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Fundamental Mechanisms for Smart Water in Sandstone and Carbonate

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What is “Smart Water”?

- “Smart water” can improve/change 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 of injected fluid.
  - No expensive chemicals are added.
  - Environmental friendly.
- Wetting condition dictates:
  - Capillary pressure curve; $P_c=f(S_w)$
  - Relative permeability; k_{ro} and $k_{rw} = f(S_w)$

Different names

- BP: LoSal TM
- Shell: Designed Water TM (Not allowed)
- Exxon: Advanced Ion Management, AIMSM
- Saudi Aramco: “Smart Water”
- Researchers: Ion Tuned Water

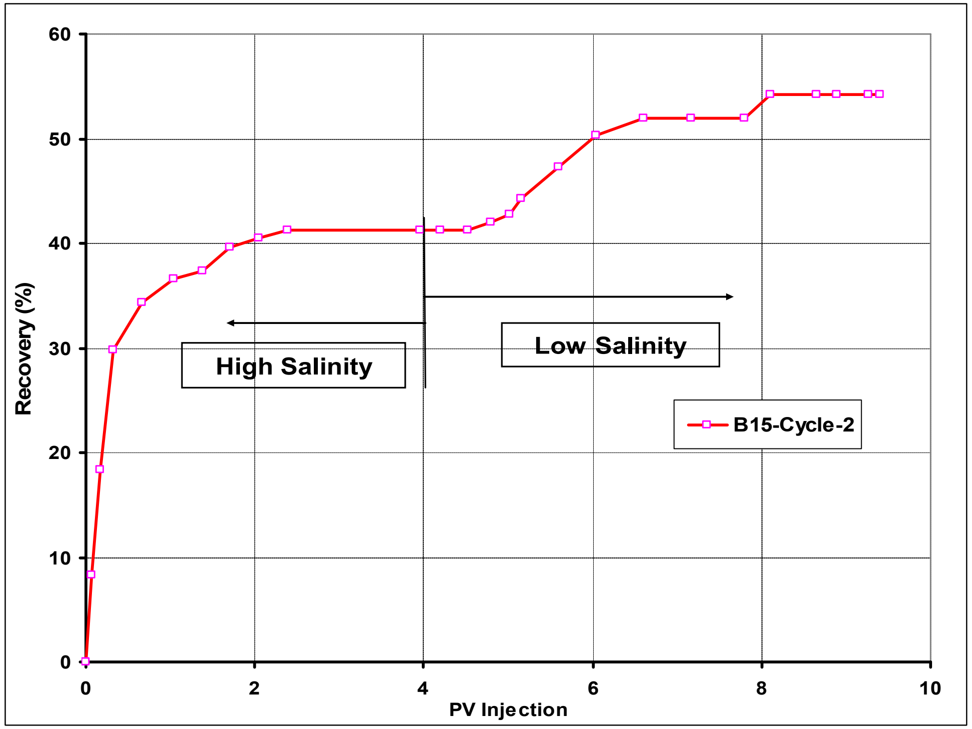
Water flooding

- 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, preferentially from the production start.

Smart Water in Sandstone

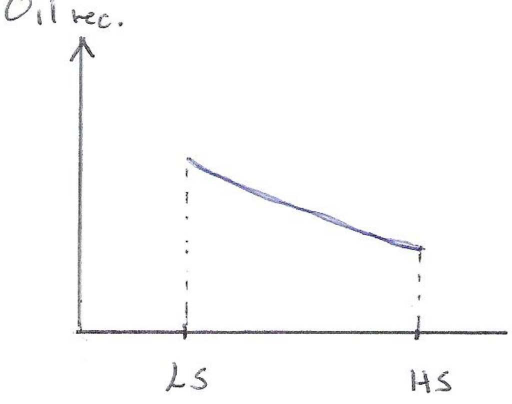
LS EOR effect in Sandstone

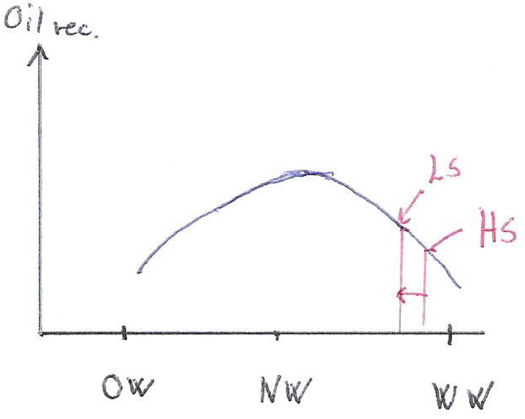
Low Salinity EOR-effect under forced displacement

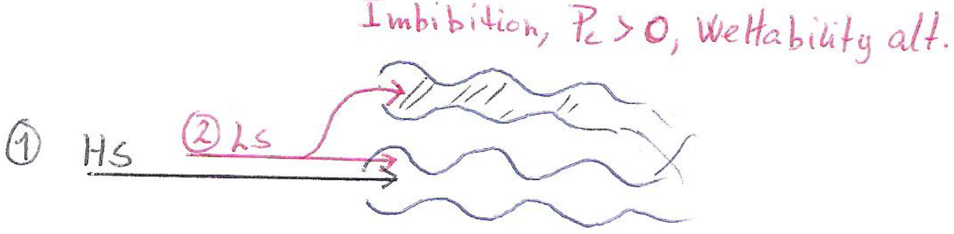


HS: 100 000 ppm; LS: 750 ppm

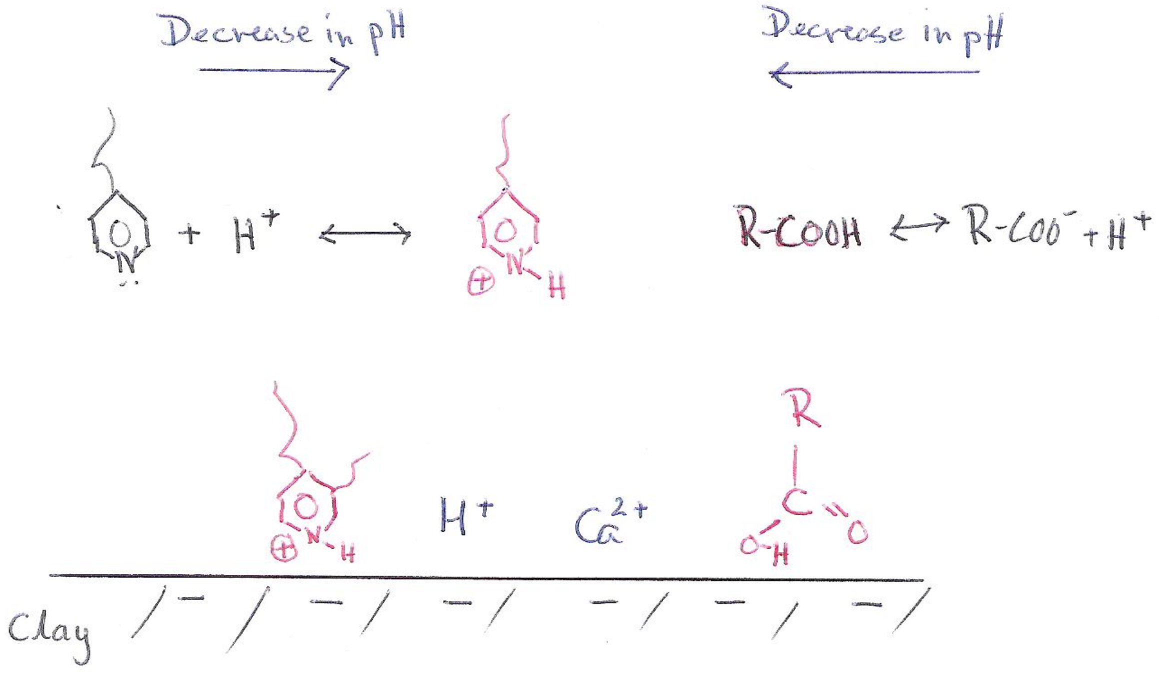
General information/knowledge







Adsorption onto clay



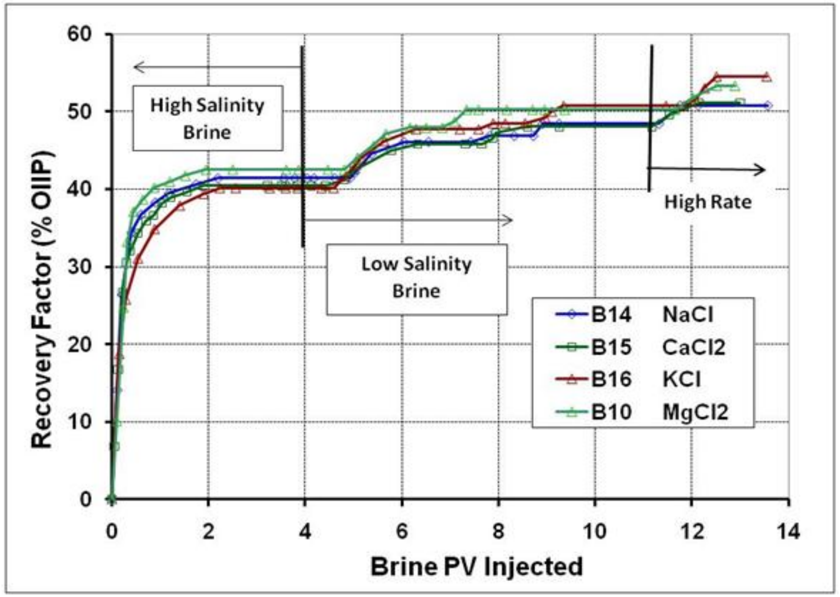
Initial pH of FW : 6 - 6.5

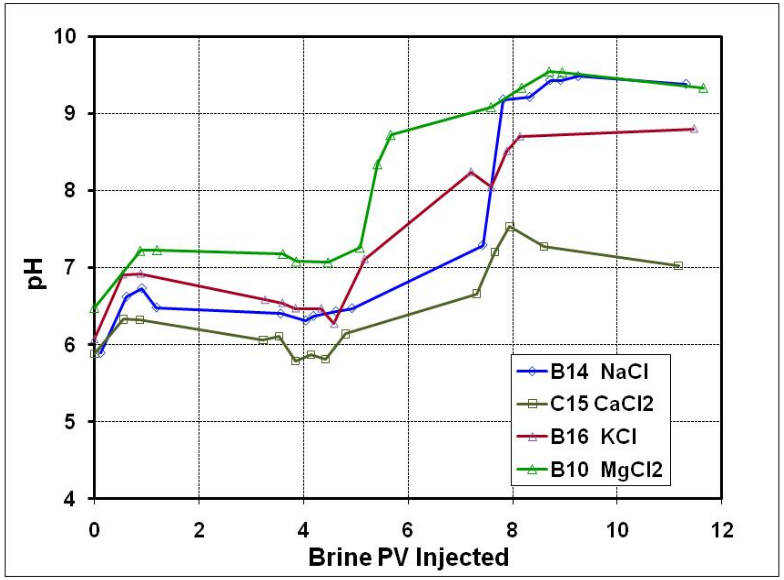
Suggested mechanisms

- Wettability modification towards more water-wet condition, generally accepted.
    - Release of clay fines (Tang and Morrow 1999).
    - Multicomponent Ion Exchange (MIE) (Lager et al. 2006).
- Mechanisms not linked to wettability modification
    - Increase in pH lower IFT; type of alkaline flooding (Mcguri et al. 2005).
    - Migration of clay fines in analogy with linked polymer particles, microscopic flow diversion (Skauge et al. 2008)
        - Later Skauge and others observed that this effect was also present at HS conditions
    - Osmotic effects due to salinity gradient in pores (should be observed using model oil and cores without clay)

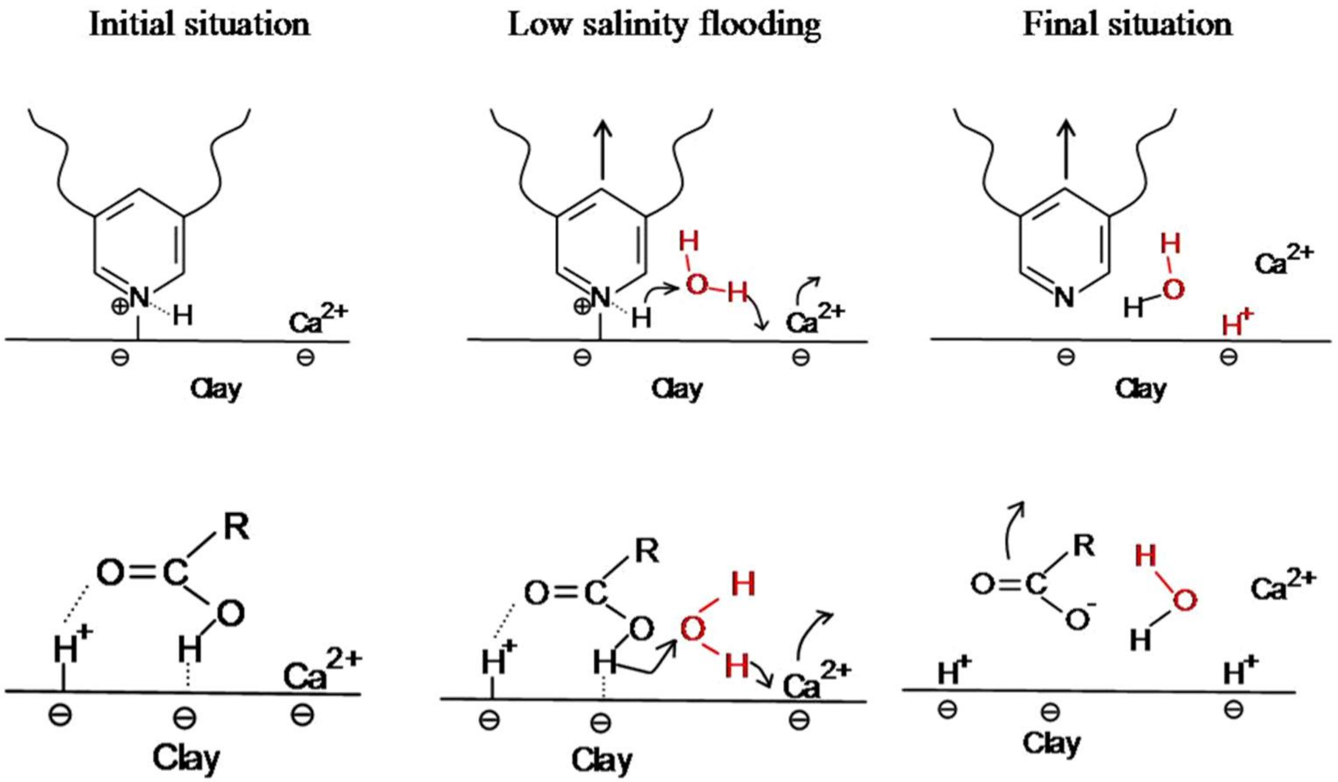
Increase in pH important

	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 5 – 6.5

Chemical equations

- Desorption of cations by LS water (slow)
  - Clay-Ca^{2+} + H_2O = Clay-H^+ + Ca^{2+} + OH^- + heat
- Wettability alteration (fast)
  - Basic material
    - Clay-NHR_3^+ + OH^- = Clay + R_3N: + H_2O
- Acidic material (fast)
    - Clay-RCOOH + OH^- = Clay + $RCOO^-$ + H_2O

Active species versus pH

- The pK_a values of protonated base and carboxylic acid are quite similar, p$K_a \approx 4.5$
  - $BH^+ \leftrightarrow H^+ + B$
  - $RCOOH \leftrightarrow H^+ + RCOO^-$
- The concentration of the active species (BH^+, and RCOOH) will have a similar variation versus pH.

Clay minerals

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

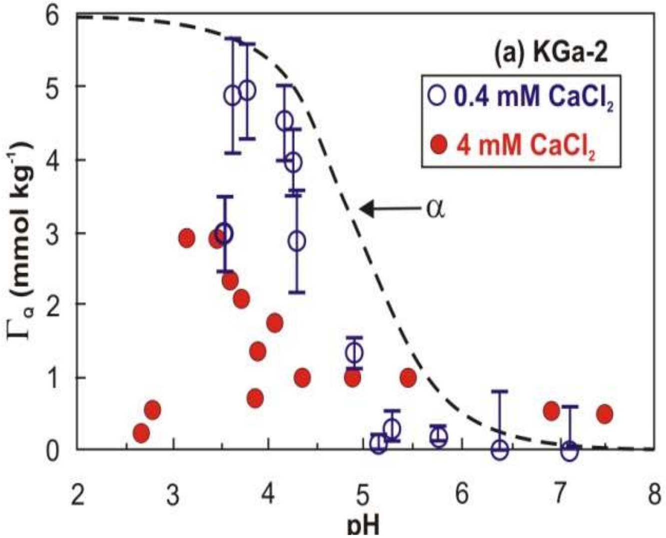
      $Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} << H^+$
  - Kaolinite and Illite are regarded as non-swelling clays

Adsorption of basic material Quinoline

Burgos et al. *Evir. Eng. Sci.*, **19,** (2002) 59-68.

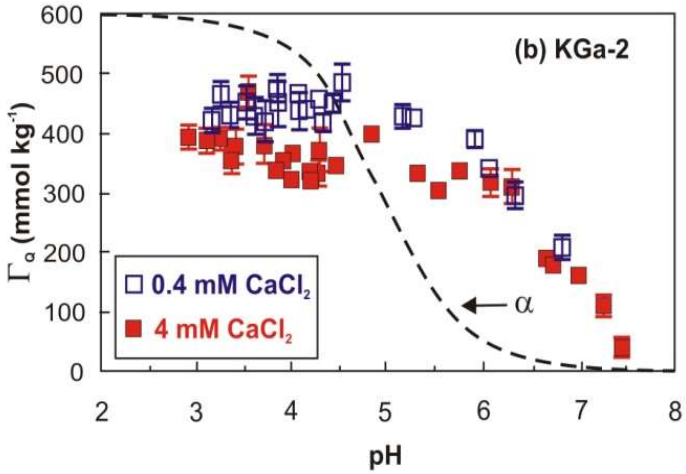
Kaolinite

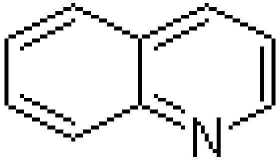
Nonsweeling(1:1 Clay)

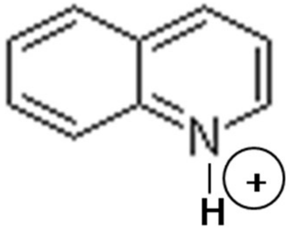


Montmorillonite

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



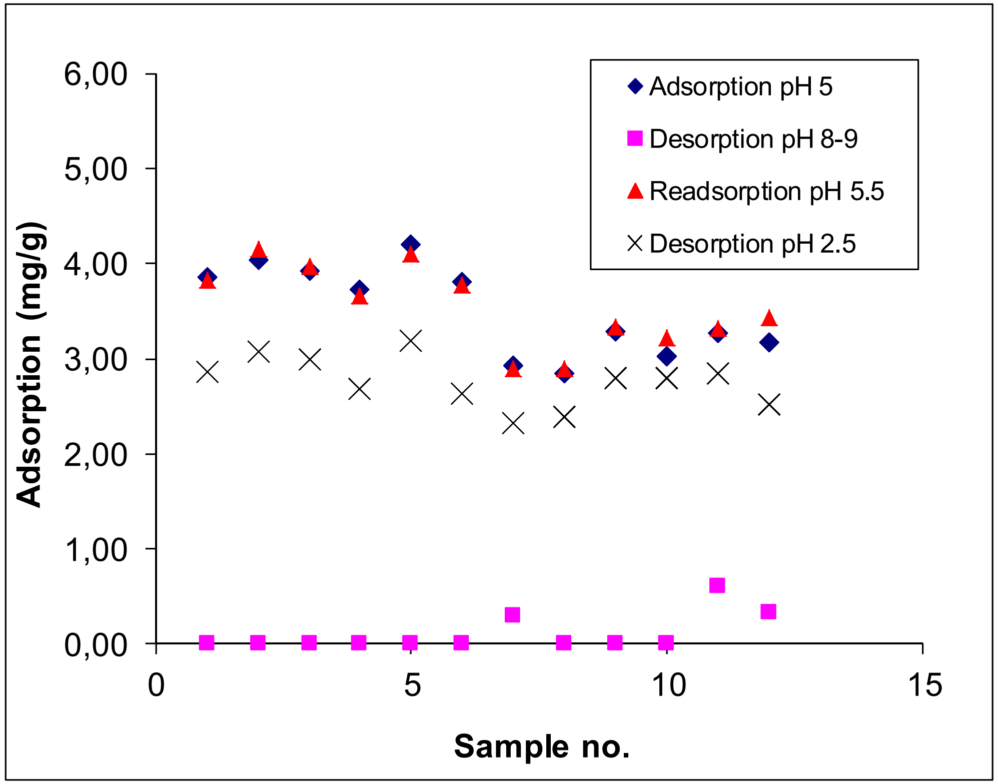




Kaolinite: Adsorption reversibility by pH

Quinoline

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



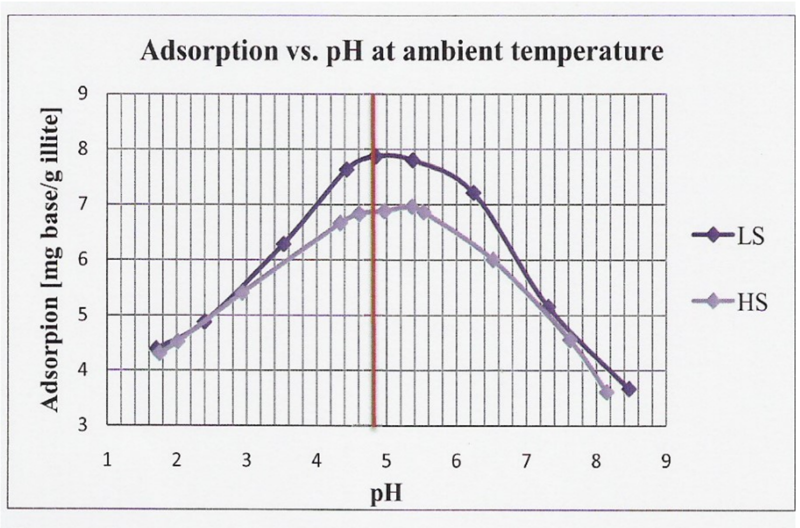
Adsorption of acidic components onto Kaolinite

