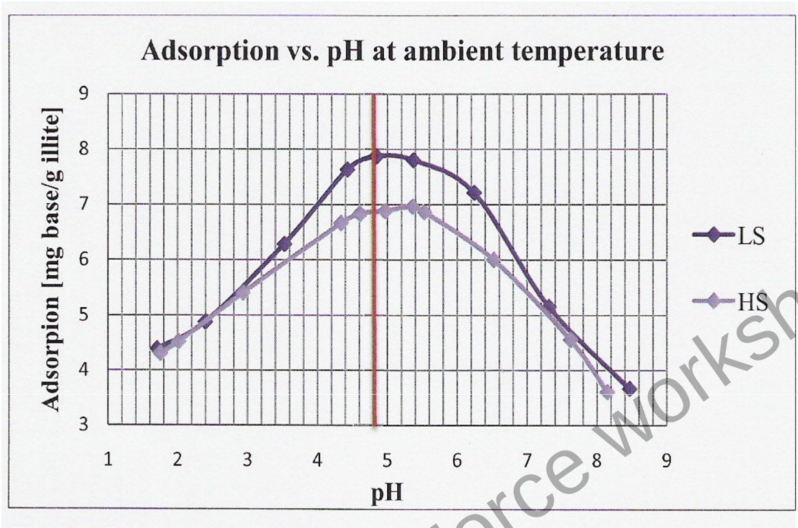
Core No.	S_{wi} %	T_{Aging} °C	$T_{Floodin}$ °g C	Oil	LS brine	Formation Brine
B18	19.7 6	60	40	TOTAL Oil Saturated With CO_2 at 6 Bars	NaCl: 1000 ppm	TOTAL FW 100 000 ppm
B14	19.4	60	40	TOTAL Oil	NaCl:1000 ppm	TOTAL FW 100 000 ppm



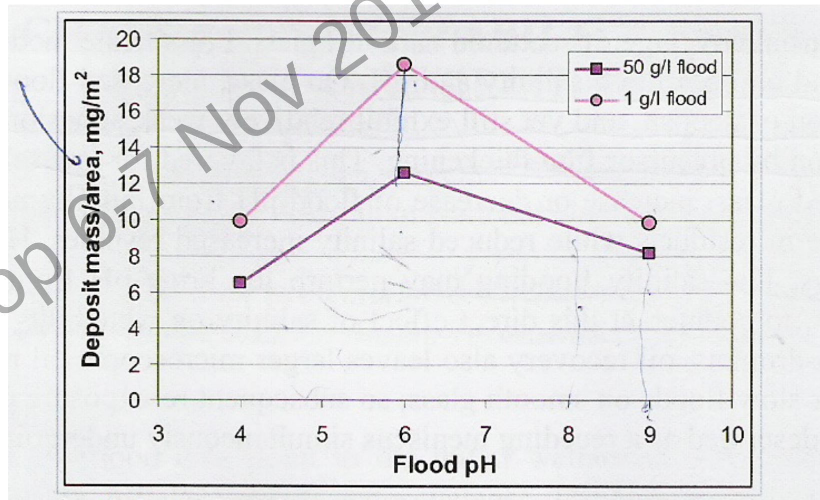


$$CO_2 + H_2O \leftrightarrow H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_20$$

LS water increases oil-wetness



Adsorption of Quinoline vs. pH at ambient temperature for LS (1000 ppm) and HS (25000 ppm) fluids.



Ref. Fogden and Lebedeva, SCA 2011-15
(Colloids and Surfaces A (2012)
Adsorption of crude oil onto kaolinite

It is not a decrease in salinity, which makes the clay more water-wet, but it is an increase in pH

Snorre field

- Lab work
  - Negligible tertiary low salinity effects after flooding with SW, on average <2% extra oil.
  - T_{res}=90 ^oC
- Single well test by Statoil
  - Confirmed the lab experiments
- Question:
  - Why such a small Low Salinity effect after flooding Snorre cores with SW ?

New study at UoS: Lunde formation

Table 1. Mineral composition

Core	Quartz [wt%]	Plagioclase [wt%]	Calcite [wt%]	Kaolinite [wt%]	Illite/mica [wt%]	Chlorite [wt%]
13	28.2	32.1	1.4	2.6	9.3	3.6
14	36.0	35.2	2.4	3.9	7.4	2.9

Table 5. Properties of the oil.

