Polysulphate: A New EOR Additive To Maximize The Oil Recovery From Carbonate Reservoirs At High Temperature

Md Ashraful Islam Khan, Iván Darío Piñerez Torrijos, Saja Hussam Aldeen, Tina Puntervold, and Skule Strand.

University of Stavanger, Norway

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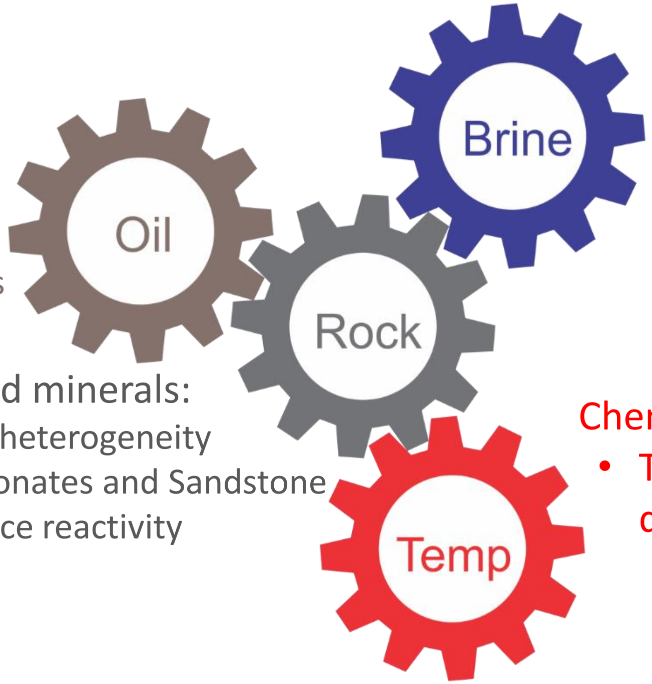
Reservoirs consist of pore systems with Mineral surfaces, Brine, and Crude Oil.

Crude Oil:
- Polar acids
- Polar bases
- Resins
- Asphaltenes



Formation Water and injection Brines:
- Salinity
- Ion composition

Rock and minerals:
- Pore heterogeneity
- Carbonates and Sandstone
- Surface reactivity

Chemical reactivity:
- Temperature dependent

Classical reservoir engineering:
- Limited knowledge …….if any

- ✓ Improved understanding of Reservoirs are needed
- ✓ Crude oil – Brine - Rock (CoBR) integrations controls:
  - Initial Reservoir wettability
  - Wettability in core restoration
  - Wettability alterations by «Smart Water»
  - Fluid flow in heterogeneous reservoirs
  - Scaling

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BRINE COMPOSITIONS – FW AND INJECTION BRINES

Formation Water ≠ Injection Water

Chemical CoBR equilibrium disturbed

«unstick» oil from rock surface!

Smart Water compositions in carbonates different from sandstone reservoirs

Ion	FW mM	SW mM	mSW mM	LS mM
Na^+	929.8	450	477.2	23.9
K^+	17.8	10	8.1	0.4
Ca^{2+}	**44.2**	**13**	**8.2**	**0.4**
Mg^{2+}	**7.0**	**45**	**13.5**	**0.7**
SO_4^{2-}	**0.0**	**24**	**0.4**	**0.02**
Cl^-	1058.8	525	527.9	26.4
HCO_3^-	7.7	2	0.3	0.02
pH	6.8	7.8	7.0	6.4
TDS, mg/kg	63 000	33.390	30 725	1 536
Ionic strength	1.128	0.657	0.551	0.028