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

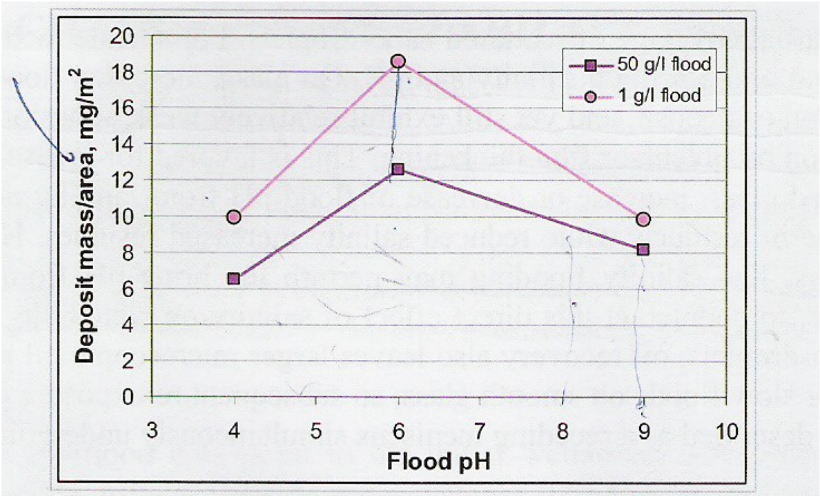
$pH_{initial}$	Γ_{max} μmole/m^2
5.3	3.7
6.0	1.2
8.1	0.1

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

LS water increases oil-wetness



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



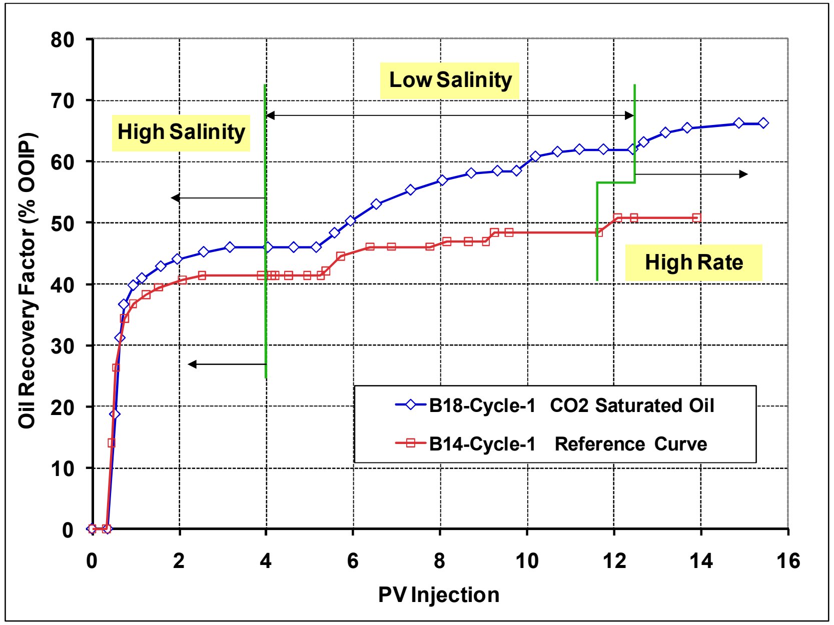
ss of asphaltenic deposits remaining, per planar area of kaolinite-coate

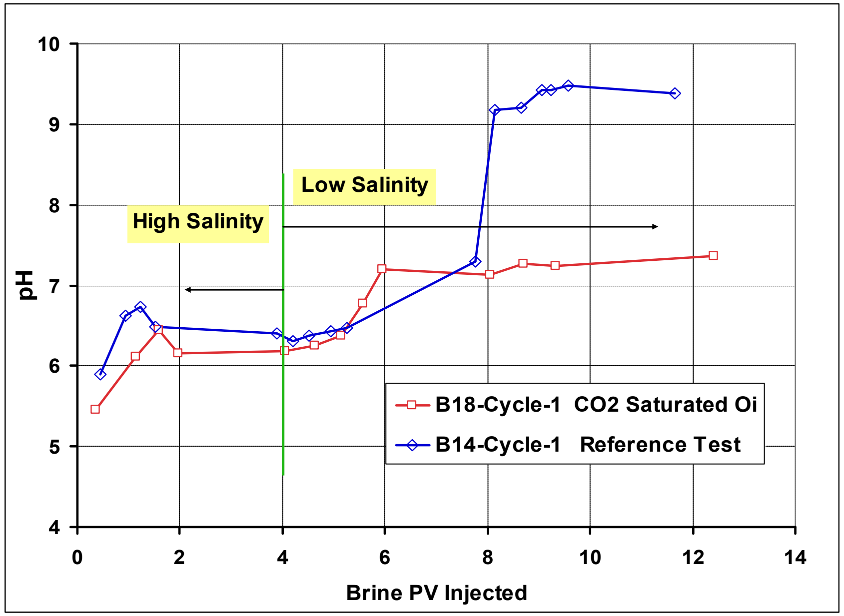
Ref. Fogden and Lebedeva, SCA 2011-15 (Colloids and Surfaces A (2012)
Adsorption of crude oil onto kaolinite

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

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	19.76	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





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

Small LS EOR effects after flooding with SW

Morrow et al. (2012) SPE 154 209
Torrijos et al. (2015) SPE 179625-MS

FW = SW : 35 604 ppm;Ca^{2+} 13 mM; LS: 20x diluted SW
Oil: AN= 1.46 and BN = 2.49 mgKOH/g
T_{res}= 60 °C

Core plug sample	Kaolinite (Mass %)	Clays & micas (Mass %)	Albite (Mass %)	Microcline (Mass %)	ΔR_t** %OOIP	Initial pH	ΔpH
Briar Hill	4.5	4.5	0	2.5	**3.65**	7.0	**0**
Idaho Gray	6.0	6.9	29	22	**3.27**	7.3	**0.5***
Leopard	2.5	3.7	0,5	1.2	**1.05**	7.2	**0.5***
Cedar Creek	5.0	8.6	7,5	8.0	**0.74**	6.6	**0.5**
Boise	5.0	5.7	29	22	**1.09**	7.2	**1***
Sister Gray	7.0	7.6	1.4	7.0	**0**	8.0	**0**

Table 3. Detailed mineralogy, tertiary recovery, initial pH and ΔpH.

** ΔR_t : Amount of oil recovered in the tertiary LS EOR process, (ref: SPE 154209)

* The pH increment was not stable during the LS flooding (decreasing trend).

ΔpH versus LS EOR effect

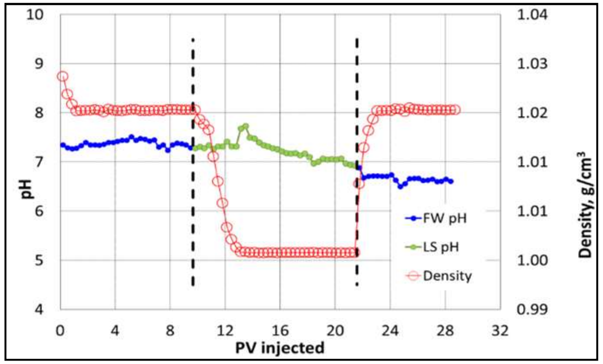


Fig. 5. pH screening for an Idaho gray core at 60 °C, flooding sequence SW-LS$_{d20}$-SW.

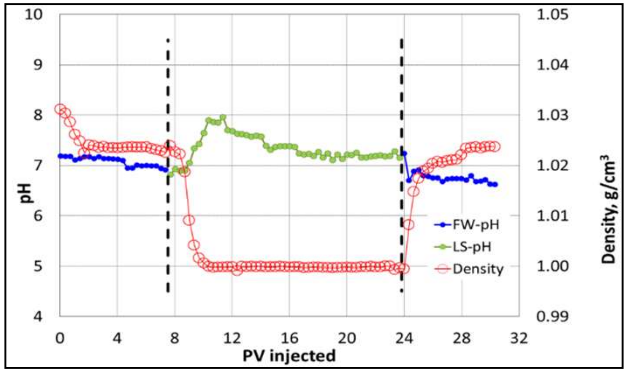


Fig. 6. pH screening for a Boise core at 60 °C, flooding sequence SW-LS$_{d20}$-SW.

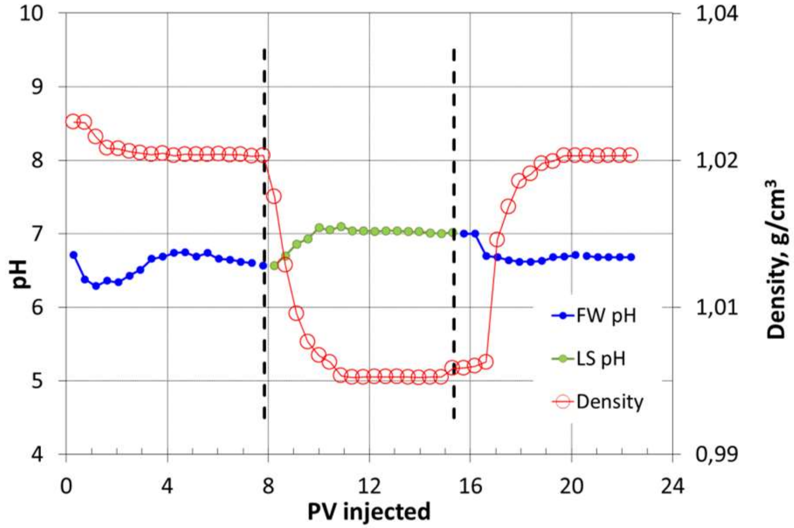


Fig. 7. pH screening for a Cedar creek core at 60 °C, flooding sequence SW-LS$_{d20}$-SW. LS EOR effect:0.74

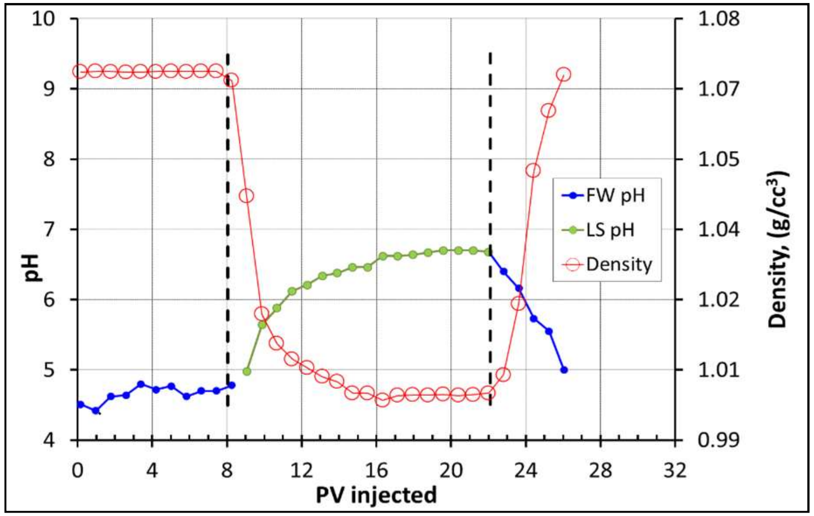


Fig. 10. pH screening for a Cedar Creek core at 60 °C with flooding sequence Total FW (100 000 ppm)-LS(1000ppm)-Total FW.

Effect of FW salinity

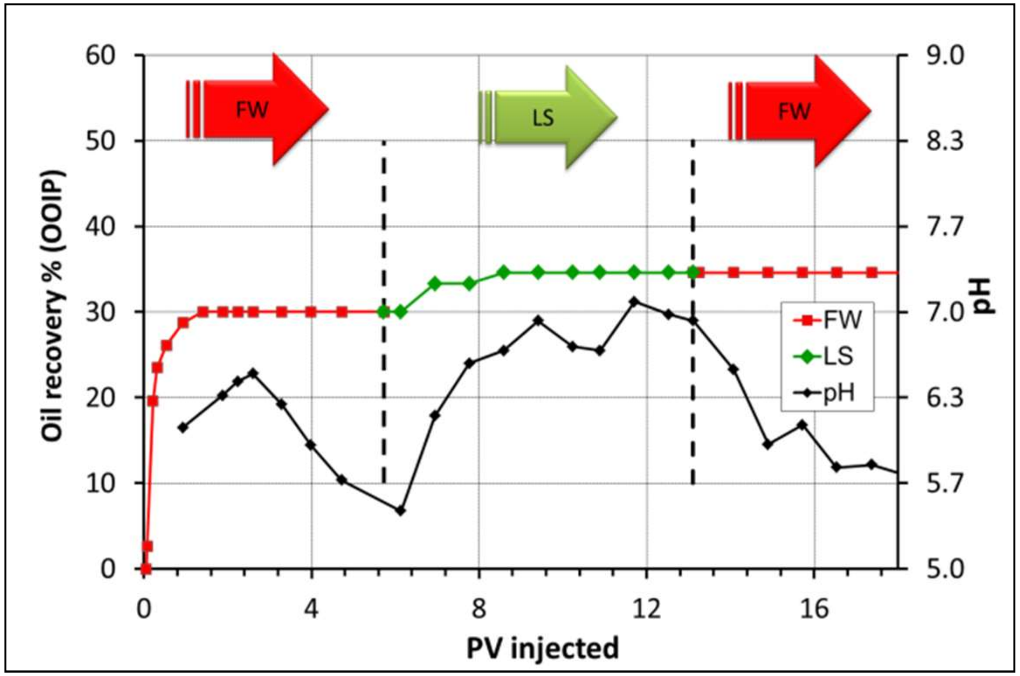


Fig 8. Oil recovery for a Cedar creek core at 60 °C, flooding sequence FW-LS-FW. LS EOR effect: **5% of OOIP**

PS!! Difficult to obtain tertiary LS EOR effects after flooding with SW.

Effect of Reservoir Temperature on the Tertiary LS EOR Potential

Relationship: T and ΔpH

(Aksulu et al. Energy & Fuel 26 (2012) 3497-3509)

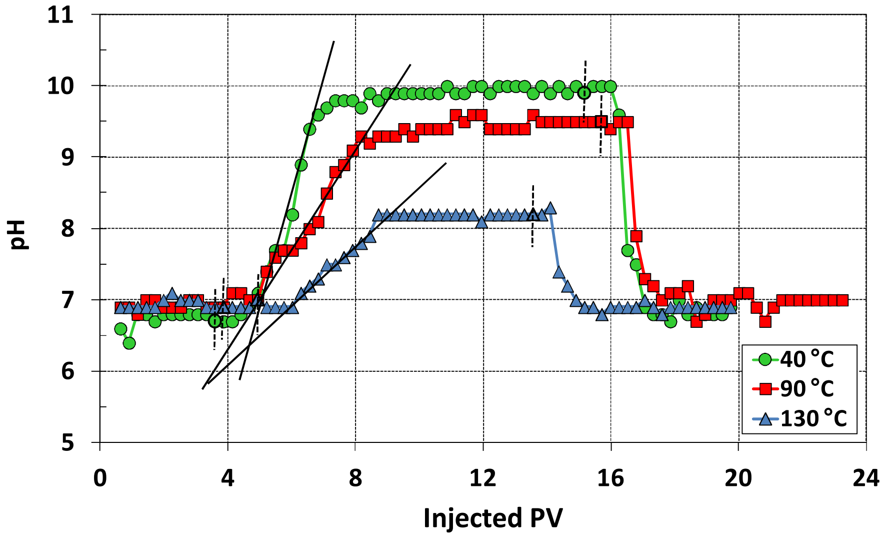
- Wettability alteration of clay by LS water:

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

- 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 will 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.

Temperature – pH screening



Change in effluent pH versus PV injection fluid in core RC2 at temperatures 40, 90, 130 °C. The brine flooding sequence was HS-LS-HS. HS: 100 000 ppm, LS: 1000 ppm.

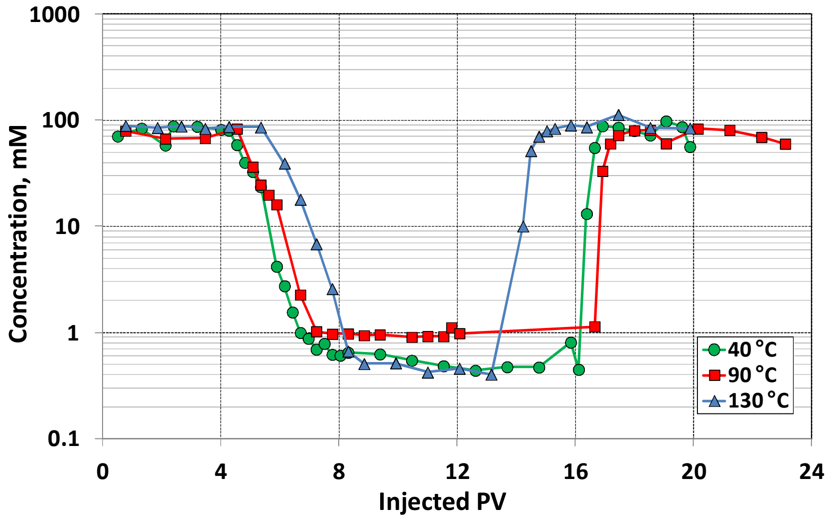


Fig. 5. The effluent concentration of Ca^{2+} when flooding RC2 successively with HS2-LS2-HS2 versus injected PV at different temperatures.

Desorption of Ca^{2+} slow process

Adsorption of Ca^{2+} fast process

PS! LS brine only contained NaCl

Reservoir minerals

Reservoir minerals minerals that can affect the equilibrium:

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

Presence of Anhydrite

- Reservoirs at high T_{res} and salinity my contain Anhydrite, $CaSO_4(s)$

- Offshore reservoirs at high T_{res} and salinity flooded by SW may also contain precipitated Anhydrite, $CaSO_4(s)$

Yme RC1: pH – HS – LS scan

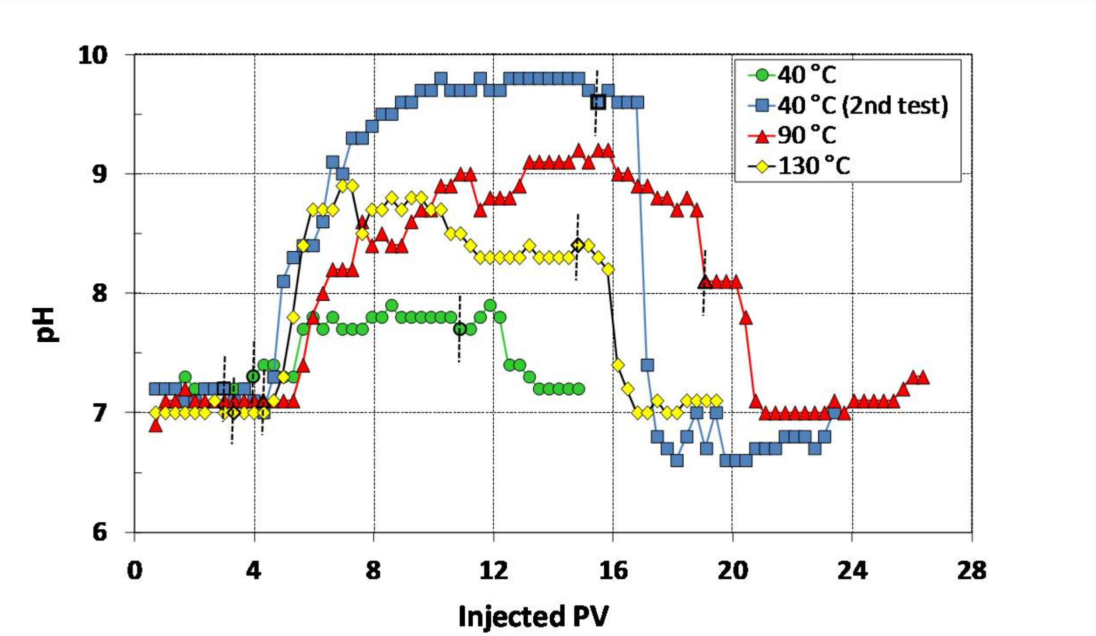


Fig. 2. pH versus PV injected for RC1. The flooding sequence was HS2-LS2-HS2, and the switching of fluids is marked by dashed lines and marked points.