AN [mgKOH/g oil]	BN [mgKOH/g oil]	Density (20˚C) [g/cm^3]	Viscosity (30˚C) [cP]	Viscosity (40˚C) [cP]
0.07	1.23	0.83653	5.6	4.0

PS!! The oil was saturated with CO_2 at 6 bar.
The core was flooded FW diluted 5x and the pH of the effluent stayed above 10.

Plagioclase gives alkaline solution: pH: 7.5 to 9.5

Plagioclase

- Anionic polysilicates give alkaline solution
  - Albite as example:

  $NaAlSi_3O_8 + H_2O \leftrightarrow HAlSi_3O_8 + Na^+ + OH^-$
- At moderate salinities, the pH of FW will be above 7, which means low adsorption of polar components onto clay; negligible LS EOR-effect.
- Due to buffer effects, the pH of FW was not decreased significantly by adding CO_2.

Snorre (Lunde) Core 13

CO_2 was added

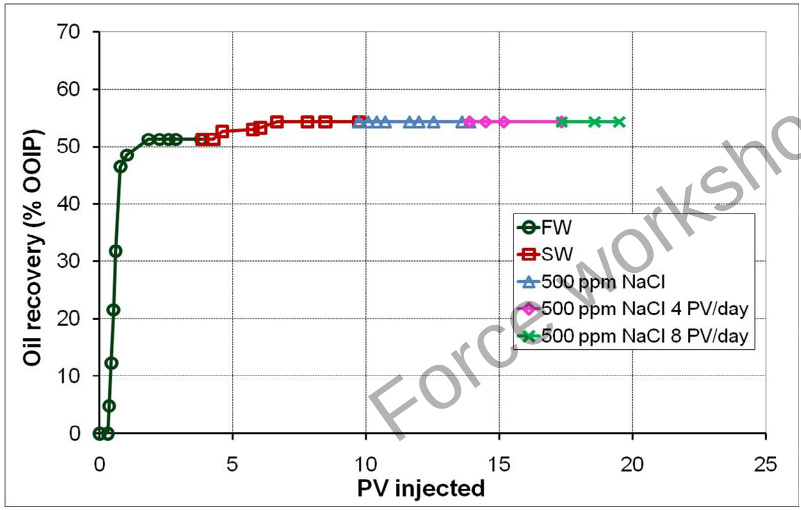
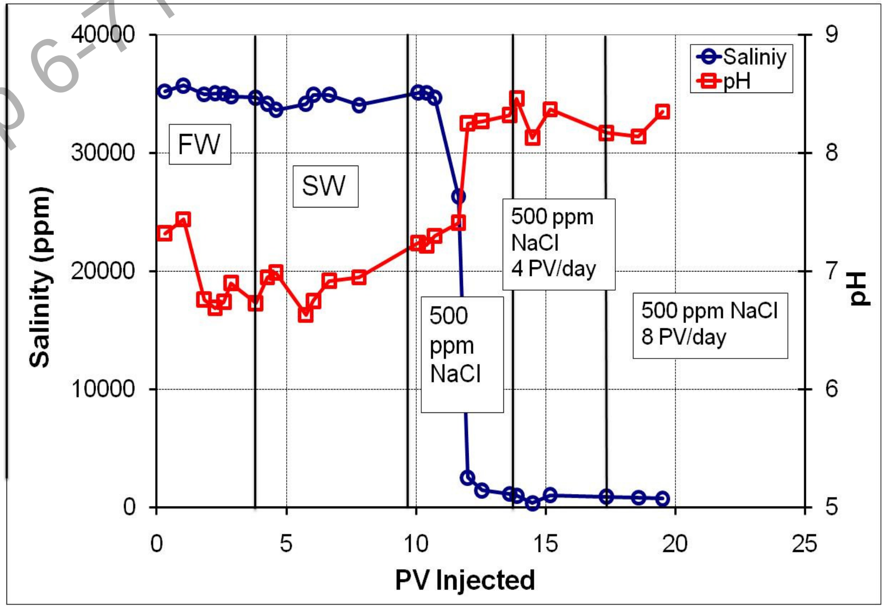


Fig. 3. Recovery vs. injected PVs for Core 13. Flooding rate of 2 PV/D; T_{res} = 90 °C.