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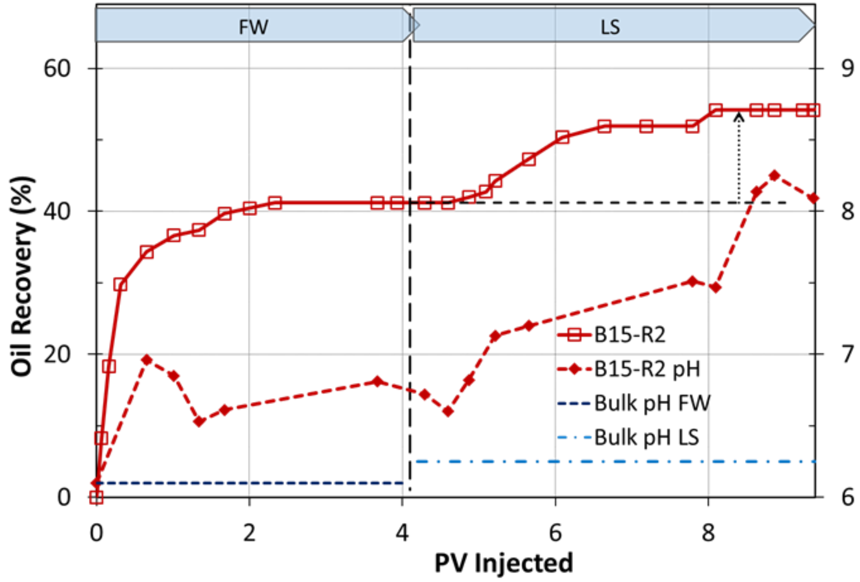
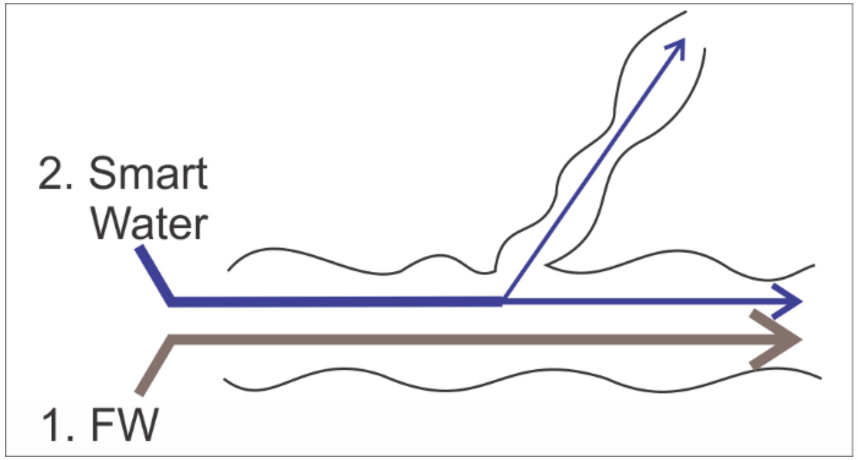
SEAWATER (SW) AS A «SMART WATER» IN CARBONATES:



- ✓ Minor changes in IFT
- ✓ Same pore distribution (FW and SW)
- ✓ Unfavorable mobility ratio with SW
  - ✓ SW viscosity lower than FW
- ➢ Wettability alteration
- ➢ Increased Microscopic Sweep



Wettability alteration towards more water wet

Increased capillary forces (F_c)
promotes increased sweep efficiency

Pressure (P):

$$P = \frac{F}{A}$$

Capillary pressure (P_c); tube model:

$$P_c = \frac{2 \cdot \sigma \cdot cos\theta}{r}$$

Capillary forces (F_c); heterogenies system:

$$F_c = \int (P, A)$$

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INTRODUCTION

EOR by modified water injection:

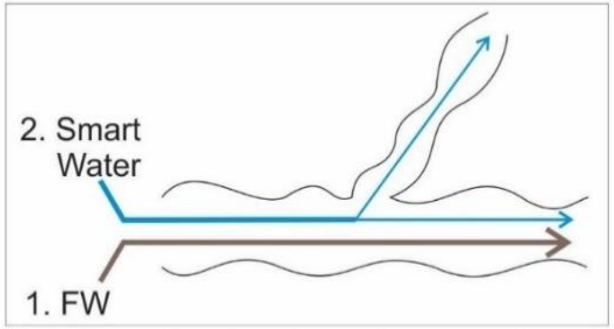
- Injection water ≠ Formation water
- Chemical equilibrium between crude oil, brine and rock must be disturbed.

- Smart Water is an injection brine with modified ionic composition.
  - No expensive chemicals are added
  - Environmentally friendly
  - Composition is dependent on reservoir mineralogy
  - Causes wettability alteration and improved sweep

- In carbonate/chalk seawater is a Smart Water

Ions	FW mM	SW mM
Na^+	996	450
K^+	5	10
Ca^{2+}	**29**	**13**
Mg^{2+}	**8**	**45**
SO_4^{2-}	**-**	**24**
Cl^-	1066	525
HCO_3^-	9	2
Ionic ... gth	1.112	0.657
... g/l)	62.8	33.39