Brines: HS2: 100 000 ppm ($CaCl_2$ and NaCl)
LS2: 1000 ppm (NaCl)

Presence of anhydrite in reservoir core

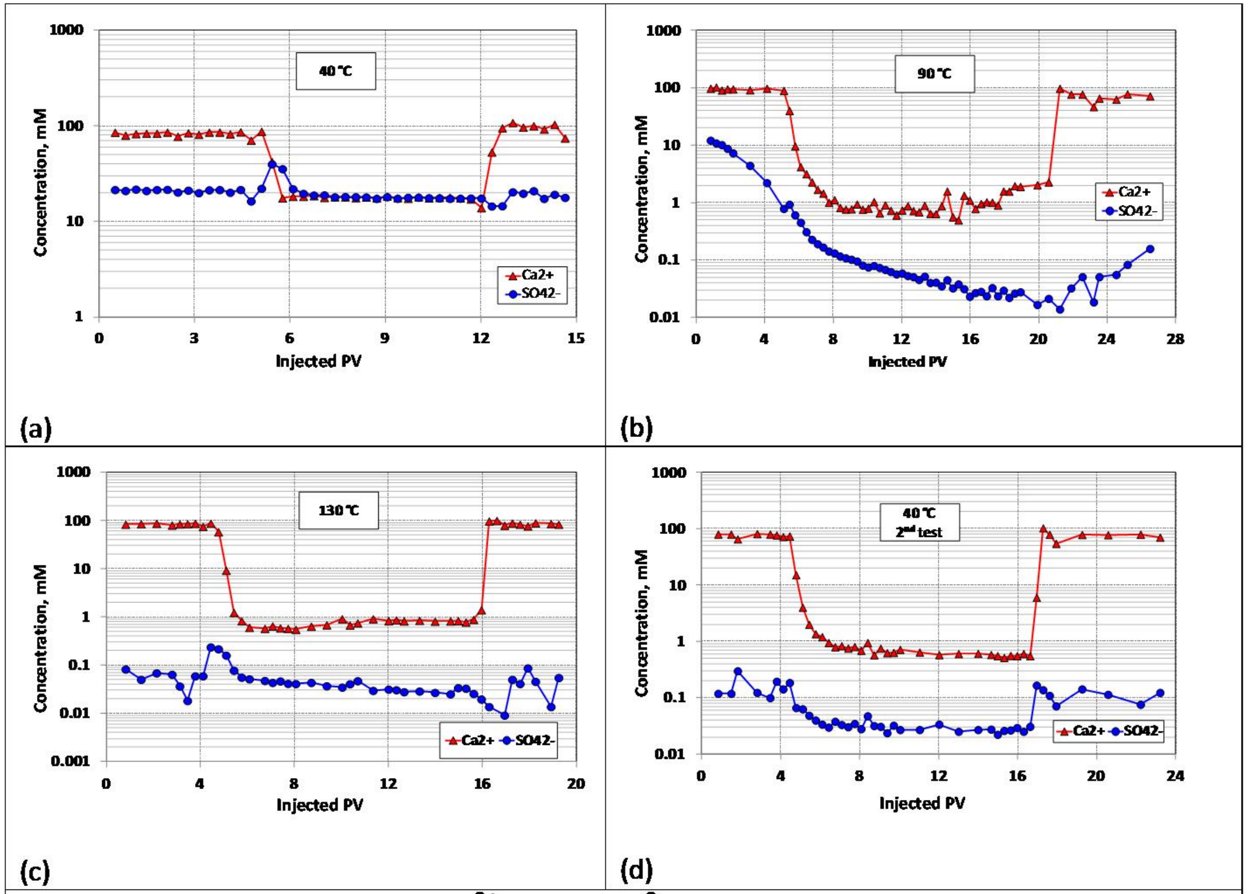


Fig. 3. Concentration of Ca^{2+} and SO_4^{2-} in the effluent versus PV injection fluid in RC1. The flooding sequence was HS2-LS2-HS2. The temperature ranged from 40 °C to 130 °C.

Plagioclase as reactive reservoir mineral

- Anionic poly silicate (Feltspar type), which is charged balanced mainly with Al^{3+}, but also with Ca^{2+} or Na^{+}.
- Albite, **$NaAlSi_3O_8$,** is a common member of the Plagioclase group. Na^{+} can be exchangeable with H^{+} which will have impact on the pH of the brine.

Chemical equilibrium: Albite as example

(Aksulu et al. *Energy Fuels* **2012,** *26*, 3497-3503).

- Chemical equilibrium:
    - **$NaAlSi_3O_8 + H_2O \leftrightarrow HAlSi_3O_8 + Na^+ + OH^-$**
- Initial FW conditions
    - Low saline FW (Alkaline solution pH>7)
        - Equilibrium moved to the right
    - High saline FW (May have acidic solution pH<7)
        - Equilibrium moved to the left, i.e. no cation exchange
- Impact on initial wetting conditions and the potential for LS EOR effects
- Hydrolysis of Albite is not very sensitive to temperature (small hydration energy of Na^+)

Outcrop: pH-HS-LS scan

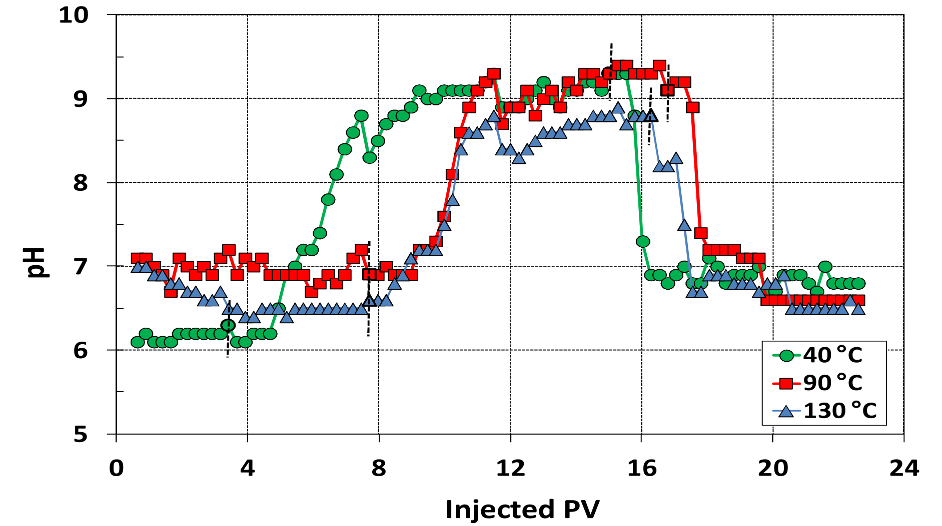


Fig. 6. Change in effluent pH versus PV injection fluid in core OC1 at 40 °C, 90 °C and 130 °C. The brine flooding sequence was HS2-LS2-HS2. The switches of injection fluids are indicated by the dashed lines.

PS!! ΔpH not sensitive to the temperature due to Eq. (1):

(1) $NaAlSi_3O_8 + H_2O \leftrightarrow HAlSi_3O_8 + Na^+ + OH^-$

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

Snorre field

(Reinholdtsen, et al. 16th European EOR Symp., Cambridge, UK,12-14 April, 2011.)

- Lab work
  - Negligible tertiary low salinity effects after flooding with SW, on average <2% extra oil.
  - T_{res}=90 °C
- 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

- **Salinity of FW: 35 000 ppm**
- 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/Albite can give initial alkaline solution: pH>7**

Snorre (Lunde) Core 13

CO$_2$ was added

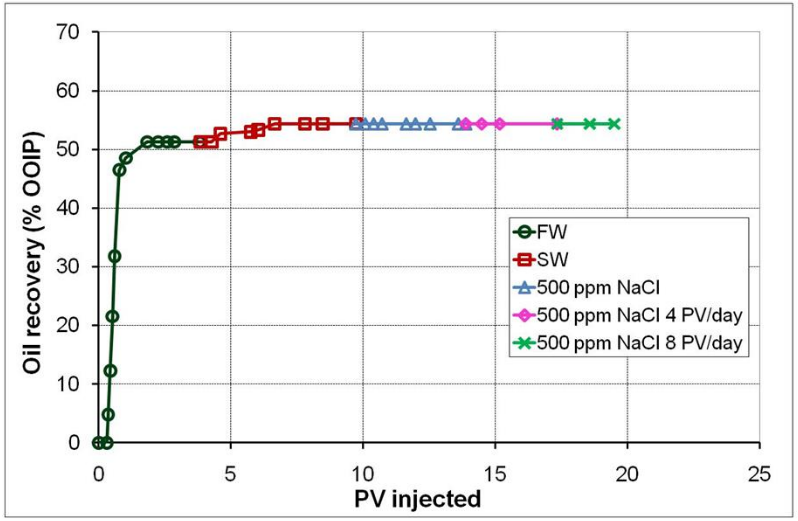
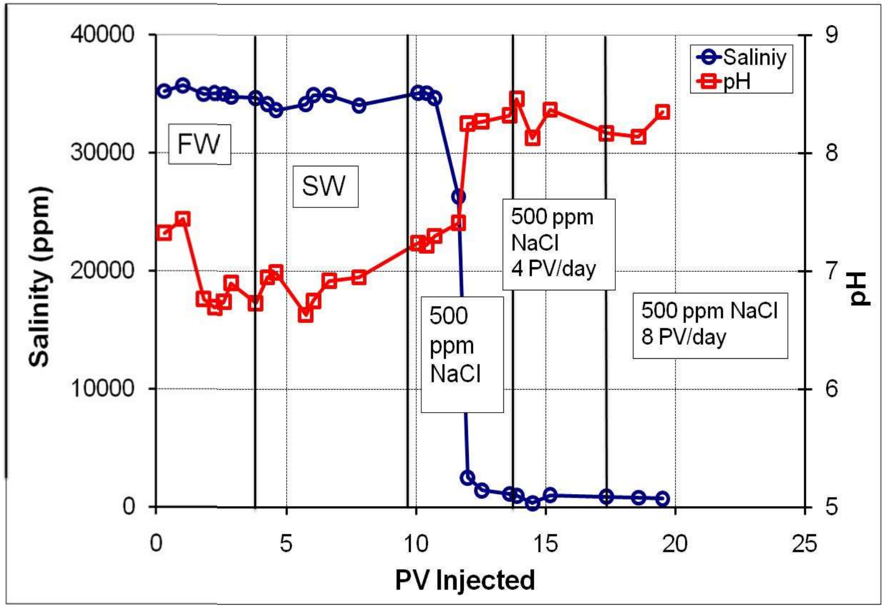


Fig. 3. Recovery vs. injected PVs for Core 13. Flooding rate of 2 PV/D; T_{res} = 90 °C.



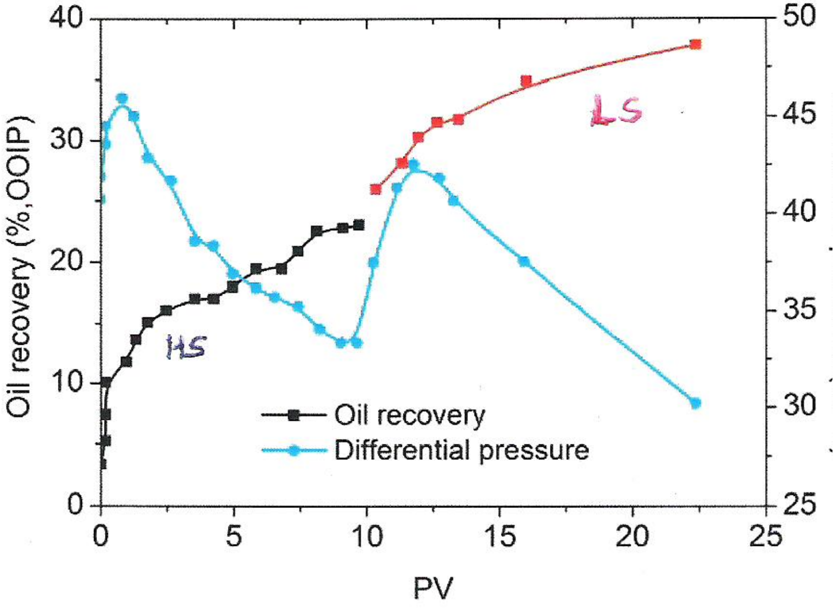
- **Low salinity EOR effect of about 3 % of OOIP with SW**
- **Initially, too water wet , pH>7, for obtaining LS EOR effects**

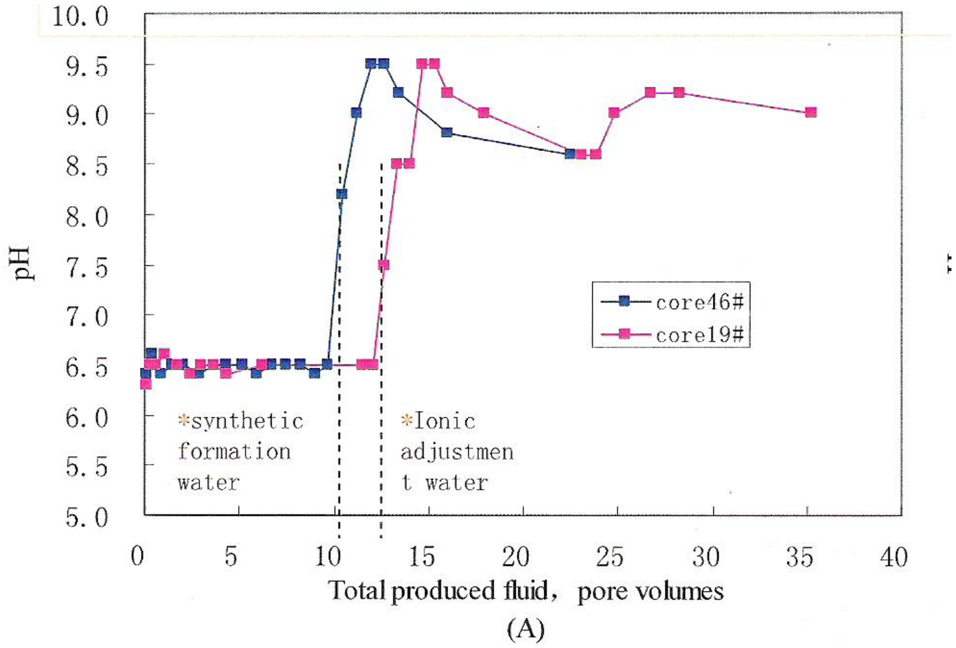
Excellent LS EOR conditions

(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

LS EOR-effect: 14.5% OOIP





Outcrop core containing Albite

(Torrijos et al. (2015) Paper under review)

Core properties: Total clay: 10 wt%; Albite: 33 wt%
Brines: HS 100 000 ppm (Ca^{2+} and Na^{+}); LS 1000 ppm (NaCl)
LS EOR effect: 60 °C 9.1 and 120 °C 8.7 %OOIP
pH gradient very similar at 60 and 120 °C

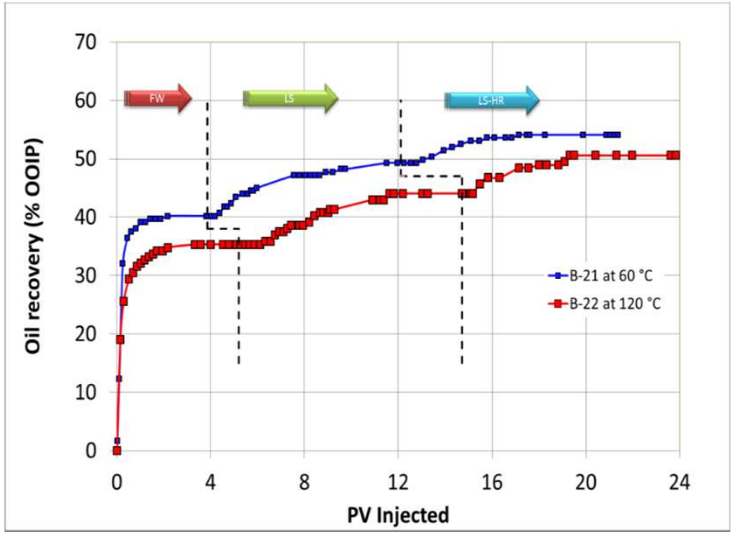


Figure 4. Oil recovery test at 60° C and 120° C

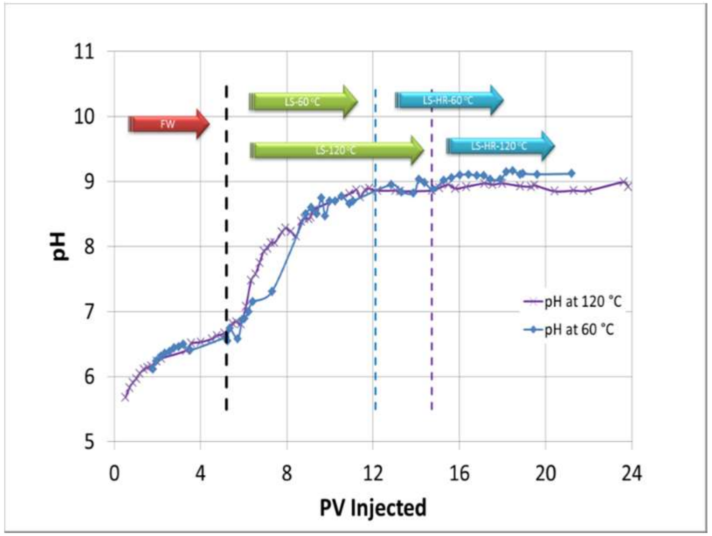


Figure 3. pH Increment during the oil recovery test, flooding sequence Total FW-LS-LS High rate.

Response time for the LS EOR effect

(Torrijos et al. Energy & Fuels (2016) accepted)

- More than 500 papers are published on LS EOR effects in sandstone.
- Field applications: very few, Why ????
- Tertiary LS EOR effect
  - Varying LS EOR effect: usually between 0 – 10% OOIP
  - Very long response time
    - Many PVs of LS brine must be injected to reach 5-10% extra oil
- Secondary LS EOR effect
  - Usually larger EOR effect
  - Much shorter response time
  - Extensive lab work is needed to verify the effect.

Test conditions

Table 2. Mineralogical properties of the outcrop cores, given as wt %.

Quartz	**Albite**	**Chlorite**	**Illite**	**Anatase**	**Apatite**	**Calcite**	**Pyrite**
57.0	32.0	1.7	8.2	0.5	0.2	0.3	0.1

Table 3. Crude oil properties.

Crude Oil	**AN (mg KOH/g)**	**BN (mg KOH/g)**	**Density* (g/cm^3)**	**Viscosity* (cP)**
Total oil	0.10	1.80	0.846	17.6

HS= FW: 100 000 ppm ($CaCl_2$ and NaCl)
LS: 1000 ppm NaCl
Test temperature: 60 ^{o}C

pH scan: FW-LS-FW

TOTAL outcrop B series: Important minerals: Illite clay and Plagioclase/Albite

LS brine: Clay-Ca^{2+} + H_2O ↔ Clay-H^+ + OH^- + Ca^{2+}

$NaAlSi_3O_8$ + H_2O ↔ $HAlSi_3O_8$ + OH^- + Na^+

HS brine: Clay-H^+ + Ca^{2+} ↔ Clay-Ca^{2+} + H^+

$HAlSi_3O_8$ + Na+ ↔ $NaAlSi_3O_8$ + H^+

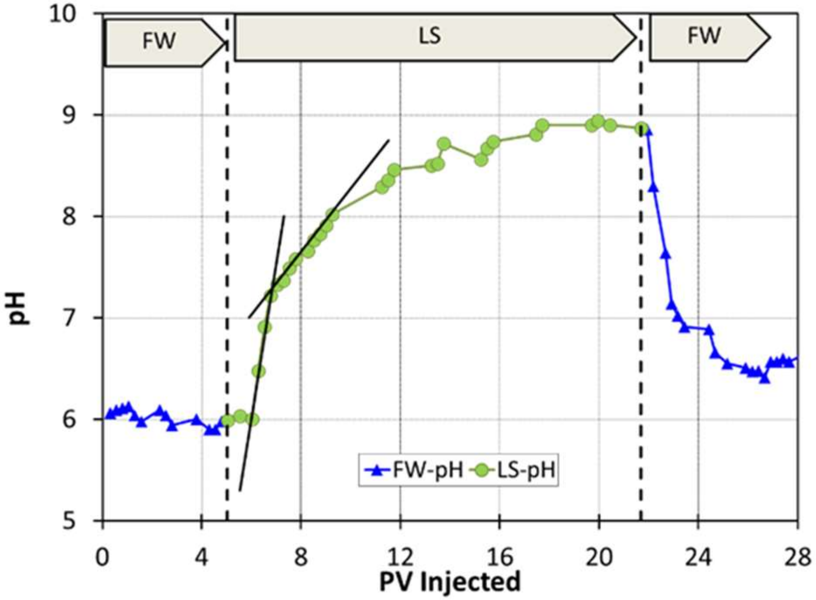


Fig. 2. pH scan at 60 °C for core B-21. Flooding sequence: FW-LS-FW. Flooding rate: 4 PV/D

Tertiary LS EOR effect

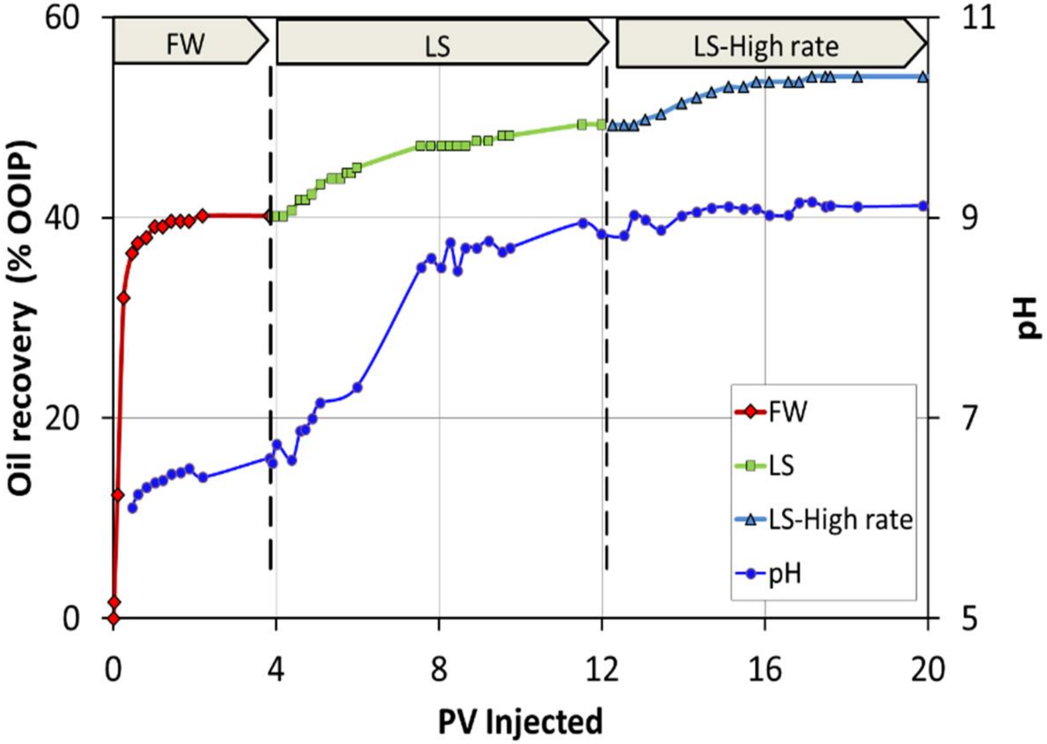


Fig. 1. Oil recovery test from core B-21 at 60 °C. The core was successively flooded with FW-LS at 4 PV/D, at the end the injection rate was increased to 16 PV/D.