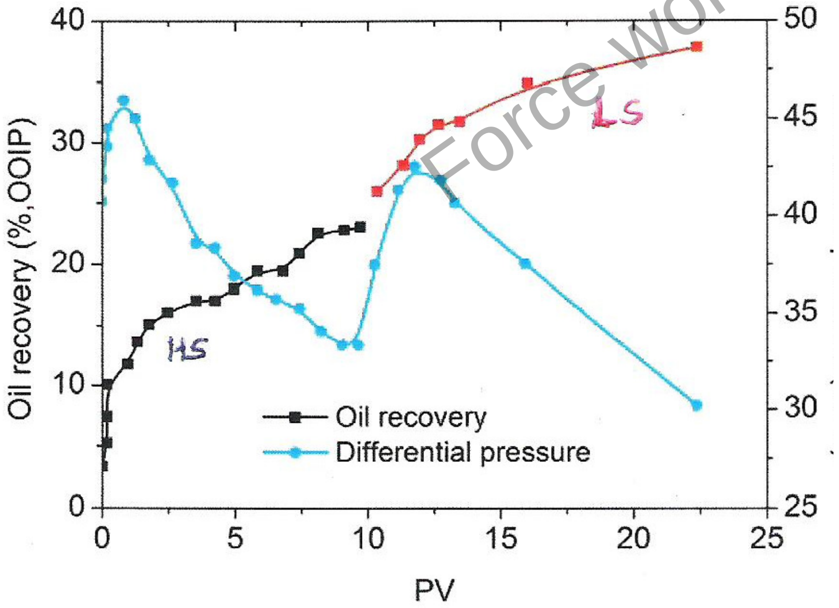
Low salinity effect of about 3-4 % of OOIP with SW as low salinity fluid

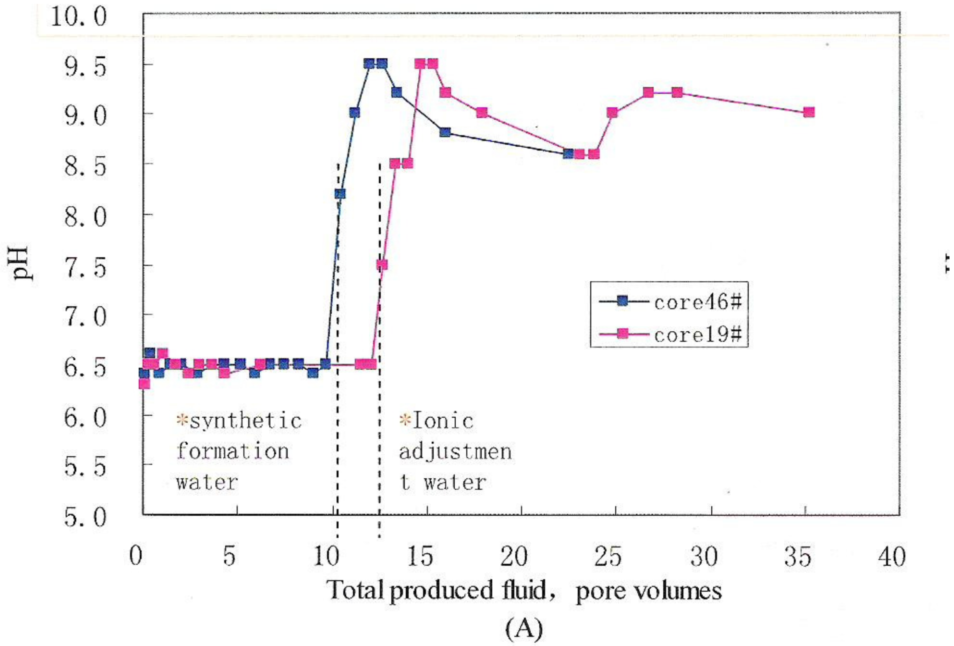
Excellent LS EOR conditions

(Quan et al. IEA EOR Symposium 2012, Regina, Canada)

Minerals: Plagioclase ≈ 22%, Total clay ≈ 25% (mostly Illite and kaolinite)
FW: Ca^{2+} : 0.061 mole/l, Total salinity 57114 ppm
T_{res} = 65 ^oC
k = 1-2 mD, Φ=0.11