«Smart Water» mechanism

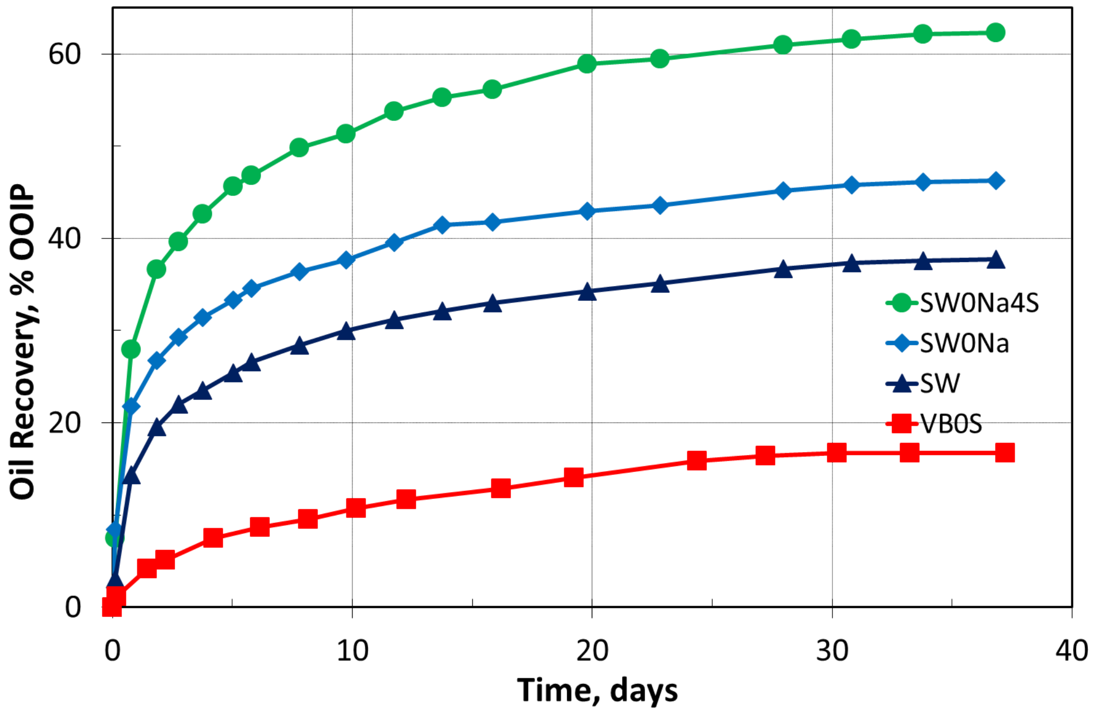


Wettability alteration towards more Water wet

$P_c > 0 \rightarrow$ Imbibition

Increased Microscopic sweep efficiency

SMART WATER EOR IN CHALK



- 4 parallel chalk cores, k = 3-5 mD
  - S_{wi}=10% with VB0S as FW
  - Crude Oil with AN=0.5 mgKOH/g
- Spontaneous imbibition at T = 90 ˚C
  - FW (VB0S) - formation water
  - SW - seawater
  - SW0Na - SW depleted in NaCl
  - SW0Na4S - SW depleted in NaCl spiked with 4 x SO_4^{2-}

Fathi et al, E&F 25 (2011)

- Low SI with FW (VB0S): initial wetting is mixed/slightly water wet
- Higher SI with SW: SW behaves as a «Smart Water» inducing wettability alteration
- Improved SI with SW0Na: Smarter water compared to SW
- Highest SI with SW0Na4S: Most efficient brine for wettability alteration