Mechanism for oil displacement

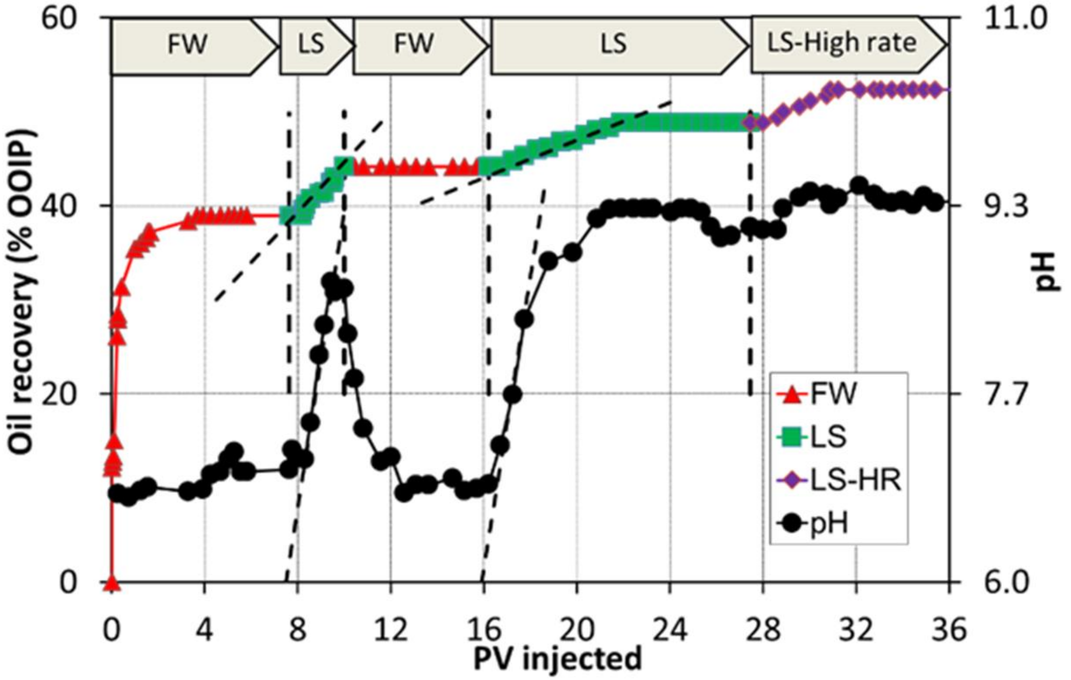
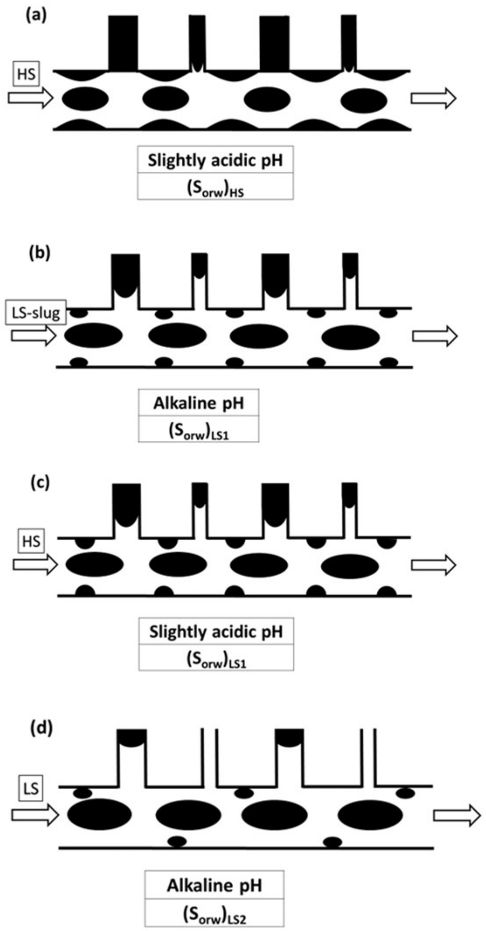


Fig. 3. Oil recovery test for core B-24 at 60 °C. The core was successively flooded with FW-LS (2PVs) - FW - LS at 4 PV/D, at the end the injection rate was increased to 16 PV/D.



Pore size distribution

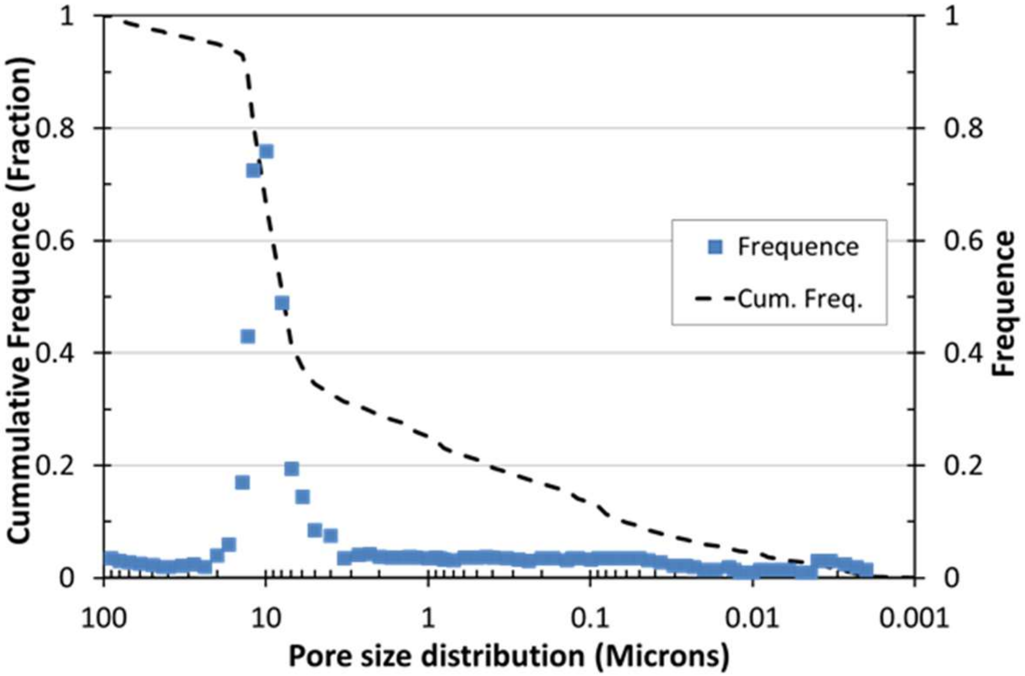


Fig. 6. Pore size distribution of a core from the same block as the tested core material. Data submitted by TOTAL E&P. The core material has heterogeneous pore size distribution, with pores ranging from ~0.01 to 100 µm. The majority of the pores is in the range of 10 µm.

Secondary LS EOR effect

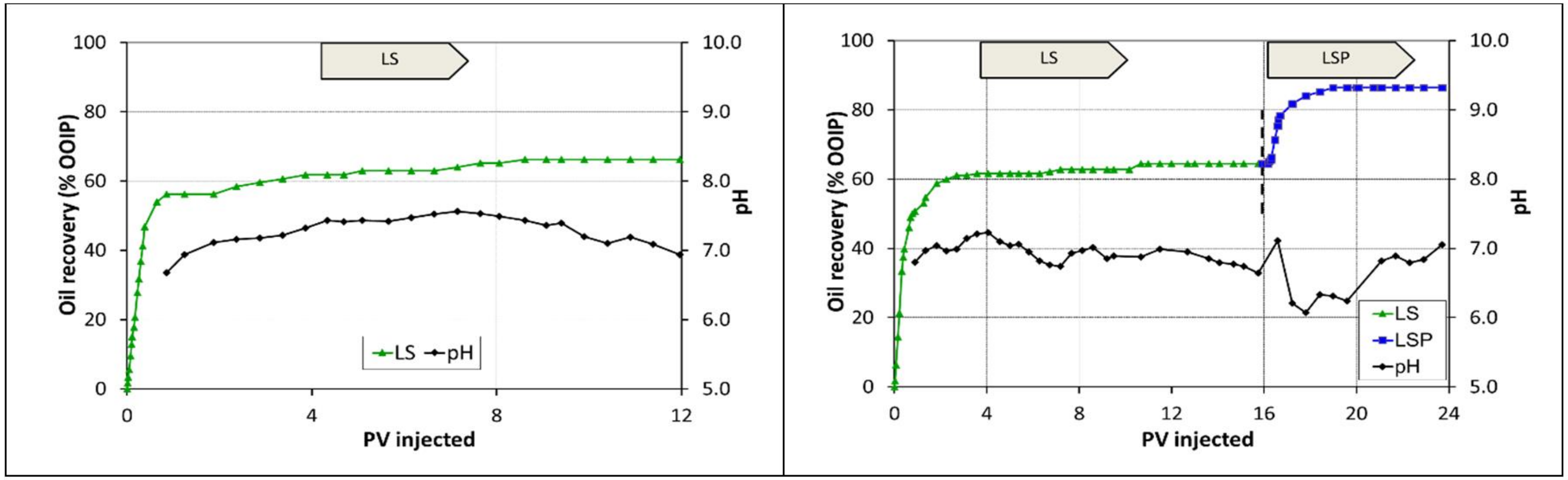


Fig. 7. Oil recovery test from core B-26 at 60 ^{o}C by **secondary injection of LS** brine. a) First restoration (left) b) Second restoration of core B-26 after mild cleaning with LS in secondary mode followed by a LSP flood (right).

The secondary LS EOR effect increased by 10% of OOIP compared to tertiary LS injection.

PS!! Restructuration of residual oil saturation after a secondary LS flood can have great effect on oil displacement using LS polymer or LPS, even when the LS EOR effect is small

Modelling

Electrostatics and low salinity effect in sandstone reservoirs.

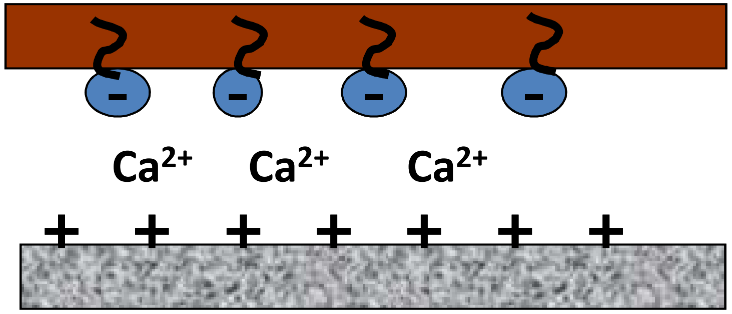
Brady, Morrow, Fogden et al. *Energy & Fuels 2015, pp. 666-677*.

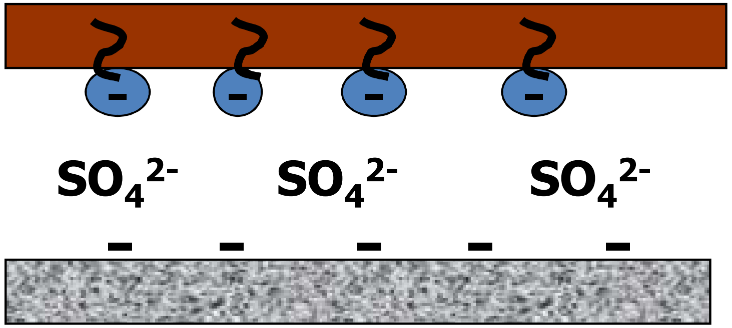
PS! Induced pH gradient was incorporated in the modelling for the first time.

Smart Water in Carbonate

Wetting properties in carbonates

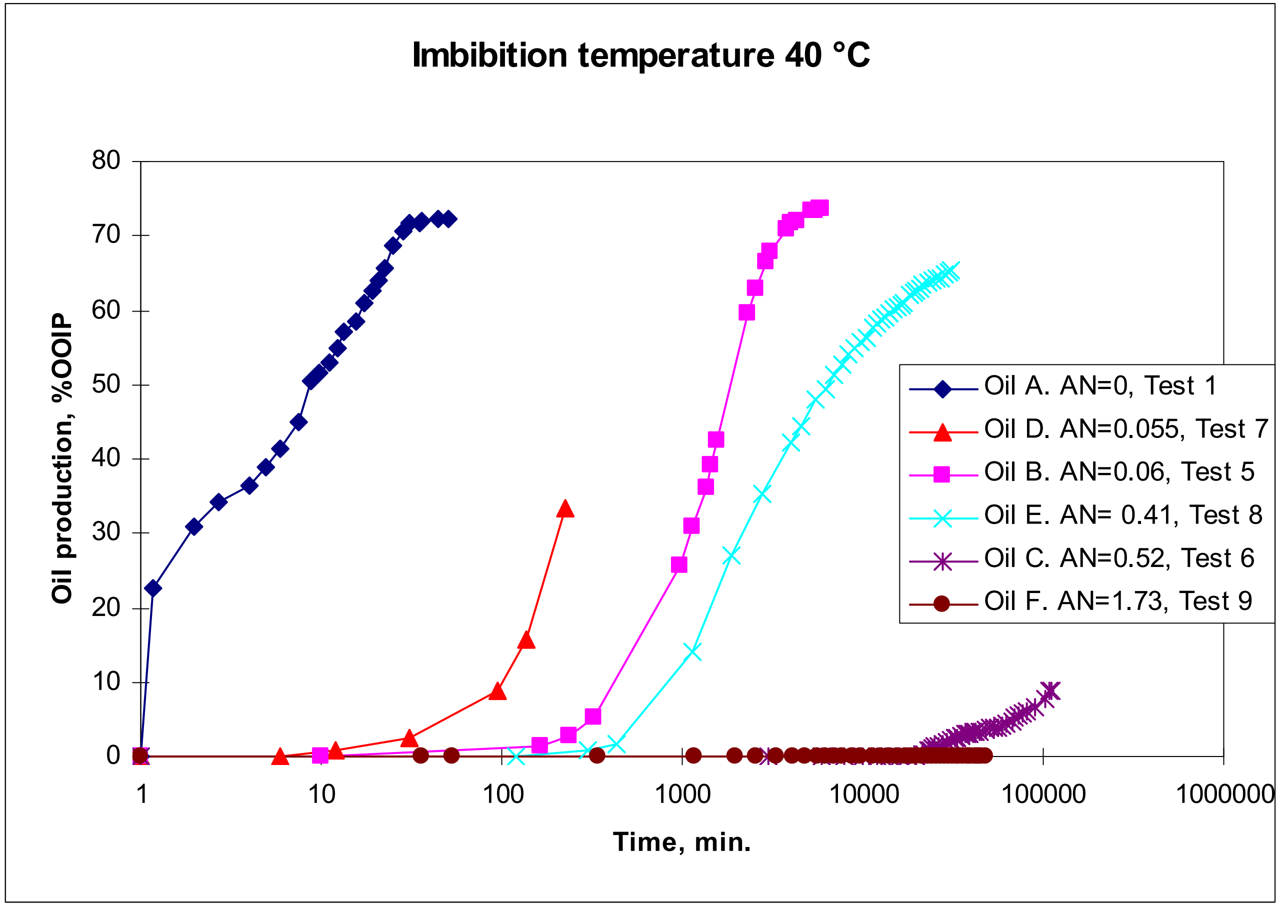
- Carboxylic acids, R-COOH
  - AN (mgKOH/g)
- Bases (minor importance)
  - BN (mgKOH/g)
- Charge on interfaces
  - Oil-Water
    - R-COO$^-$
  - Water-Rock
    - Potential determining ions
      - **Ca^{2+}, Mg^{2+},**
      - **(SO_4^{2-}, CO_3^{2-}, pH)**





Impact of AN on spontaneous imbibition

(Standnes and Austad, J. Pet. Sci. Eng. 28 (2000) 111-121)



Seawater as Smart EOR fluid in carbonates

Questions asked

- Why is injection of seawater such a tremendous success in the fractured Ekofisk field? T_{res}= 130 °C

- Can SW act as a wettability modifier in chalk at high temperatures?

Model 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**

Potential determining ions

(Zhang and Austad, *Coll. and Surf.* A 279 (2006) 179-187)

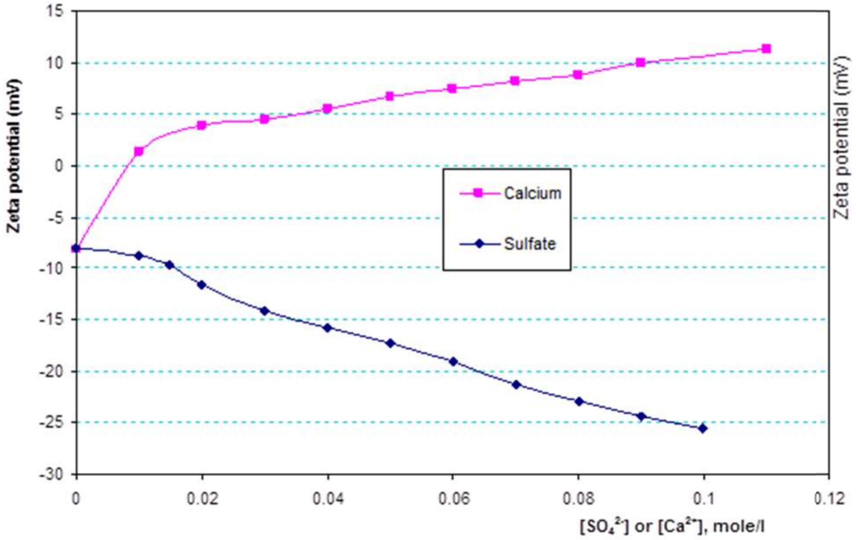


Fig.2 Zeta potential measurements on an aqueous chalk suspension system by adding SO_4^{2-} or Ca^{2+} (pH = 8.4). Initially 4wt% milled chalk powders were mixed with brine ZP.

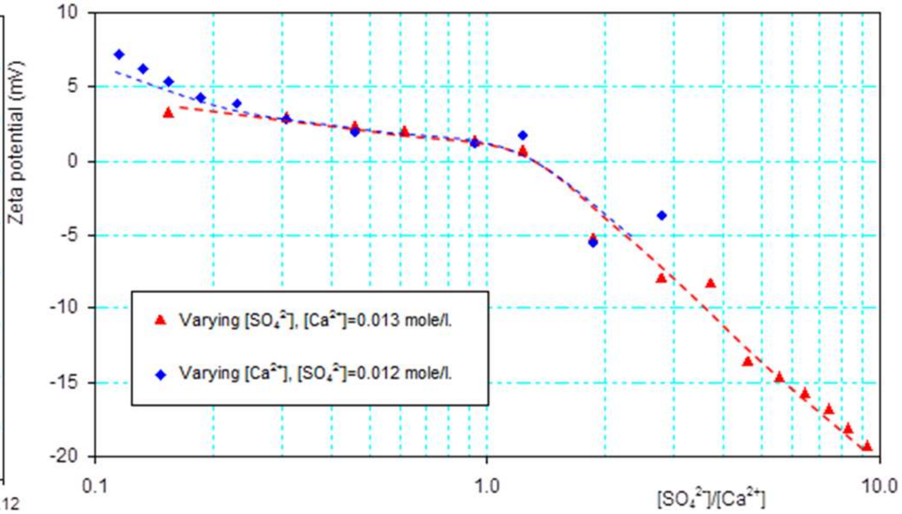
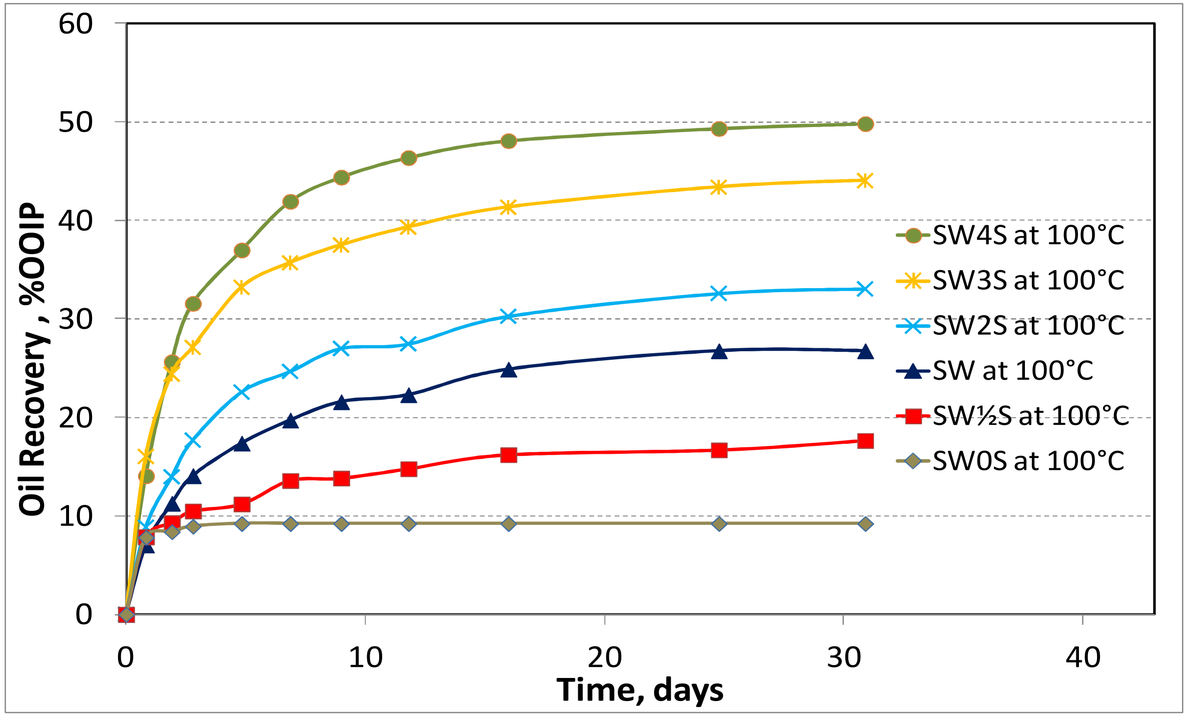


Fig.3 Zeta potential measurements on a aqueous chalk suspension system (pH=8.4) by varying $[SO_4^{2-}]$ (keeping $[Ca^{2+}]$=0.013mole/l) or varying $[Ca^{2+}]$ (keeping $[SO_4^{2-}]$=0.012mole/l). Initially 4wt% milled chalk powders were mixed with brine ZP at room temperature.