14.5% LS EOR-effect

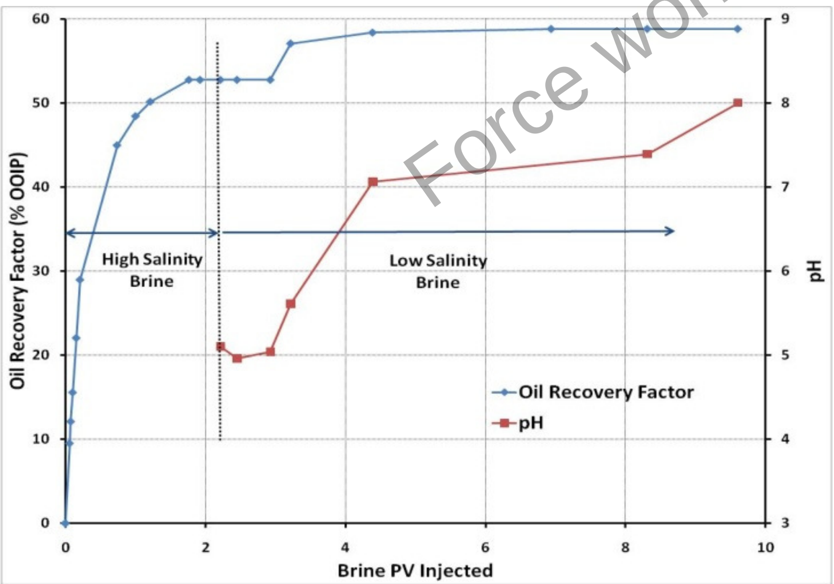




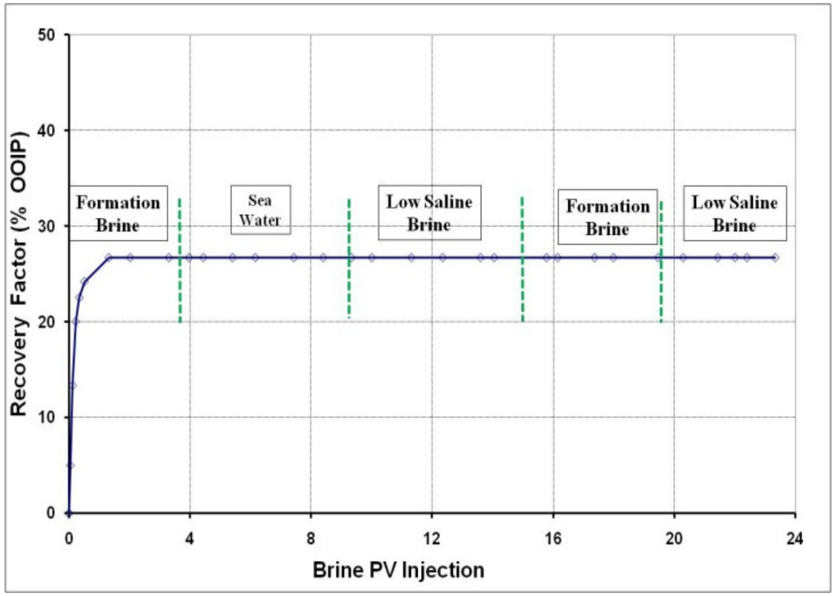
Varg field: SPE 134459

- Reservoir temperature: 130 °C
- Salinity 201 000ppm
- Brine composition;