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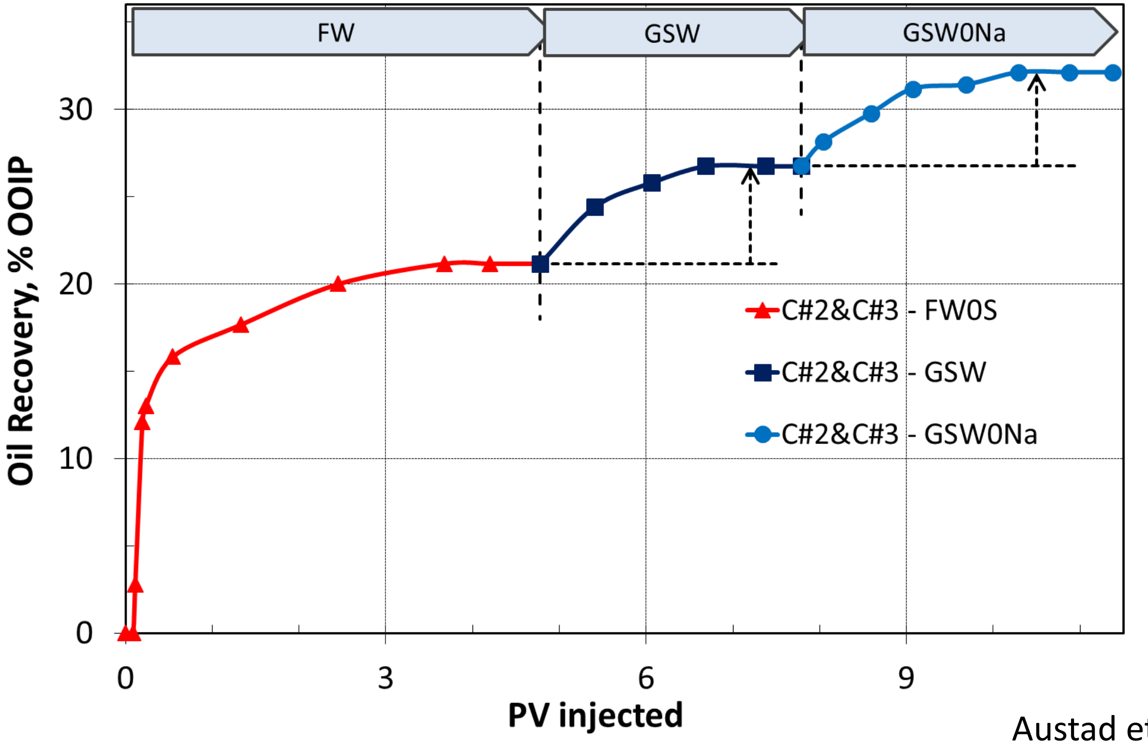
SMART WATER EOR IN RESERVOIR LIMESTONE

Oil recovery by viscous flooding on composite reservoir limestone cores at 100 °C



- 2 Middle East Reservoir limestone cores:
  - Mildly cleaned
  - S_{wi} = 10% with FW
  - Reservoir crude oil.
- Oil recovery test at 100 °C by waterflooding:
  - Composite cores
  - Rate 0.6 PV/D
  - FW (Reservoir formation water without SO_4^{2-})
  - GSW (58 000 ppm Gulf seawater)
  - GSW0Na (Gulf seawater depleted in NaCl)

Austad et al., E&F 29 (2015)

➢ Both Gulf seawater (GSW) and modified Gulf seawater (GSW0Na) behave as «Smart Water»:

- – Significant improved recovery compared to formation water
- – Modified GSW gave 52 % extra oil after FW

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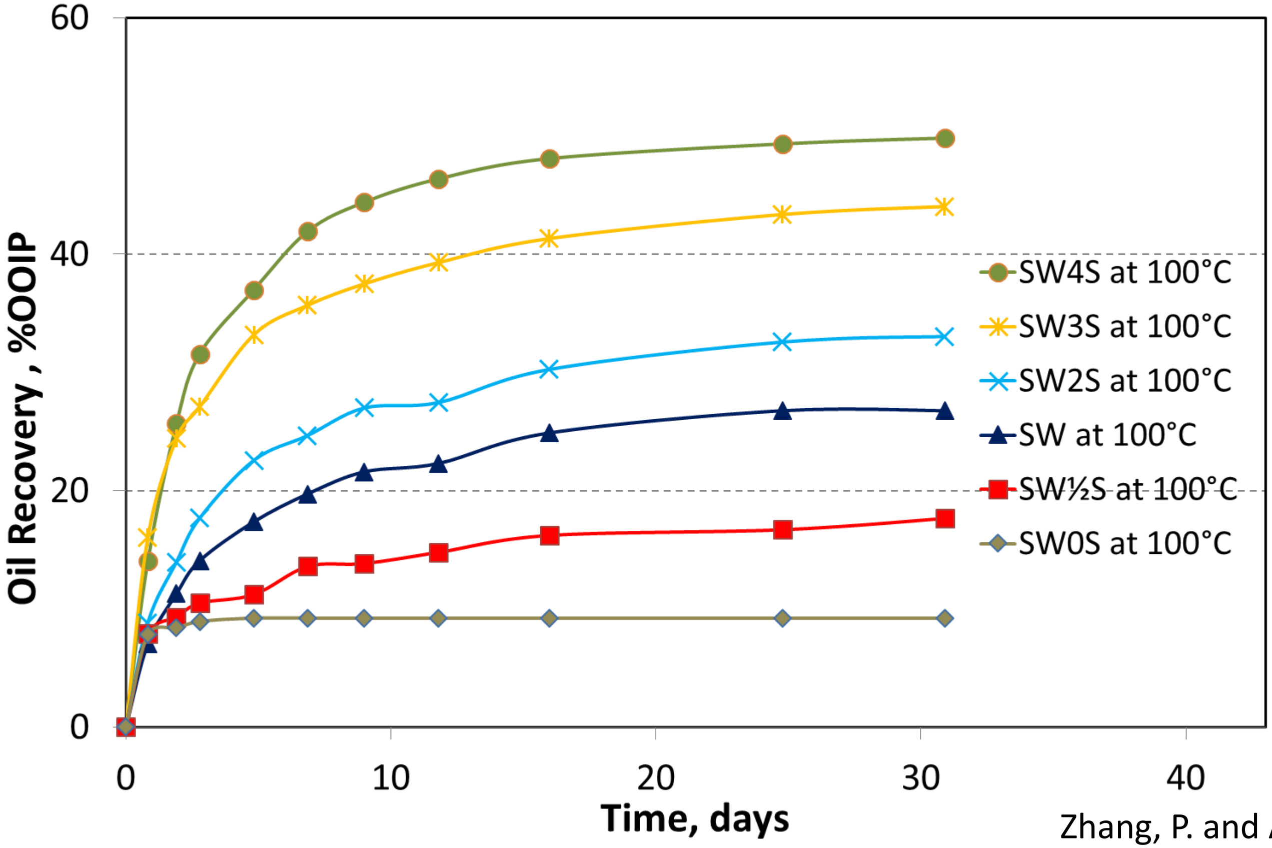
EFFECT OF SULFATE ON SMART WATER