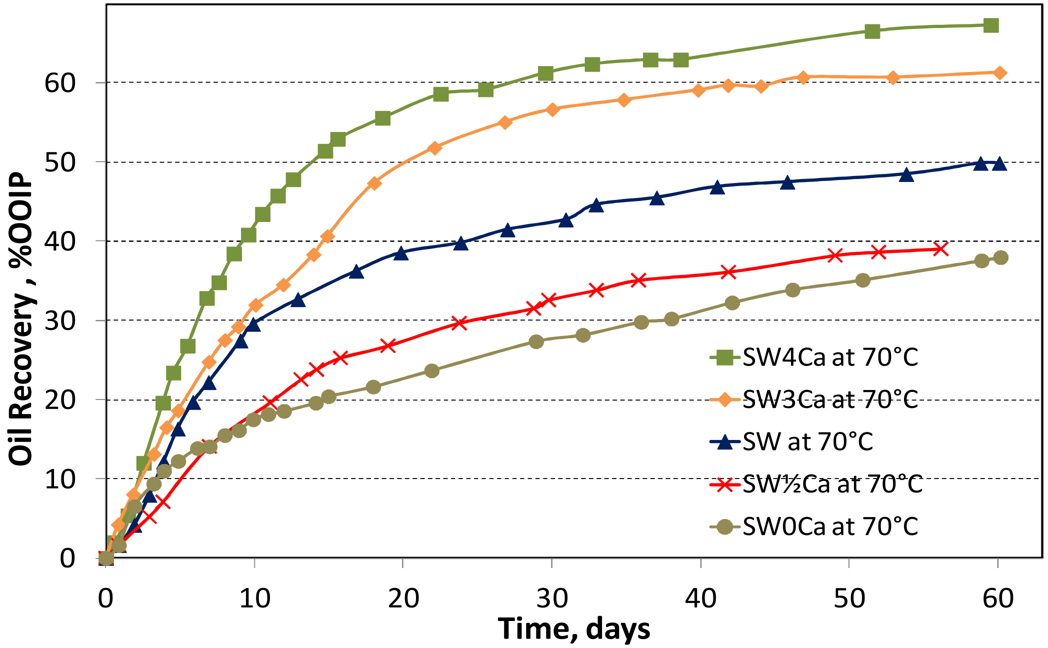
Effect of Sulfate in SW

- Crude oil: AN=2.0 mgKOH/g
- Initial brine: EF-water
- Imbibing fluid: Modified SW (SO_4^{2-}: 0-4x SW conc.)
- Spontaneous imbibition at 100 ^oC



Effect of Ca^{2+} in SW

- Crude oil: AN=0.55 mgKOH/g
- S_{wi} = 0;
- Imbibing fluid: Modified SW
- T = 70 ^{o}C



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

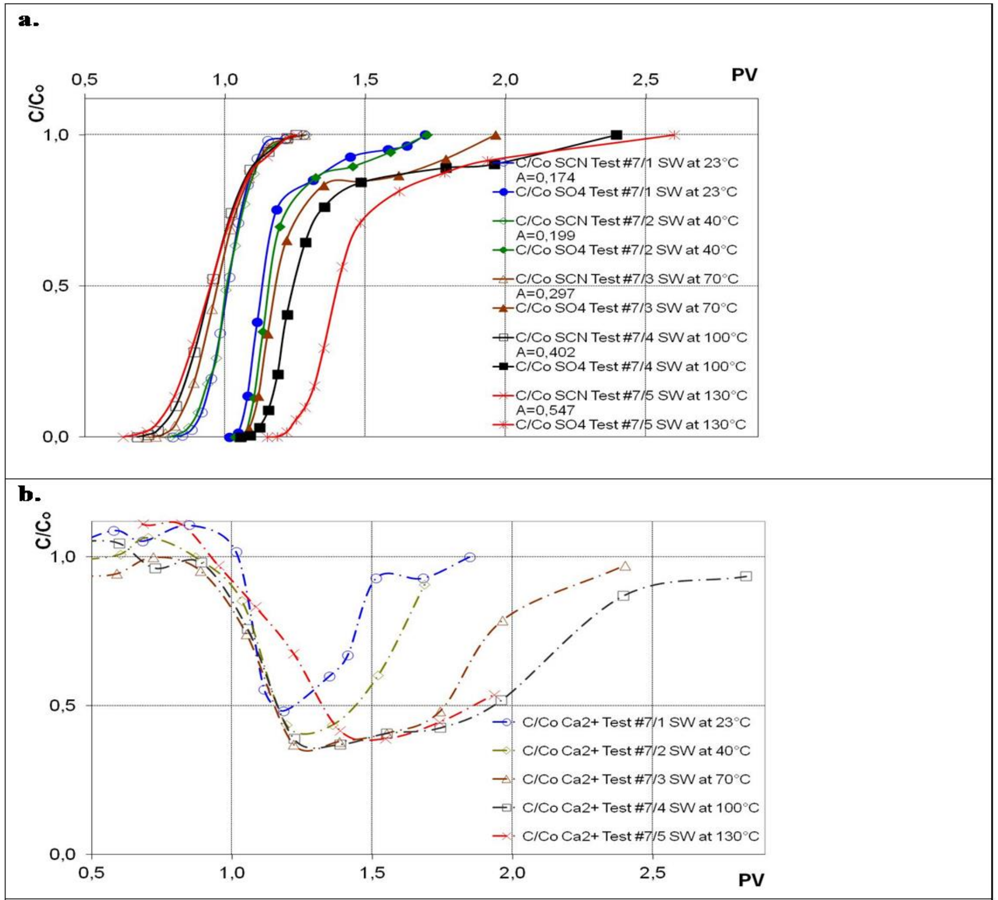


Fig. 6. (a): The retardation of sulfate increases as the temperature increases.
(b): The decrease in Ca^{2+} concentration increases as the temperature increases (Strand et al., 2006a).

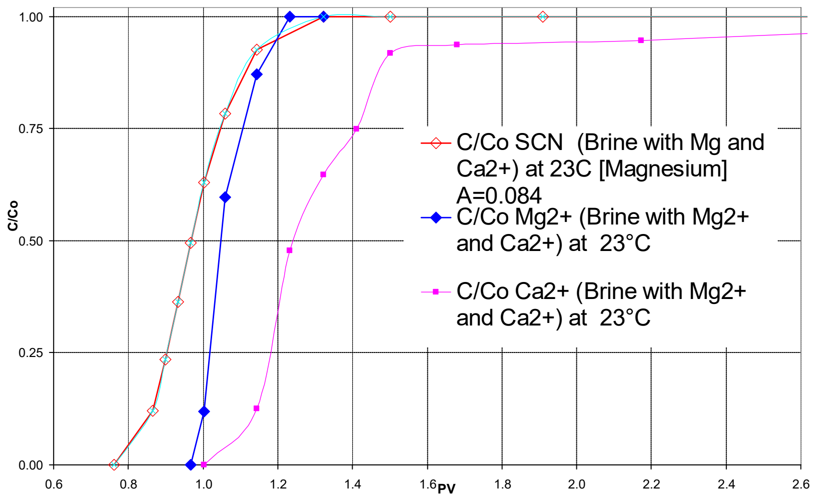
Method:

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-})

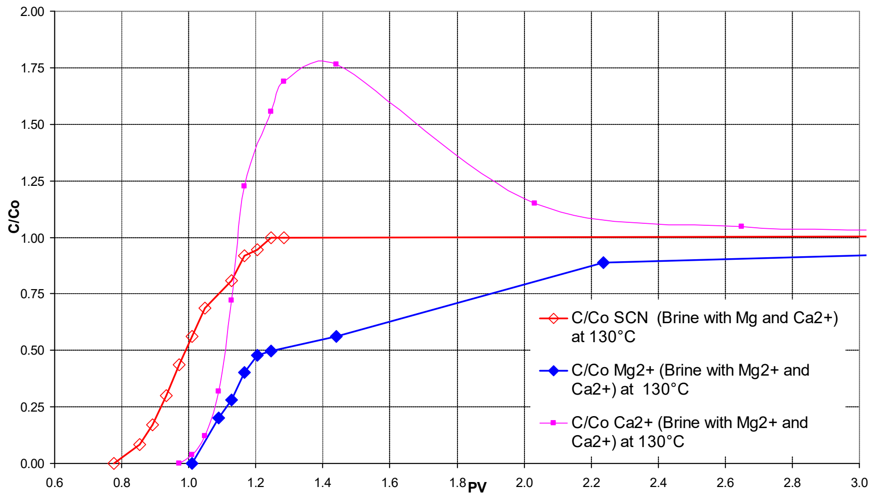
Affinities of Ca^{2+} and Mg^{2+} towards the chalk surface

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

T=20 °C



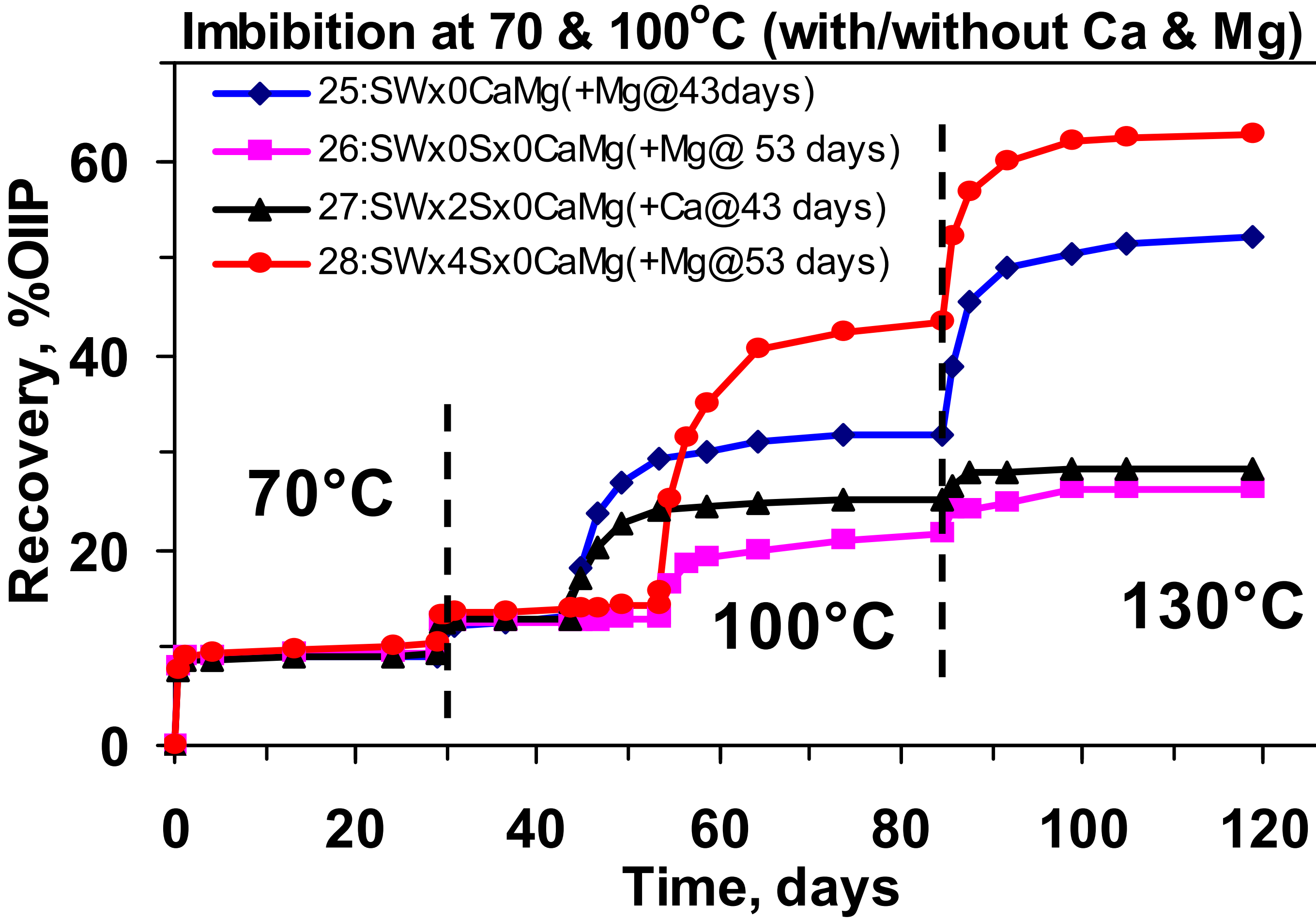
T=130 °C



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

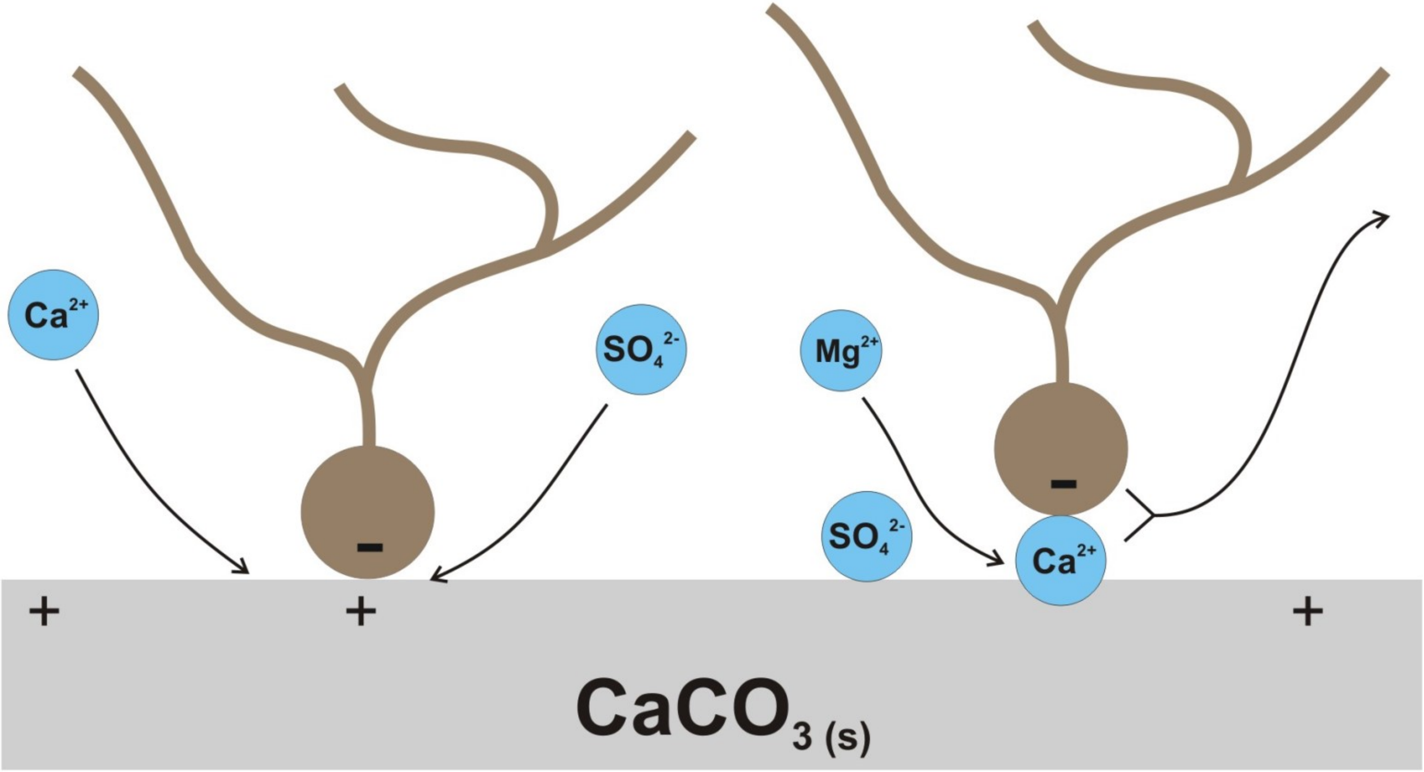
Effects of potential determining ions and temperature on spontaneous imbibition

Zhang et al. Colloids and Surfaces A: 301 (2007) 199-208)



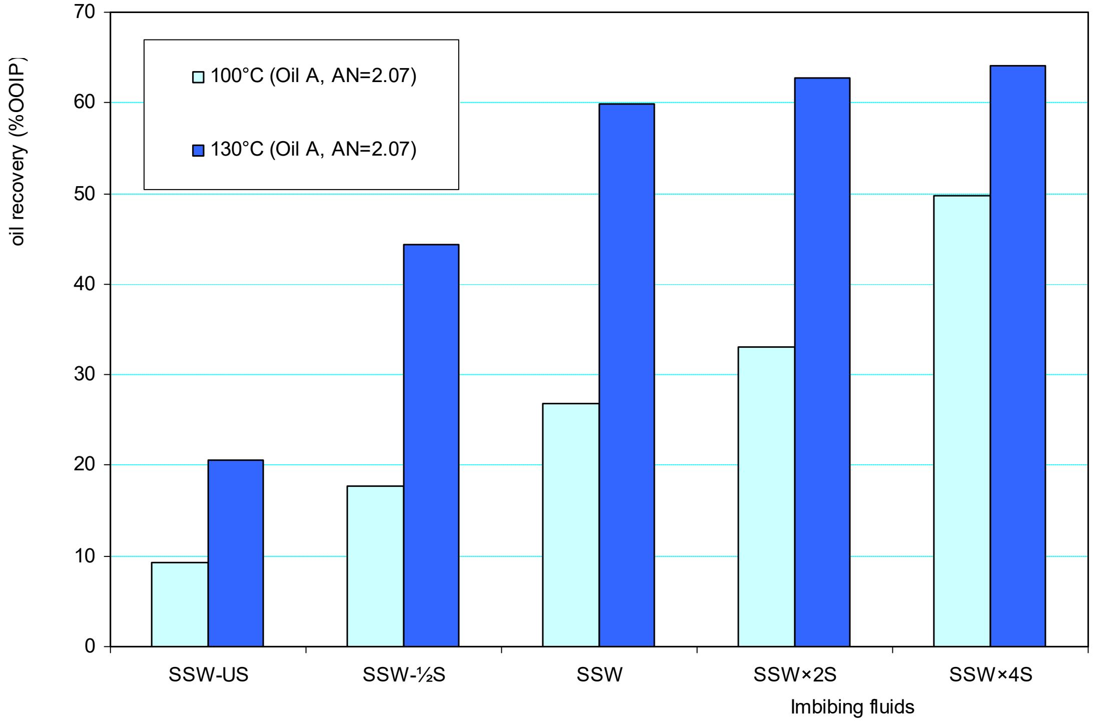
Suggested wettability mechanism

Zhang et al. Colloids and Surfaces A: 301 (2007) 199-208)



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

(Zhang and Austad Colloids and Surfaces A: 279 (2006) 179-187)



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 of brines

Molar compositions (mole/l) of PW/SSW-mixtures for Ekofisk

	SSW	**PW***	**FW***
HCO_3^-	0.002	0.008	0.004
Cl^-	0.525	0.765	1.423
SO_4^{2-}	**0.024**	**0.007**	**0.000**
Mg^{2+}	**0.045**	**0.021**	**0.022**
Ca^{2+}	**0.013**	**0.049**	**0.100**
Na^+	0.450	0.635	1.156
K^+	0.010	0.007	0.007
Ba^{2+}	0.0E+00	8.2E-06	0.002
Sr^{2+}	0.0E+00	2.2E-03	0.009
Li^+	0.0E+00	9.8E-04	0.000
Ionic strength	0.657	1.150	1.559
TDS (g/l)	**33.39**	**45.81**	**83.09**

* Data received from ConocoPhillips, Norway.