T_a=90 , T_f=130°C



T_a=130 , T_f=130°C



Relationship: T and pH

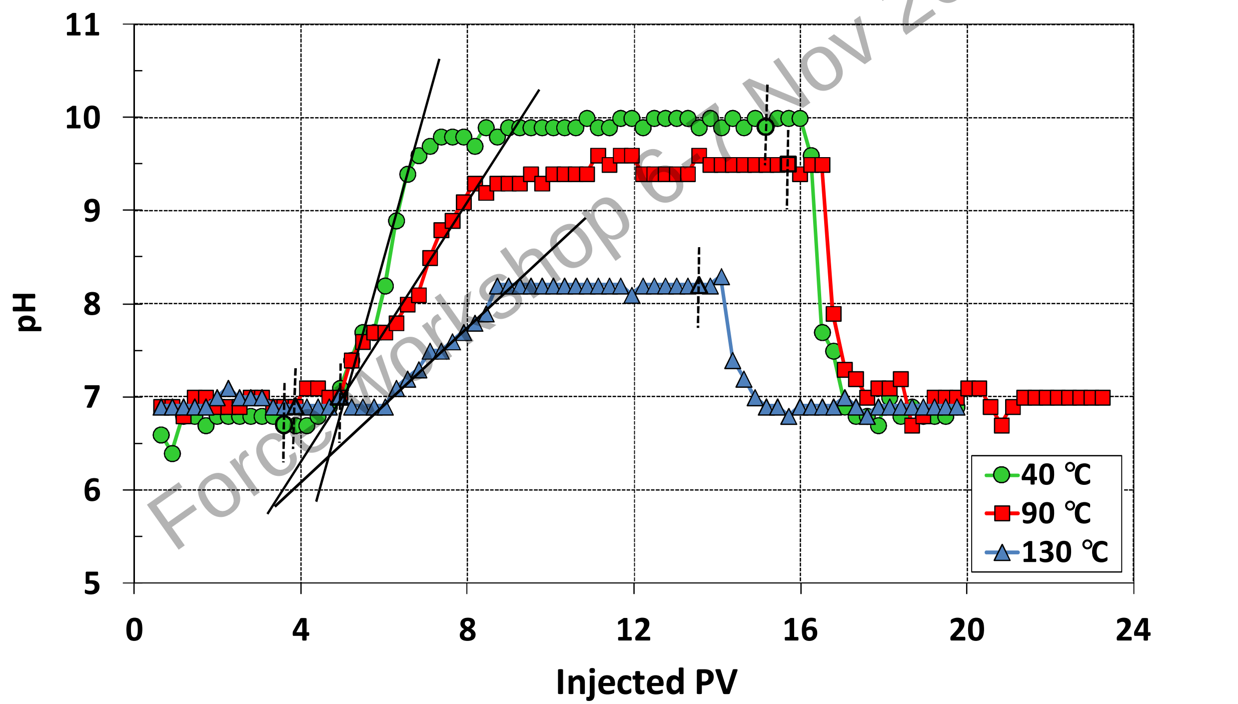
- Wettability alteration of clay by LS water:

  $Clay\text{-}Ca^{2+} + H_2O \leftrightarrow Clay\text{-}H^{+} + Ca^{2+} + OH^{-} + heat$

- Desorption of active cations from the clay surface is an exothermic process, $\Delta H<0$.
  - Divalent cations (Ca^{2+}, Mg^{2+}) are strongly hydrated in water, and as the temperature increases the reactivity of these ions increases, and the equilibrium is moved to the left.
  - The change in pH should decrease as the temperature increases.
  - Dissolution of anhydrite, $CaSO_4$(s), will move the equilibrium to the left.

Gamage, P., Thyne, G. *Systematic investigation of the effect of temperature during aging and low salinity flooding of Berea sandstone and Minn*, 16th European Symposium on Improved Oil Recovery, Cambridge, UK, 12-14 April, 2011.

Temperatur – pH screening



Change in effluent pH versus PV injection fluid in core RC2 at temperatures ranging from 40 °C to 130 °C. The brine flooding sequence was HS-LS-HS.

Summary

- «Smart water» EOR in Carbonates
  - Optimal brine composition
    - Modified SW: Depleted in NaCl and spiked with SO_4^{2-}: Active ions SO_4^{2-}, Ca^{2+}, Mg^{2+}
  - T_{res}>70 °C
  - Conditions for LS EOR-effects
    - Formation must contain dissolvable anhydrite, $CaSO_4$.

Summary

- «Smart Water» EOR effects in Sandstone
  - Formation water:
    - pH < 6.5
    - Reasonable high Ca^{2+} and total salinity.
  - Clay must be present (Illite and kaolinite)
  - Plagioclase can affect the pH both in a positive and negative way LS EOR effects depending on initial salinity.
  - Combination of high T_{res} (>100 ^oC) and high conc. of Ca^{2+} can make the formation too water-wet.
  - A pH-HS/LS scan can give valuable information of the potential for LS-EOR effects.

Acknowledgement

Statoil,

ConPhil,

NFR

Total,

Talisman,

BP,

Maersk,

Shell,

Saudi Aramco,

DNO International.