Zhang, P. and Austad, T. (2006)

- 6 outcrop chalk cores
  - S_{wi} = 10 % FW
  - Crude oil and aging
- Oil recovery by spontaneous imbibition 100 °C
  - Modified SW with increasing SO_4^{2-} concentration

- SO_4^{2-} in SW has a dramatic effect on oil recovery
- «Smart Water» EOR effect is catalyzed by SO_4^{2-}

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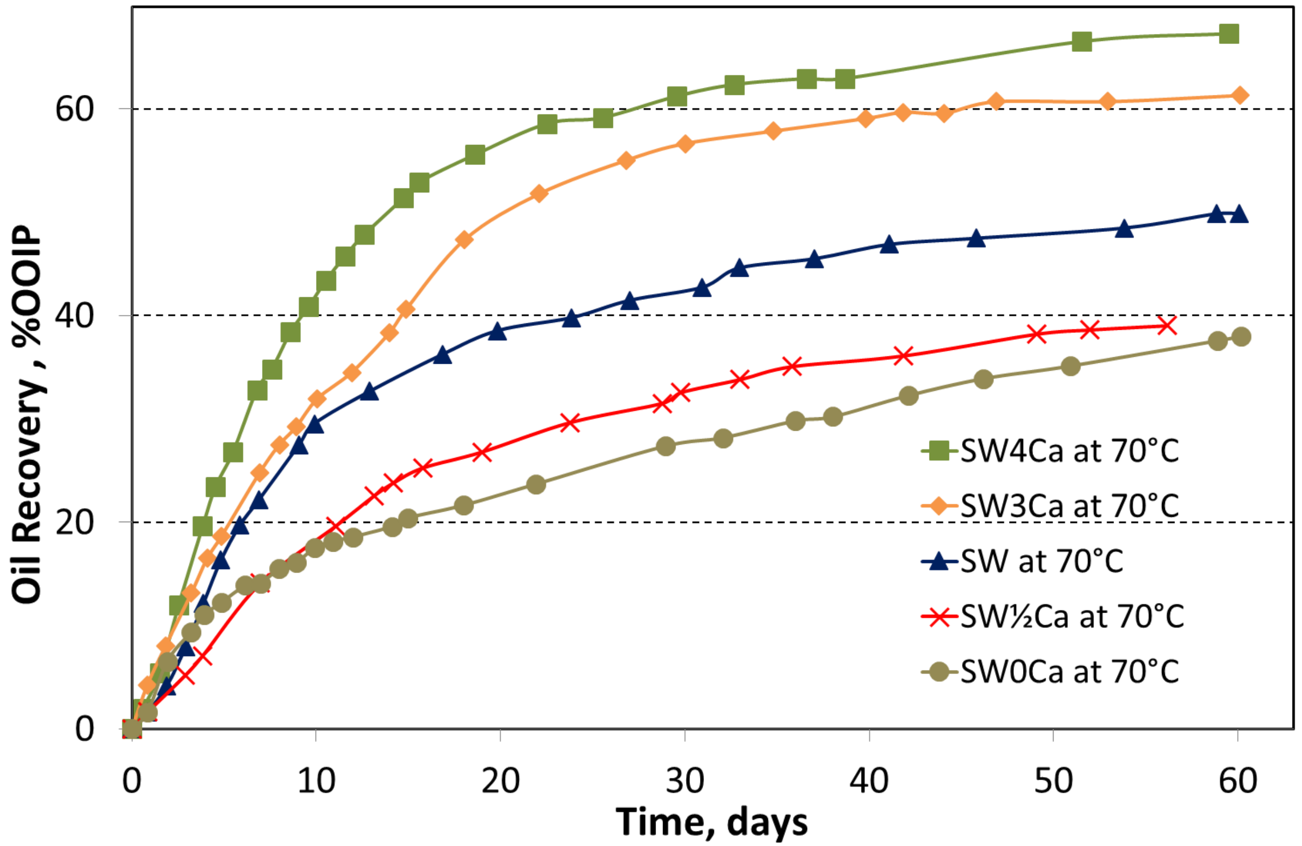
EFFECT OF CALCIUM ON SMART WATER