Ion composition in PW from Ekofisk

PW contained 73.6 vol% SW and 26.4 vol%FW

T_{res}=130 °C

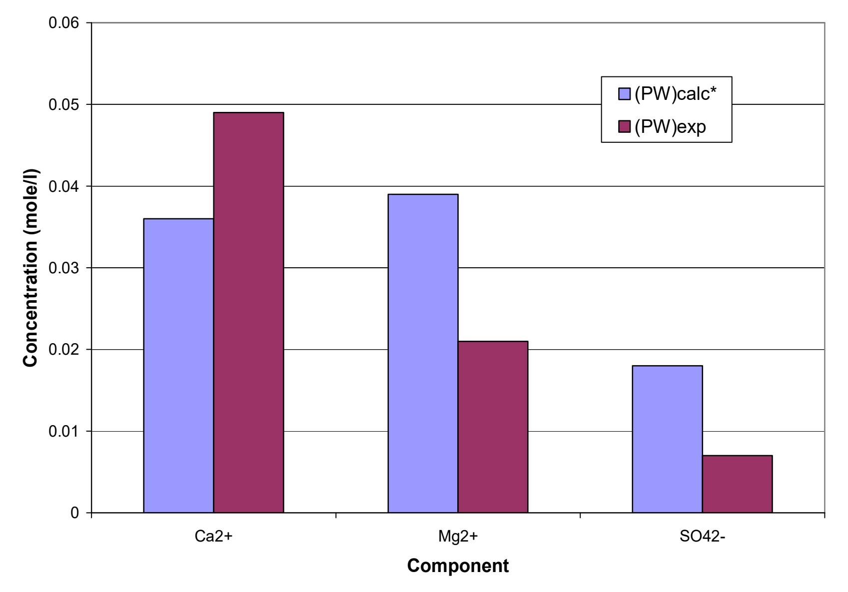


Fig. 3 Calculated and measured component concentration in PW linked to substitution of Ca^{2+} by Mg^{2+} at the rock surface, adsorption of SO_4^{2-} onto the rock and precipitation of $CaSO_4$.

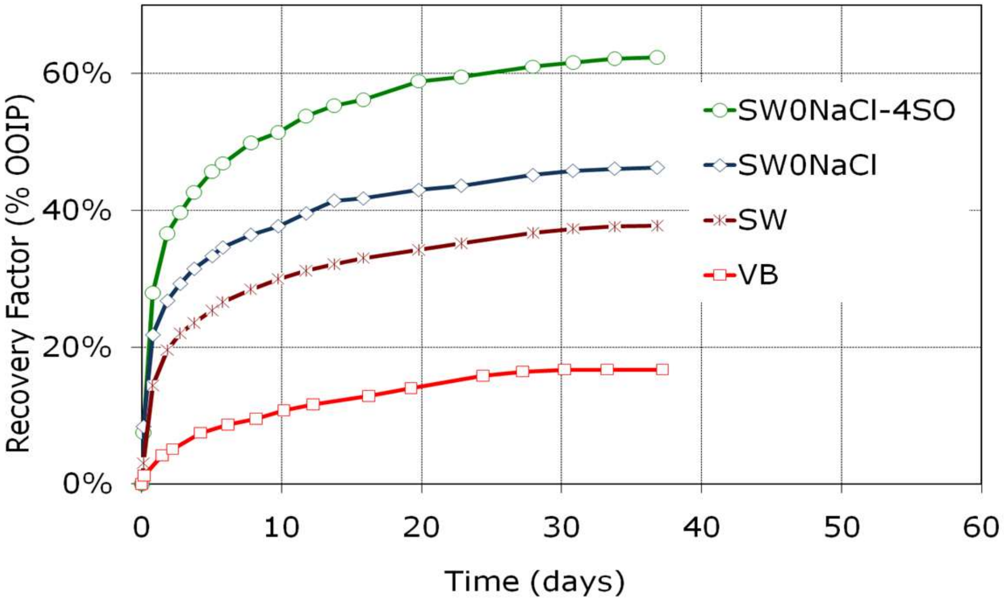
Question

Can SW be improved as a wettability modifier?

“Modified SW” as EOR-fluid

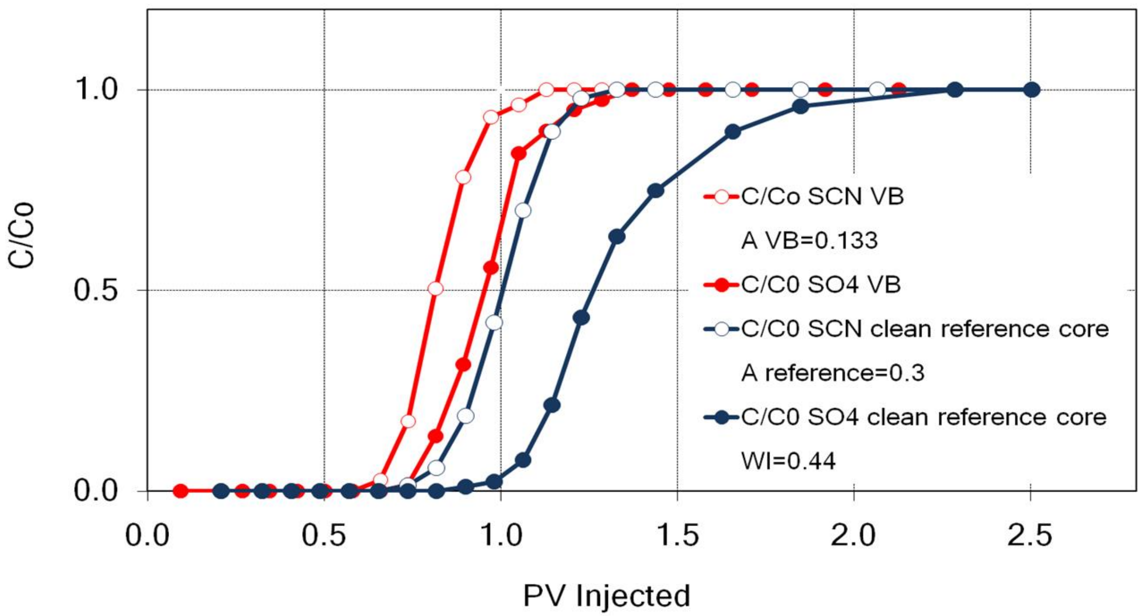
Fathi et al. *Energy & Fuels*: 24 (2010) 2514-2519; 25 (2011) 5173-5179)

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



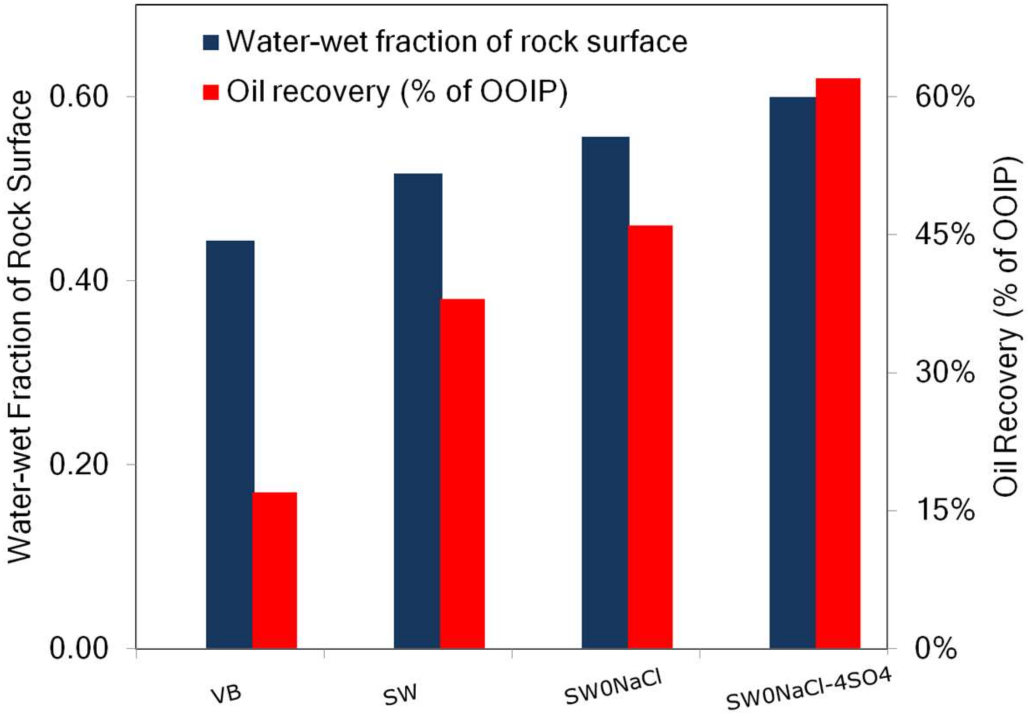
- Formation water: VB
- Seawater: SW
- Seawater depleted in NaCl
- Seawater depleted in NaCl and spiked with 4x sulfate

Chromatographic wettability test



Chromatographic wettability analysis after spontaneous imbibition at 90ºC by using formation brine, the cores was saturated with Oil–B with acid number of 0.5 mgKOH/g.

Relationship: Wettability-Oil recovery



Relationship between oil recovery and water–wet fraction of the rock surface **after spontaneous imbibition** with VB, SW, SW0NaCl, and SW0NaCl–4SO_4^{2-} **at 90 °C.**

”Smart Seawater” in Chalk

110 °C

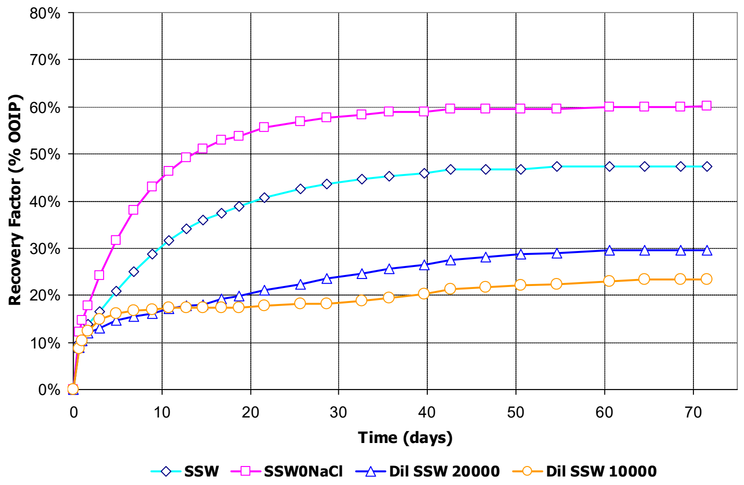


Fig. 3. Spontaneous imbibition at 110 °C

120 °C

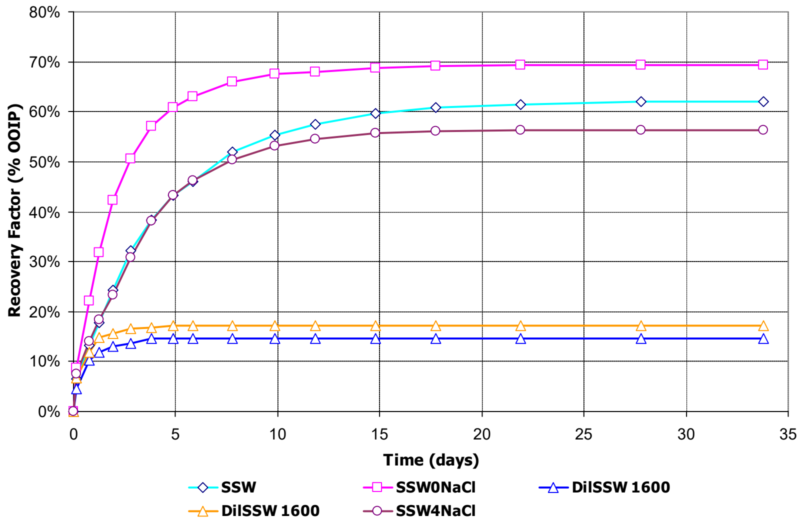
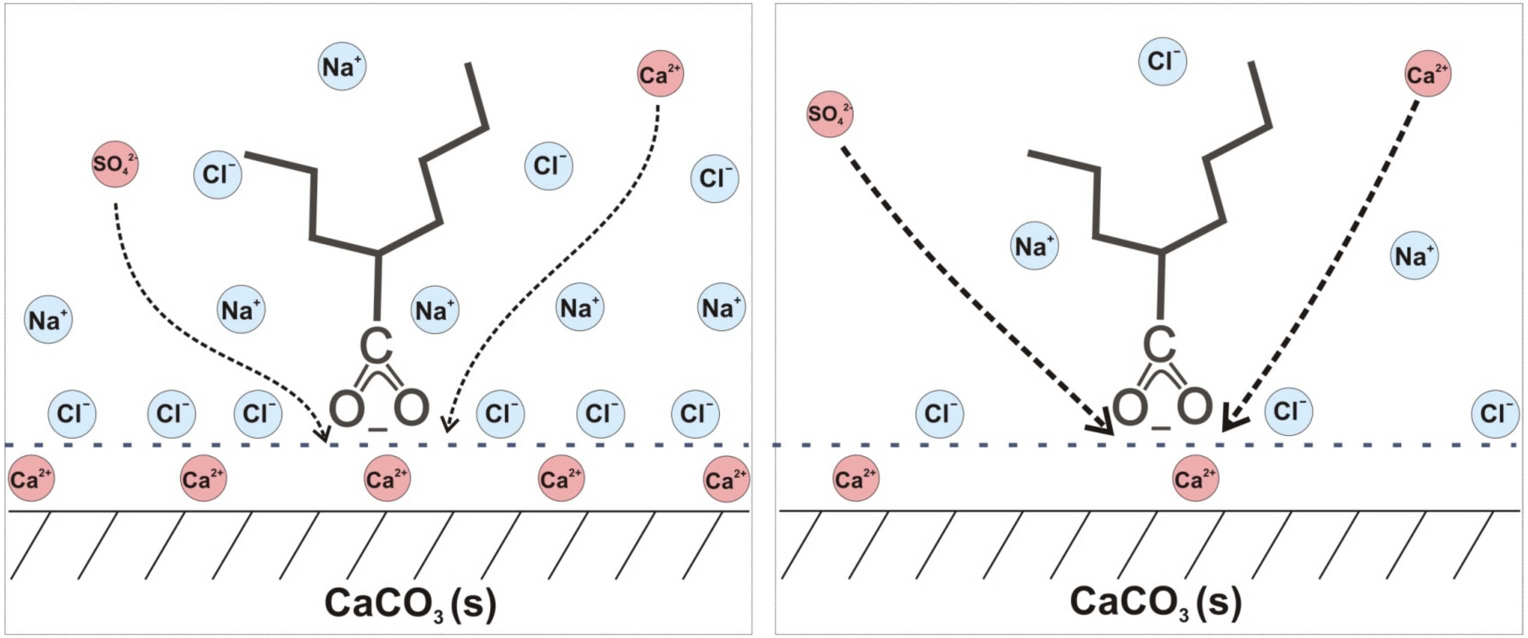


Fig. 4. Spontaneous imbibition at 120 °C using different imbibing fluids with different salinities and ionic composition.

EOR-potential by ”Smart Seawater” (depleted in NaCl) in Ekofisk may increase recovery by 10 % of OOIP.

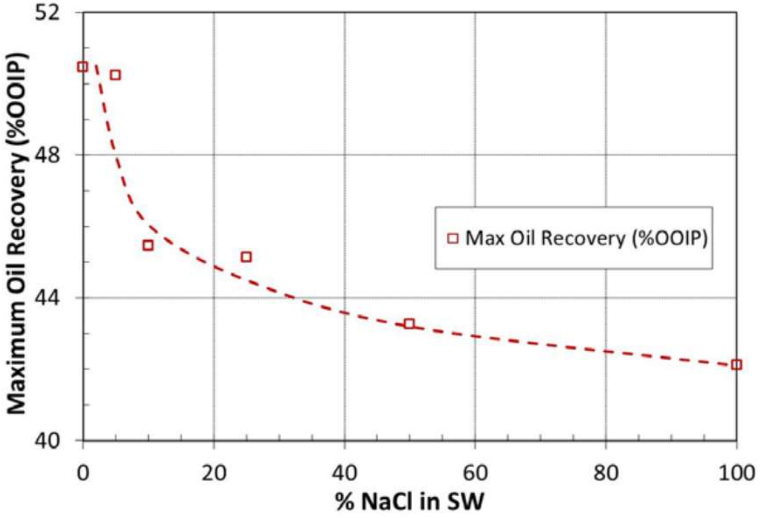
Effect of Salinity and Ion concentration

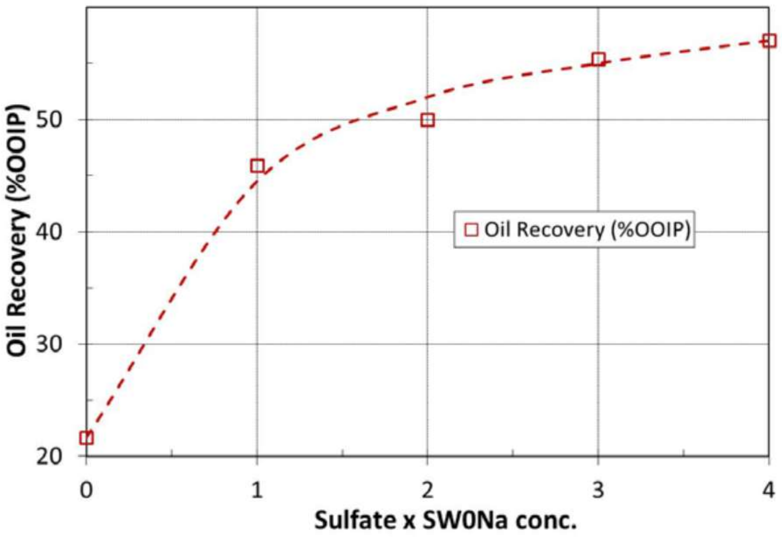


The access of potential determining ions to the calcite surface
is affected by the concentration of non active ions in the double layer

Effects of NaCl and SO_4^{2-}

(Puntervold et al. JPSE: 133 (2015) 440-443)





How much NaCl must be removed from SW?

How much sulfate must be added to SW depleted in NaCl?

Forced displacement from reservoir limestone core

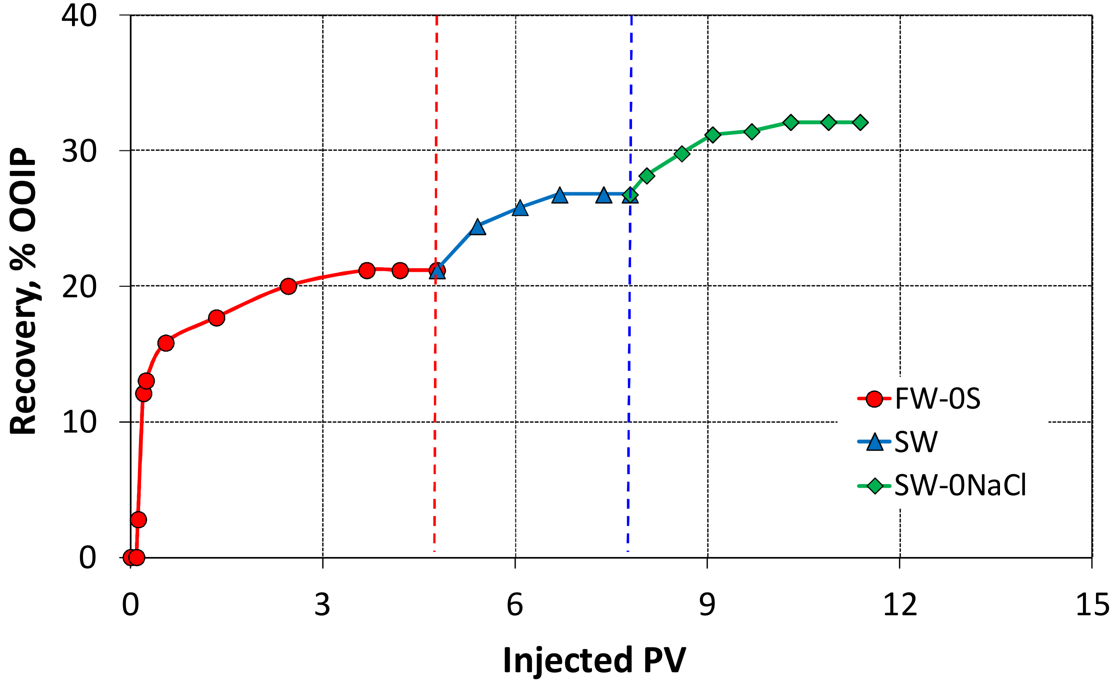


Fig. 5. Oil recovery by forced displacement from the composite core, **Core 2** and **Core 3**. Successive injection of FW-0S, SW and SW-0NaCl. T_{test}: 100°C; Injection rate: 0.01 ml/min (≈0.6 PV/D).

North Sea Chalk Fields

- Suggestions
  - Upper Ekofisk most oil-wet.(130 ^{o}C, not flooded ??)
    - Injection of SW depleted in NaCl could increase recovery in the range of 10% of OOIP compared to SW.
  - Valhall (90 ^{o}C)
    - Injection of SW depleted in NaCl and spiked by SO_4^{2-} can increase the recovery significantly compared to SW (20% of OOIP).
  - Involve service companies to make modified SW cheaply by membrane technology.

Is dissolution of chalk a mechanism for wettabilit alteration???

Hiorth, A.; Cathles, L. M.; Kolnes, J.; Vikane, O.; Lohne, A.; Madland, M. V. ***A chemical model for the seawater-CO_2-carbonate system - Aqueous and surface chemistry***, Paper SCA2008-18 presented at the International Symposium of the Society of Core Analysts, Abu Dhabi, U. A. E., 29 Oct - 2 Nov, 2008.