- 5 equally restored outcrop chalk cores
  - S_{wi} = 0 % FW
  - Crude oil and aging
- Oil recovery by spontaneous imbibition 70 °C
  - Modified SW with increasing Ca^{2+} concentration
    Note that SO_4^{2-} is present in all brines

Zhang, P. and Austad, T. (2006)

➢ Ca^{2+} in SW has a significant effect on oil recovery by spontaneous imbibition

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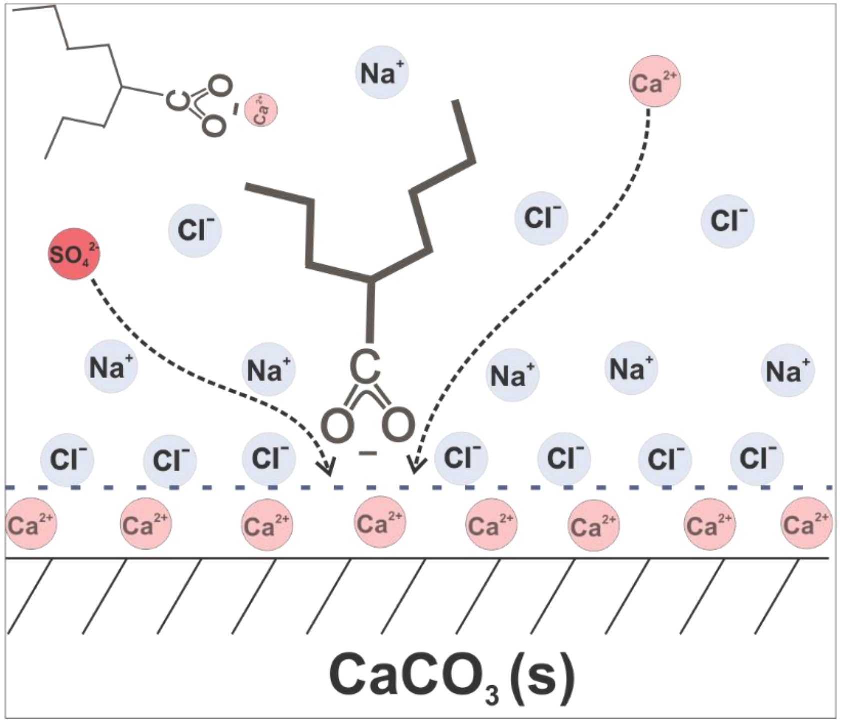
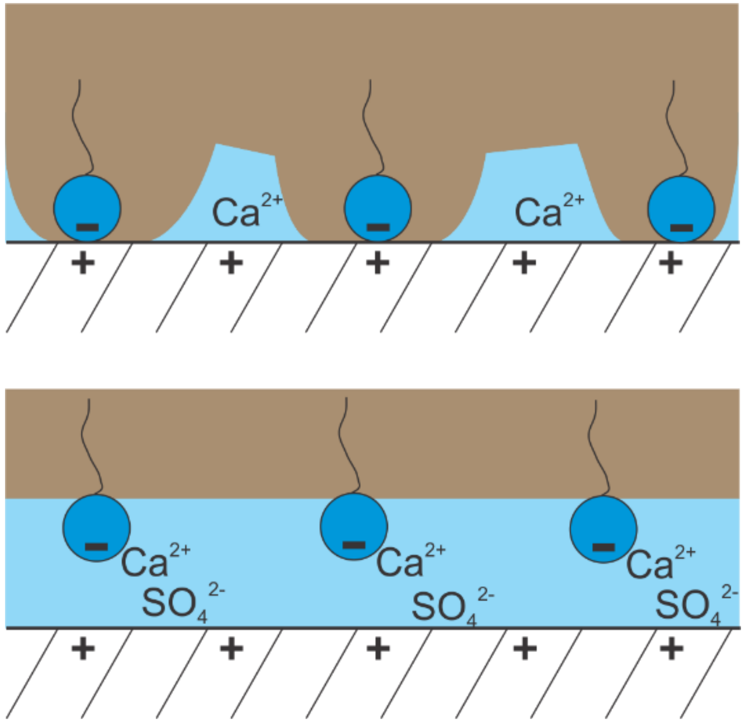
SMART WATER EOR MECHANISM IN CARBONATES