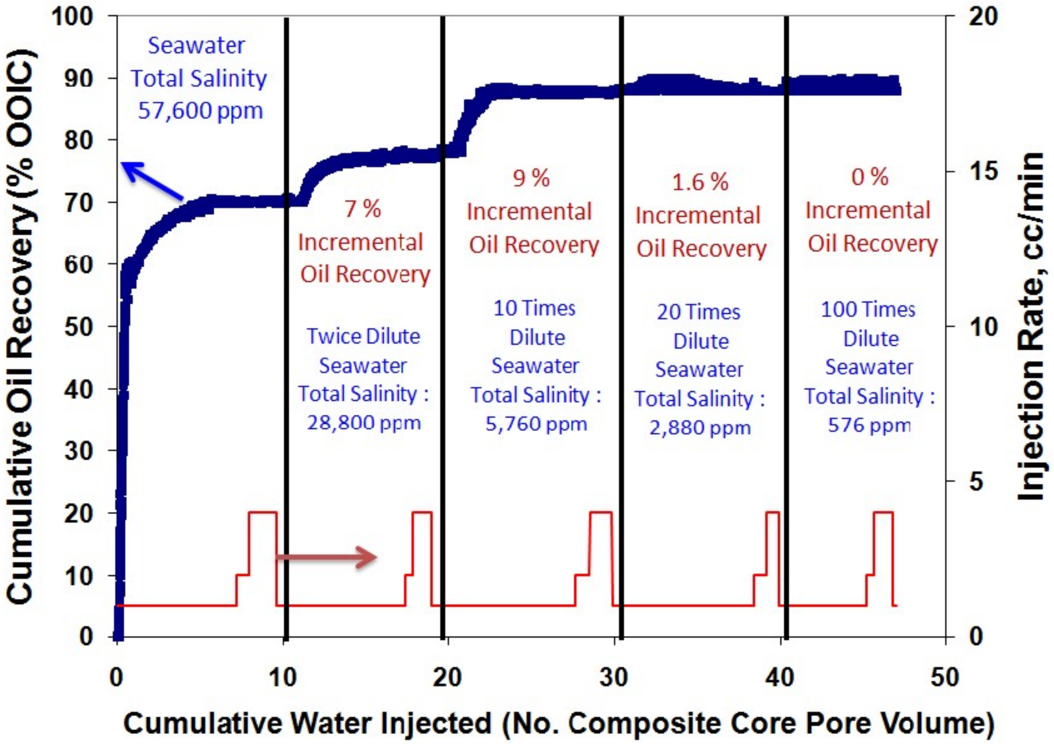
Austad, T.; Strand, S.; Puntervold, T. ***Is wettability alteration of carbonates by seawater caused by rock dissolution?*****,** Poster SCA2009-43 presented at the International Symposium of the Society of Core Analysts, Noordwijk, The Netherlands, 27-30 September, 2009.

Mahani, H.; Keya, A. L.; Berg, S.; Bartels, W.-B.; Nasralla, R.; Rossen, W. ***Driving Mechanism of Low Salinity Flooding in Carbonate Rocks***, Paper SPE 174300 presented at EUROPEC 2015, Madrid, Spain, 1-4 June, 2015. 10.2118/174300-MS.

Low salinity EOR-effects in carbonates:

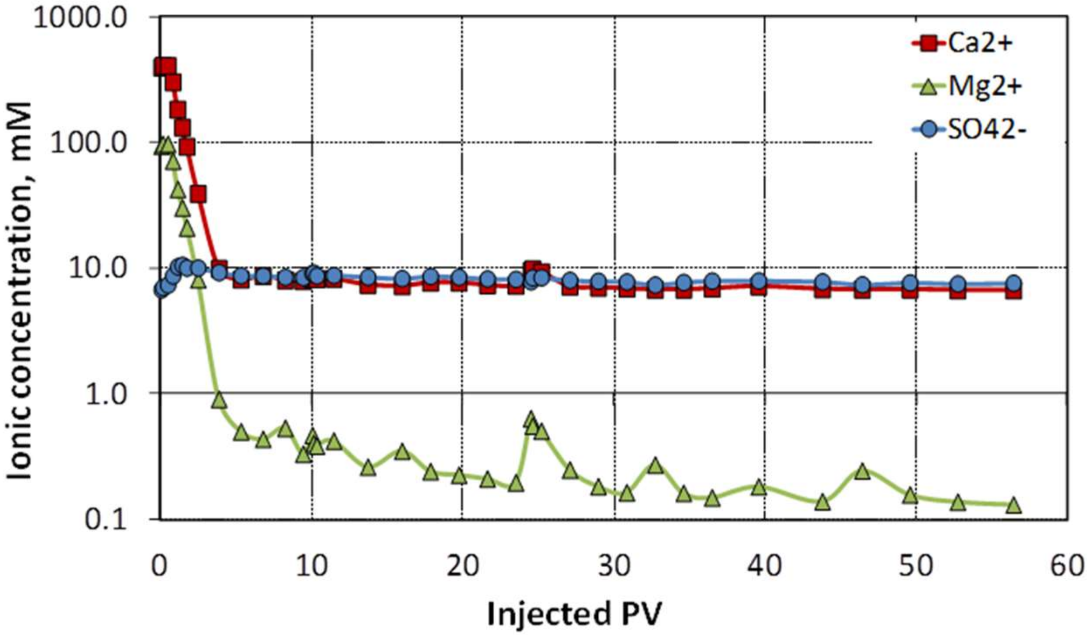
What is the condition?

Low salinity EOR-effects in carbonates



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

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.

Codition for observing low salinity EOR-effects in carbonates

Austad et al. *Energy & Fuels* 26 (2012) 569-575)

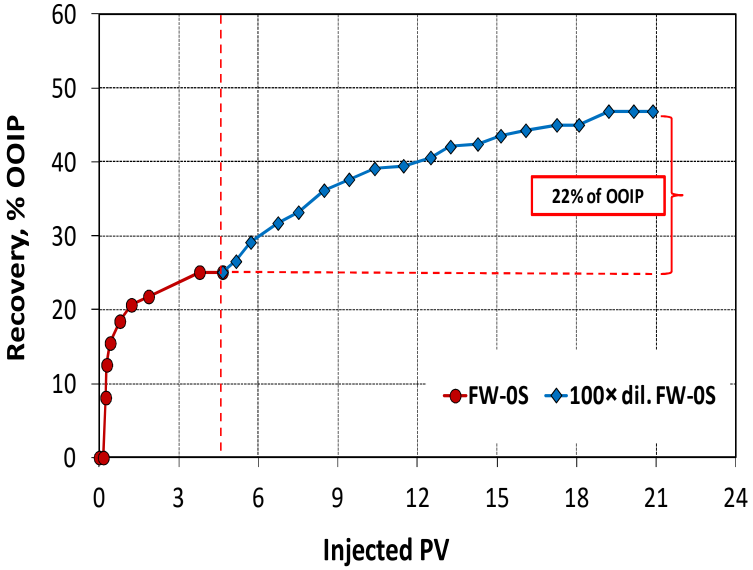
- The carbonate rock must contain anhydrite, $CaSO_4$(s)
- Chemical equilibrium:

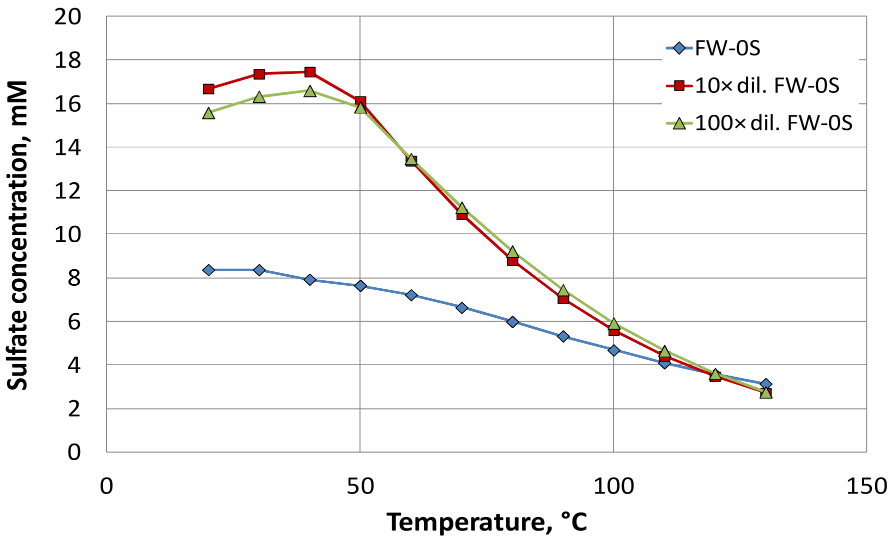
$$\mathbf{CaSO_4(s) \leftrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) \leftrightarrow Ca^{2+}(ad) + SO_4^{2-}(ad)}$$

- The concentration of SO_4^{2-}(aq) depends on:
  - Temperature: Decreases as T increases
  - Brine salinity/composition: Decreases as Ca^{2+} concentration increases
- Wettability alteration process:
  - Temperature: (increases as T increases)
  - Salinity: (increases as NaCl conc. decreases)
- Is it an optimal temperature window?
  - 90-110 °C ?

FW: Low salinity EOR-effect

(Austad et al.: Energy & Fuels 2015)

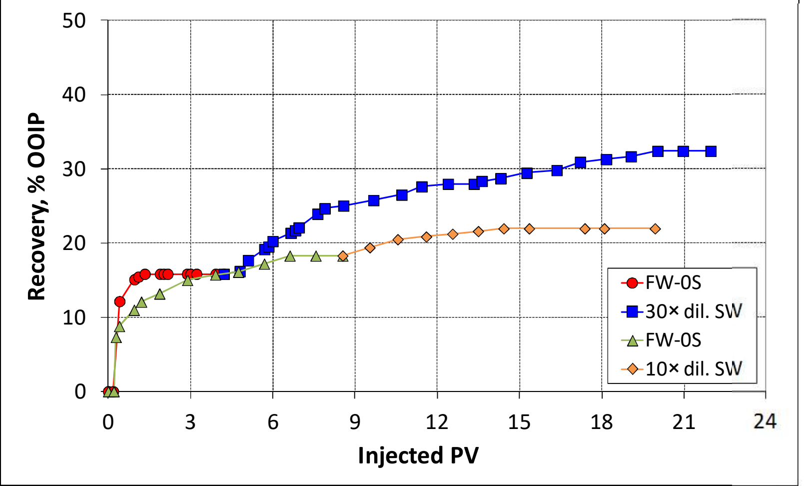




Oil recovery by forced displacement from a reservoir limestone core containing anhydrite. Successive injection of FW, and 100× diluted FW. T_{test}: 100°C. Injection rate: 0.01 ml/min (≈1 PV/D).

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

SW: Low salinity EOR in Carbonates



Low salinity effects by using 10× diluted SW (5700 ppm) and 30× diluted SW (1900 ppm) as low salinity fluids, after first flooding with FW-0S (213000 ppm). Temperature 100 °C; flooding rate 0.01 ml/min.

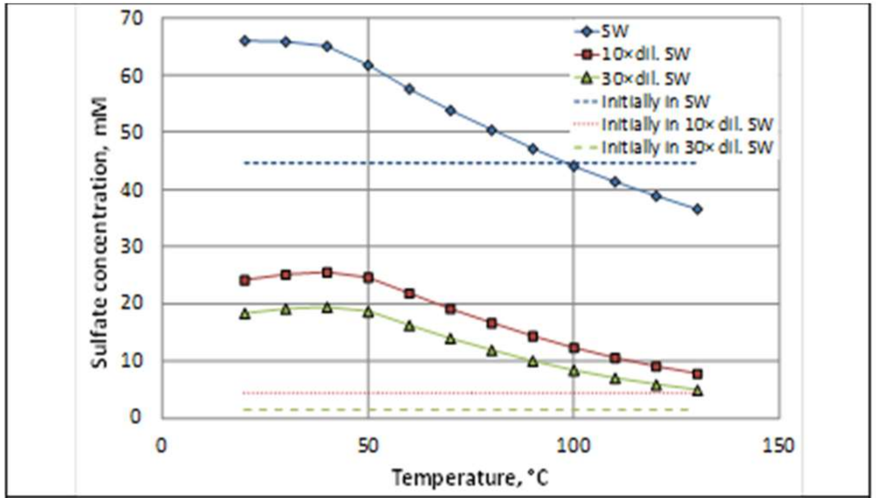


Fig. 14. Simulated dissolution of $CaSO_4(s)$ when exposed to SW, 10× and 30× diluted SW at different temperatures.

Diluted FW and SW as EOR fluid

Table 5 The relationship between extra oil recovery and effluent concentration of sulfate and NaCl under tertiary water flood using 100x dil. FW-0S, SW, 10x and 30x diluted SW, after the core was first flooded with FW-0S. T= 100 °C.

	FW-0S	**100× dil. FW-0S**	**SW**	**10× dil. SW**	**30× dil. SW**
Extra oil (% of OOIP)	-	**22**	5	5	**18**
Sulfate (mM)	2.8	**5.3**	10	7.5	**4**
NaCl (mM)	2580	**25.8**	796	79.6	**26.6**
Salinity (ppm)	213000	**2130**	57760	5776	**1925**

Anhydrite: Impact on Initial wetting condition

Farzad et al. *Energy & Fuel* 25 (2011) 3021-3028

$$CaSO_4(s) \leftrightarrow Ca^{2+} + SO_4^{2-}(aq) \leftrightarrow CaCO_3(s)\text{---}SO_4^{2}(ad)$$

Table 2. Equilibrium between SO_4^{2-}(aq) and SO_4^{2-}(ad) at different temperatures, when VB-2 (2 mM SO_4^{2-})was used as formation water

Temp. °C	**SO_4^{2-}(aq)** mg	**SO_4^{2-} (ad)** mg	**SO_4^{2-} (aq)+ SO_4^{2-} (ad)** mg	**SO_4^{2-} (aq)/ SO_4^{2-} (ad)**
20	**1.6**	**3.0**	**4.6**	**0.69**
50	**1.4**	**3.1**	**4.5**	**0.53**
90	**0.36**	**3.4**	**4.0**	**0.26**
130	**0.03**	**2.8**	**2.9**	**0.10**

Quantification of SO_4^{2-}(aq) and SO_4^{2-}(ad)

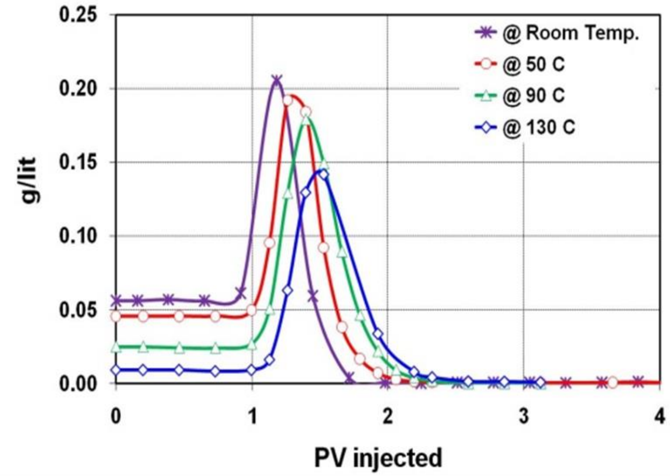


Fig. 14. Relative amount of sulfate dissolved in the pore water and sulfate adsorbed onto the rock at different temperature. The cores was saturated and aged at elevated temperatures in VB-2 and then flooded at the same temperature with DI water. Injection rate: 0.2 ml/min.

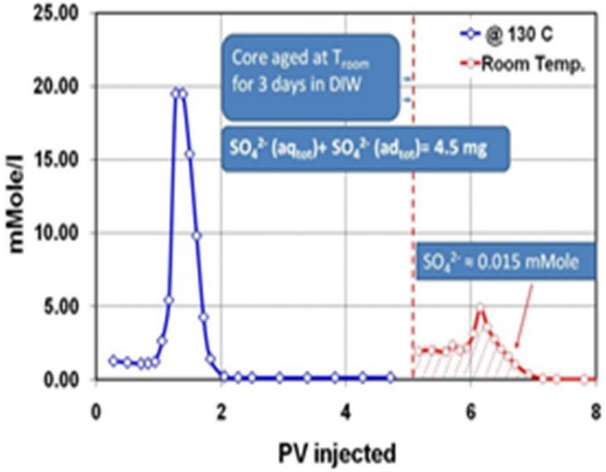
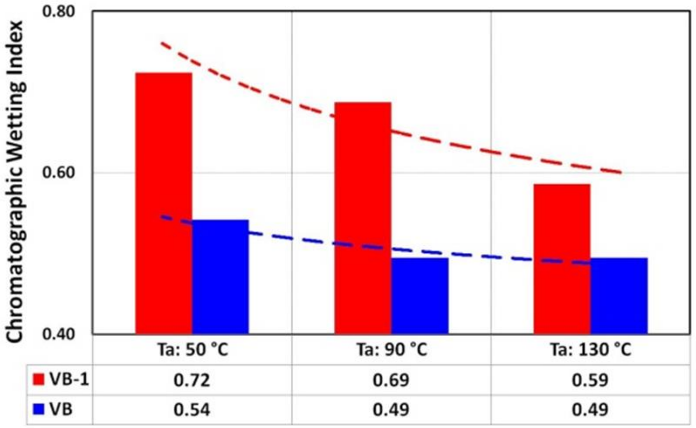


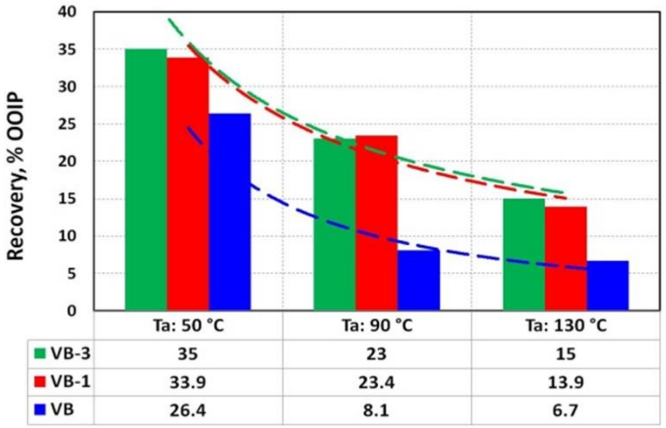
Fig. 13. Relative amount of sulfate dissolved in the pore water and sulfate adsorbed onto the rock at 130 °C and room temperature using 10 times diluted VB-2. The core was flooded with DI water. After switching to room temperature, the core was aged for 3 days prior to further flooding with DI water. Injection rate: 0.2 ml/min.

Anhydrite: Impact in Initial wetting and oil recovery



	Ta: 50 °C	Ta: 90 °C	Ta: 130 °C
🟥 VB-1	0.72	0.69	0.59
🟦 VB	0.54	0.49	0.49

Fig. 12. Chromatographic Water Index of the cores containing VB and VB-1 at different aging temperatures. Chromatographic brines, SW0T and SW1T; tests at room temperature; C/C$_o$, relative concentration of SCN$^-$ and SO$_4^{2-}$



	Ta: 50 °C	Ta: 90 °C	Ta: 130 °C
🟩 VB-3	35	23	15
🟥 VB-1	33.9	23.4	13.9
🟦 VB	26.4	8.1	6.7

Fig. 13. Oil recovery of the cores containing VB, VB-1 and VB-3 at different aging temperatures. Oil with AN=0.55 mgKOH/g was used and VB without sulfate was used as imbibing brine.

VB-1=VB-2: 2 mM SO$_4^{2-}$
VB-3 : 17 mM SO$_4^{2-}$

Recent work

- Patrick et al. (*J. Pet. Sci. Eng. 2012*)
  - Modelling showed that SO_4^{2-} protected actitve Ca^{2+}-sites on carbonate from beeing adsorbed by carboxylic material.
- Zeng et al. (*Enery & Fuels 2012*)
  - Experimental verification that SO_4^{2-} decreased adsorption of carboxylic acids onto calcium carbonates.
- ShamsiJazeyi et al. *Colloids and Surfaces A*. (2014 ??)
  - Used polyacrylate as sacrificial agent to lower adsorption of anionic surfactant.
  - Functioned badly when anhydrite was present
  - Sulfate prevented adsorption of polyacrylate onto the rock

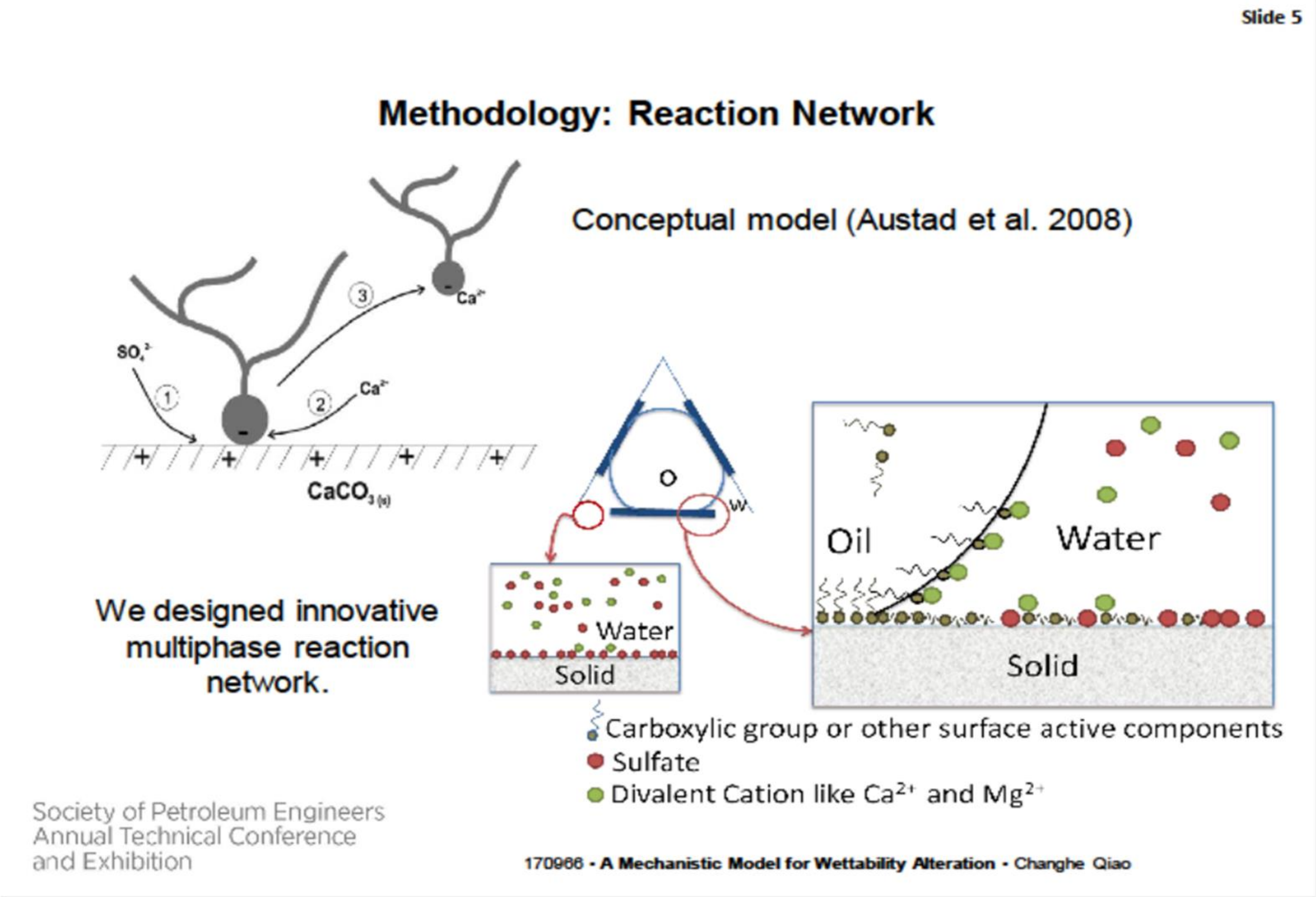
Modelling of oil recovery by wettabily alteration

- The Univ. of Texas at Austin.
  - Al-Shalabi, Sepehrnoori, Pope, Mohanty, *J. Pet. Sci. Eng.* (2014 ?)
  - Termed their model: **LSWI Fundamental Model for Carbonates**
    - Modelled data from Yousif and Mohanty successfully
  - The model incorporates wettability alteration effect through contact angle and trapping parameter, which are supposed to be dictated only by salinity.
  - Thus, changes in parameters like P_c, k_{ro}, k_{rw}, are linked to salinity gradients only.
- This **is not** a fundamental understanding of the mechanism. The model must contain:
  - Interaction between carboxylic material and the rock surface
  - Impact of specific ions, Ca^{2+}, SO_4^{2-}, Mg^{2+}
  - Impact of temperature
  - Dissolution of Anhydrite, $CaSO_4$.

Modelling of oil recovery by wettabily alteration

- Pennsylvania State Univ.
  - Qiao, Li, Johns, Xu, SPE 170966 (2014)
- Some comments
  - The model was based on our understanding of the chemical mechanism.
  - The use of advanced geochemical models is not the best tool for modelling EOR effects by wettability modification.
  - Salinity should not be a single factor for the efficiency of chemically tuned water.
- Recent work: SPE-175018-MS
  - Modelling LS EOR effects; Dissolution of Anhydrite, $CaSO_4$.

Conceptual model used



Methodology: Reaction Network

Conceptual model (Austad et al. 2008)

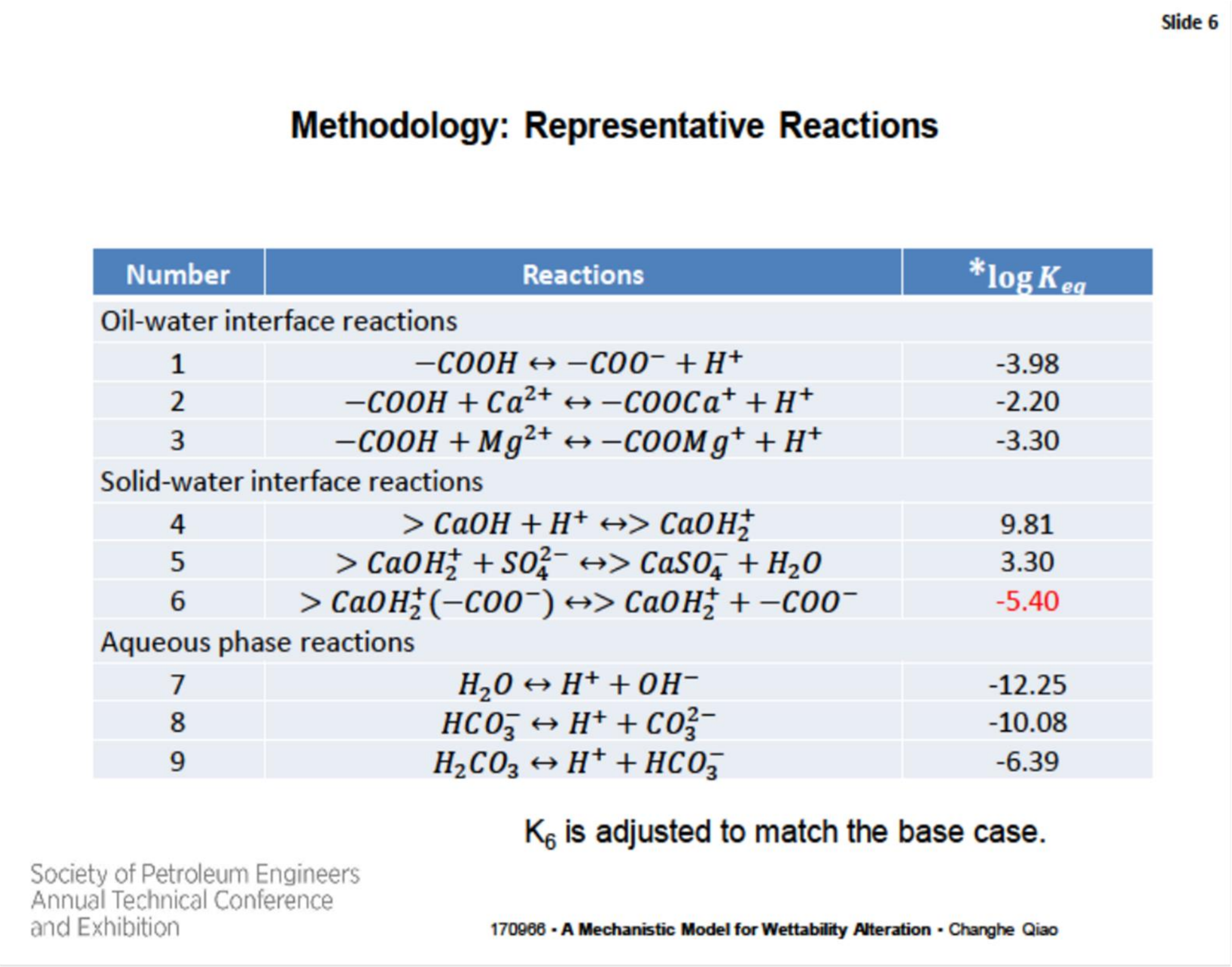
We designed innovative multiphase reaction network.

- Carboxylic group or other surface active components
- ● Sulfate
- ● Divalent Cation like Ca^{2+} and Mg^{2+}

Society of Petroleum Engineers
Annual Technical Conference
and Exhibition

170966 - **A Mechanistic Model for Wettability Alteration** - Changhe Qiao

Chemical equilibria used



Methodology: Representative Reactions

Number	Reactions	*$\log K_{eq}$
Oil-water interface reactions		
1	$-COOH \leftrightarrow -COO^- + H^+$	-3.98
2	$-COOH + Ca^{2+} \leftrightarrow -COOCa^+ + H^+$	-2.20
3	$-COOH + Mg^{2+} \leftrightarrow -COOMg^+ + H^+$	-3.30
Solid-water interface reactions		
4	$> CaOH + H^+ \leftrightarrow > CaOH_2^+$	9.81
5	$> CaOH_2^+ + SO_4^{2-} \leftrightarrow > CaSO_4^- + H_2O$	3.30
6	$> CaOH_2^+(-COO^-) \leftrightarrow > CaOH_2^+ + -COO^-$	-5.40
Aqueous phase reactions		
7	$H_2O \leftrightarrow H^+ + OH^-$	-12.25
8	$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	-10.08
9	$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	-6.39

K_6 is adjusted to match the base case.

Dolomite

- Does Dolomite respond like calcite towards Smart Water ?
- The affinity between R-COO$^-$ and Ca^{2+} and Mg^{2+} is a factor of 10 in favour of Ca^{2+}

Dolomite outcrop: Affinity of Sulfate

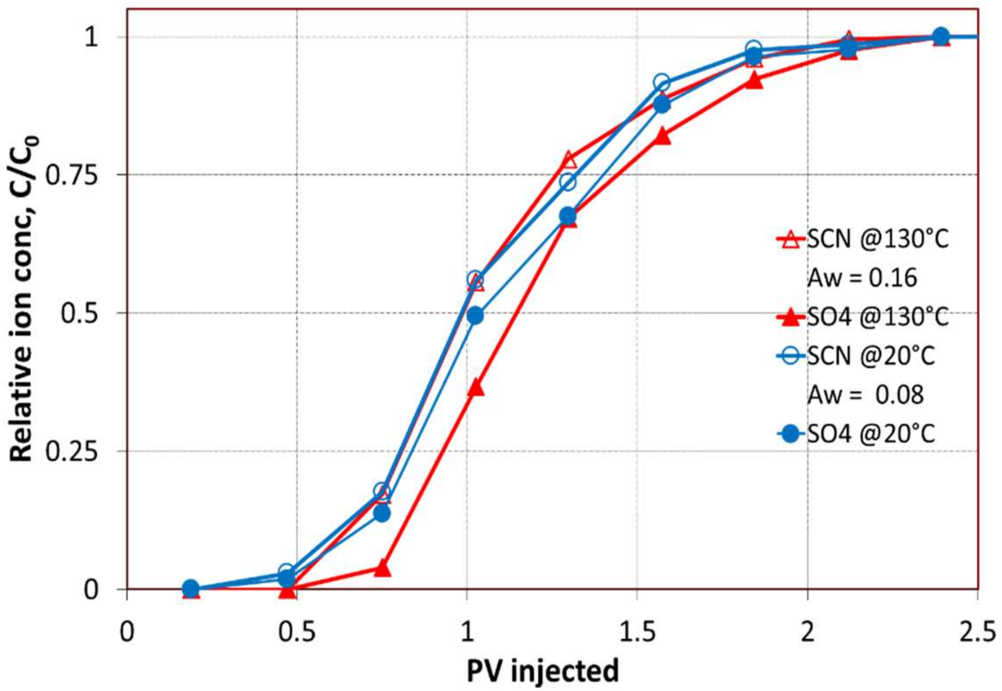


Fig. 7. Surface reactivity test on outcrop dolomite rock. The core SIL#7 was equilibrated with SW0T prior to SW½T injection at a rate of 0.1ml/min. The affinity of SO_4^{2-} towards rock surface was chromatically verified at 20 and 130 °C.

Oil recovery by SI

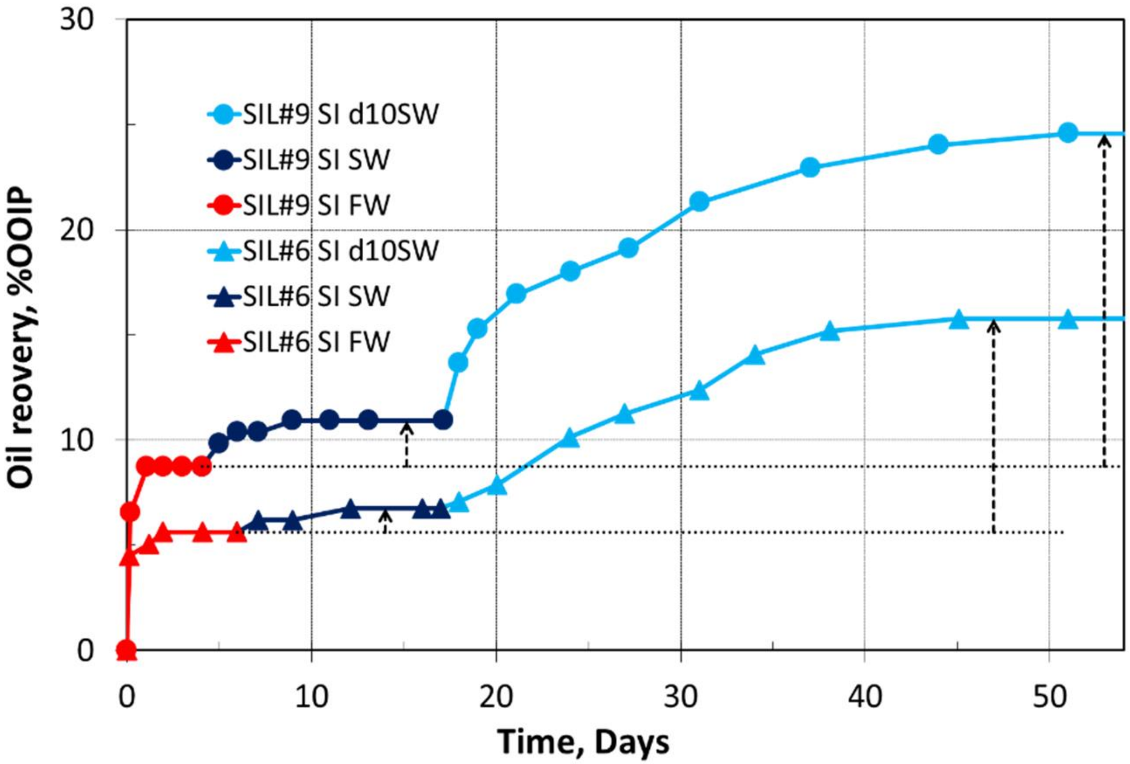


Fig. 9. Oil recovery from dolomite cores SIL#6 and SIL#9 by using FW, S_{wi}=0.15; salinity 222 000 ppm, as formation water. Oil 3 with AN=0.52 mgKOH/g was used. The cores were spontaneous imbibed at 70°C, with FW, SW and d_{10}SW.

Review papers available

Water based EOR from Clastic Oil Reservoirs by Wettability Alteration: A Review of Chemical Aspects.

JPSE 2016, Tina Puntervold, Skule Strand, Tor Austad

“Smart Water” EOR Effects in Carbonates: A Chemical Review of Wetting Properties and Oil Recovery.

To be submitted to JPSE, Tina Puntervold, Skule Strand, Tor Austad

Request of pdf files to :

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Acknowledgement

Statoil,
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Maersk,
Shell,
Saudi Aramco,
DNO International.

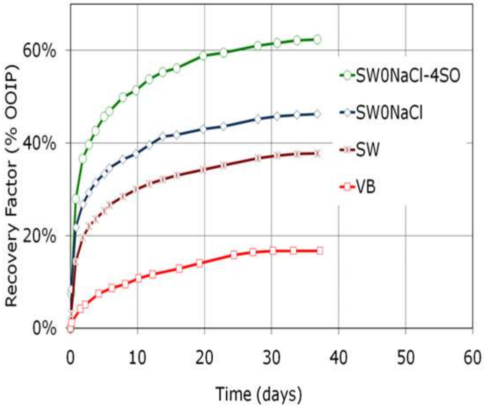

TATNEFT

IOR Aqua

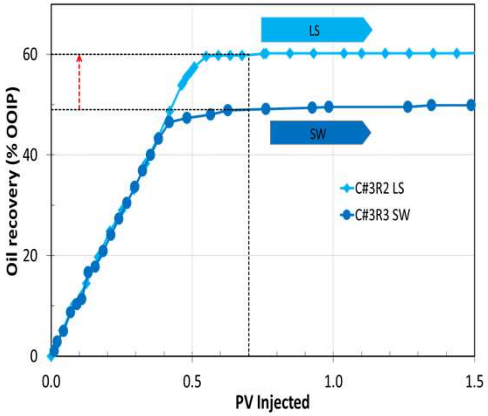
Smart Water EOR

Smart Water injection could improve oil recoveries by 10 - 50 % and significant reduce reservoir and production scale

In Carbonate:



In Sandstone:



IOR Aqua AS in collaboration with University of Stavanger, Norway, offers:

- Screening of Smart Water EOR potential in Sandstone or Carbonate reservoirs
  - Desk evaluation of Smart Water EOR potential
  - Core screening tests evaluating Smart Water EOR potential
  - Oil Recovery tests evaluating Smart Water EOR potential
  - Optimization of injection water composition

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- Morten Lerbrekk, Morten.Lerbrekk@tyrfing.no, +4795052663

References:

- «Prisverdig krittgjennombrudd» - published in «Norsk Sokkel», an NPD journal, nr. 2, 2011
- Strand, S., Puntervold, T. and Austad, T. 2016. Water based EOR from clastic oil reservoirs by wettability alteration: a chemical evaluation. *Journal of Petroleum Science and Engineering (accepted).*
- RezaeiDoust, A., Puntervold, T. and Austad, T. 2011. Chemical verification of the EOR mechanism by using low saline/smart water in sandstone. *Energy & Fuels* **25**: 2151-2162.
- Puntervold, T., Strand, S., Ellouz, R. and Austad, T. 2015. Modified seawater as a smart EOR fluid in chalk. *Journal of Petroleum Science and Engineering* **133**: 440-443.

BP: Endicott field test SPE 129692

- Background data
  - Clay content ranged from a few to 20 wt%
  - Kaolinite dominated followed by Illite
  - Average permeability: 1400 mD
  - Average porosity: 22%
  - Initial oil saturation: 95%
  - Injection of HS brine: S_{or}=41%
  - Tertiary LS brine injection: S_{or}=27%
  - Increased LS EOR displacement efficiency: 26%

Endicott two well field test observations

- LS EOR effect: 10% of total PV in swept area
- Produced water observations:
  - Increase in alkalinity, i. e. HCO_3^-
    - $CO_2(g) + H_2O \leftrightarrow [H_2CO_3] \leftrightarrow H^+ + \mathbf{HCO_3^-}$
    - $H^+ + OH^- = H_2O$
  - Decrease in $H_2S(g)$
    - $\mathbf{H_2S} + OH^- \leftrightarrow H_2O + HS^-$
  - Increase in Fe^{2+}
    - $FeS(s) + OH^- \leftrightarrow [FeOH]^+ + S^{2-}$ $K_1=10^{5.7}$
  - Decrease and increase in Mg^{2+}

Solubility of $Mg(OH)_2$ vs. pH

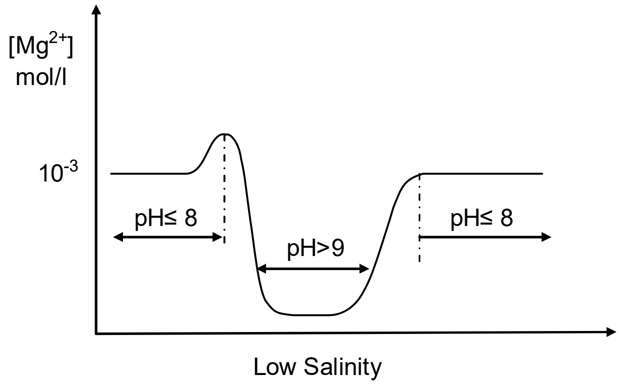
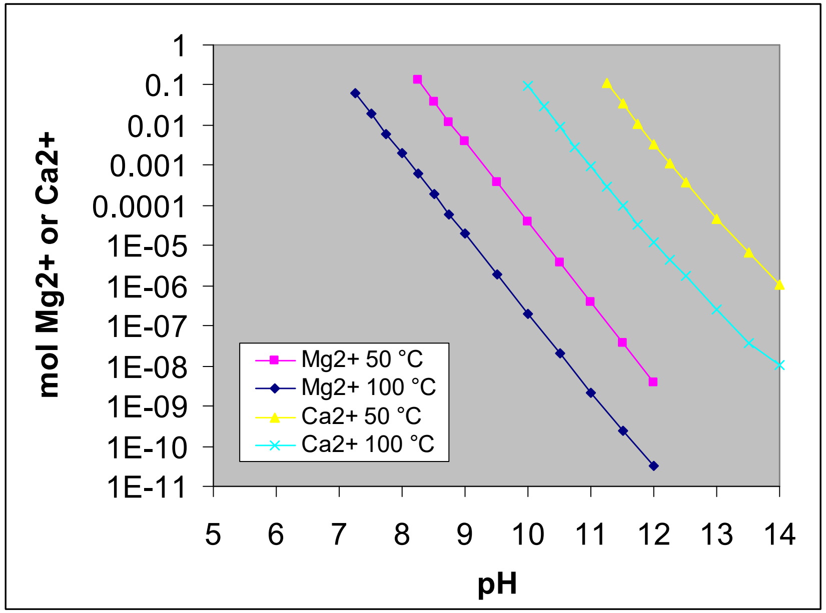


Fig. 11. Schematically change in Mg^{2+} concentration in the produced water during a low salinity flood. The concentration of Mg^{2+} is suggested to be quite similar for the initial FW and low saline brine.



Modeling solubility of $Mg(OH)_2$ and $Ca(OH)_2$ versus pH at 50 and 100 °C in a 50 000 ppm NaCl brine and 6 bars.

Mg^{2+}: 10^{-3} M, 100 °C:

At pH< 8: No precipitation of $Mg(OH)_2$

At pH >8: Precipitation: $Mg^{2+} + 2OH^- = Mg(OH)_2(s)$

HS brine: $Clay\text{-}H^+ + Ca^{2+} = Clay\text{–}Ca^{2+} + H^+$

$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2\,H_2O$

BP: Clare Ridge LS EOR prospect

Upstream Technology, Q1 2013

- Investments: $ 7.3 billions
- On steam 2016, oil production up to 120 000 bbl/D at peak
- Reversed osmosis desalt capacity: 45 000 bbl/D
- Estimated oil recovery
  - Flooding with SW: 640 millon bbl
  - Additional 42 million bbl by LS EOR, i. e. 6.6% extra oil.
  - Cost: $ 3 per bbl of extra oil compared to about 20 for other EOR techniques.