Model proposed by Zhang and Austad, University of Stavanger, 2006:





- Chemical interaction between surface active ions at the rock surface
- Acidic polar organic components (carboxylates) need to be “unsticked”
- Wettability alteration is temperature dependent - more efficient at higher temperatures

➢ Both Ca^{2+} and SO_4^{2-} are needed for wettability alteration

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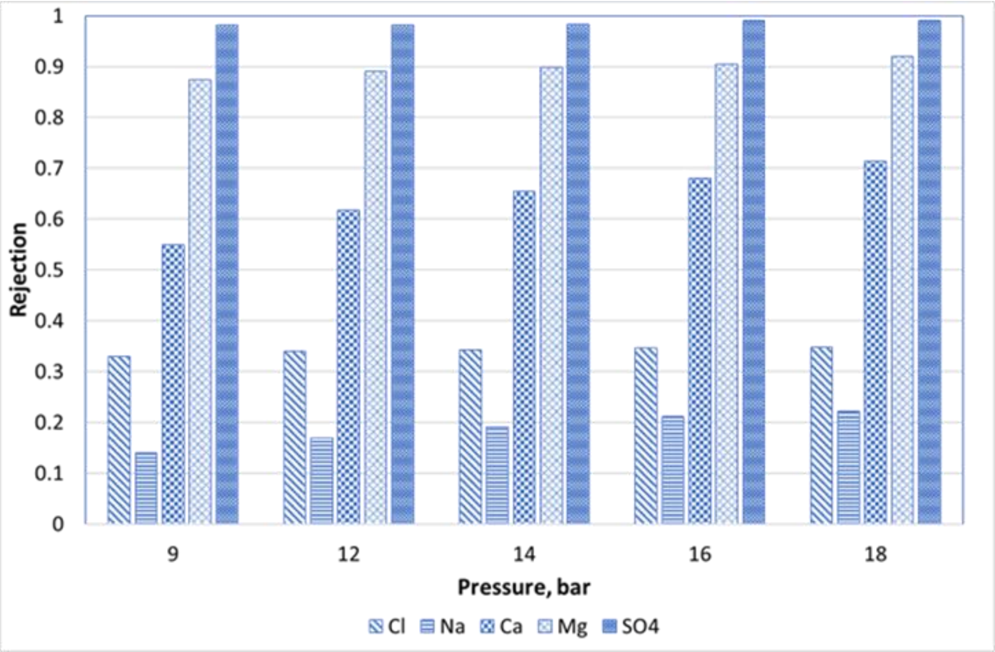
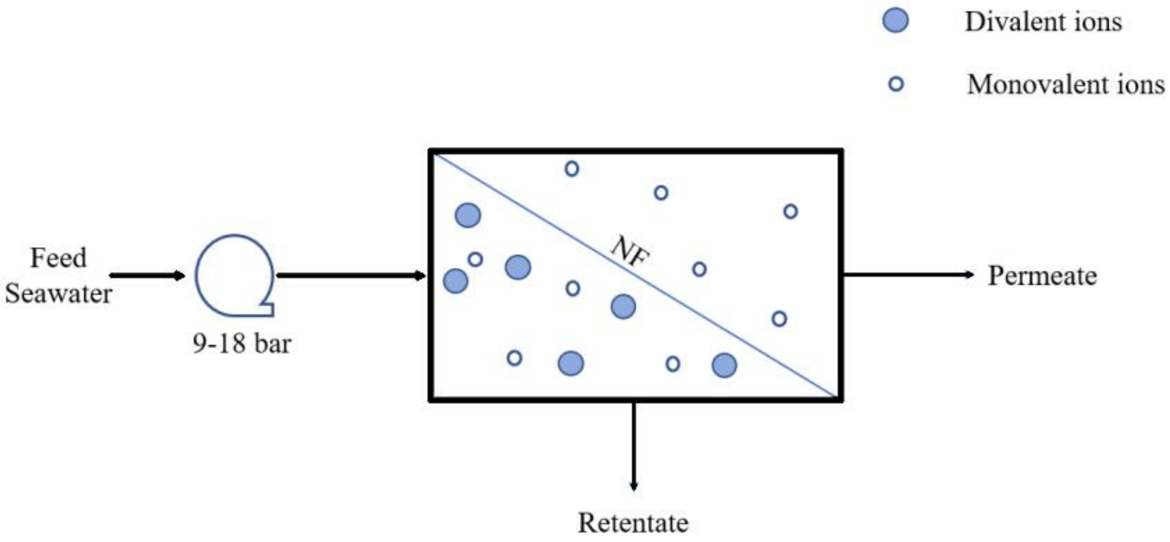
OBJECTIVE OF STUDY

SMART WATER PRODUCTION

Nanofiltration for modified brines:





Nair, PhD-thesis (2019)

- Expensive / Technical challenging
- Retentate/Reject:
  - High salinity
  - High conc. of sulfate
  - Reduced conc. of Mg and Ca
  - Sulphate will precipitate at high temperatures
- Needs for making cheap Smart Water
  - Easily preparable
  - No precipitate at higher temperatures.

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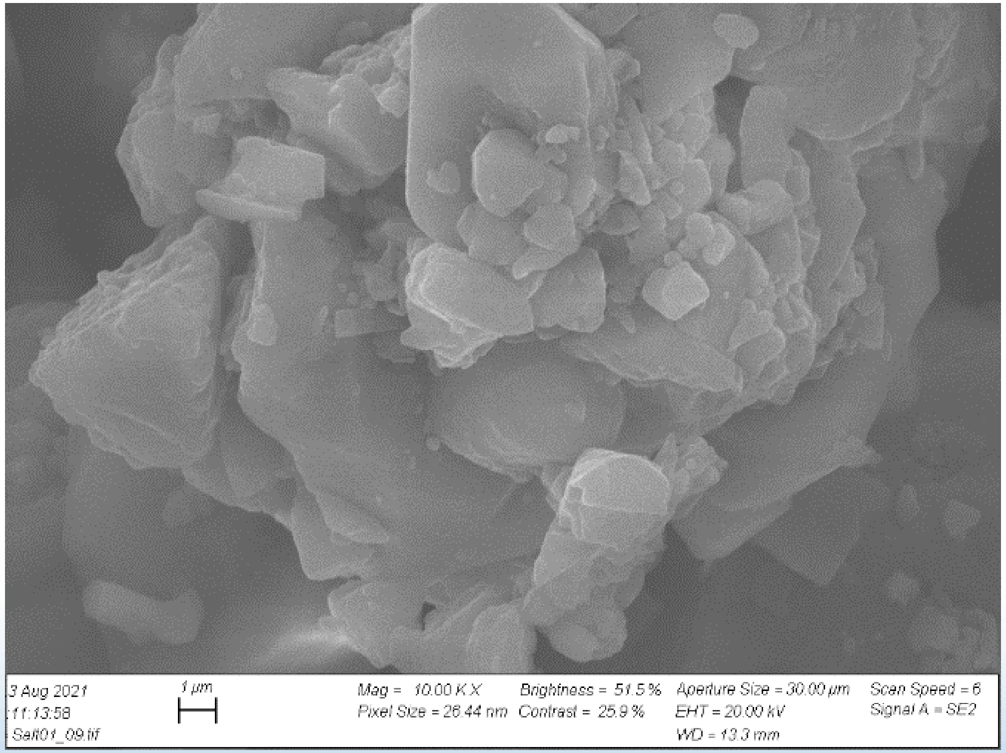
WHAT IS POLYSULFATE?

- Polysulphate/Polyhalite is a naturally occurring salt - $(K_2Ca_2Mg(SO_4)_4 \cdot 2\ H_2O$
- Deposited 260 million years ago during the Permian period
- Can be mined near the North Yorkshire coast, UK
- Dissolves easily in water with low residue
- Provides the essential ions for inducing wettability alteration; SO_4^{2-} and Ca^{2+}



Cations		Anions	
Element	Atomic weight %	Element	Atomic weight %
Sodium	9.3	Sulfur	85.4
Magnesium	21.9	Chloride	14.6
Aluminium	3.2		
Silica	3.3		
Potassium	25.5		
Calcium	36.9		

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Can polysulphate be used as a
water additive for EOR-purposes?

Can polysulphate be used
to make Smart Water with
potential for wettability alteration and
enhanced oil recovery?

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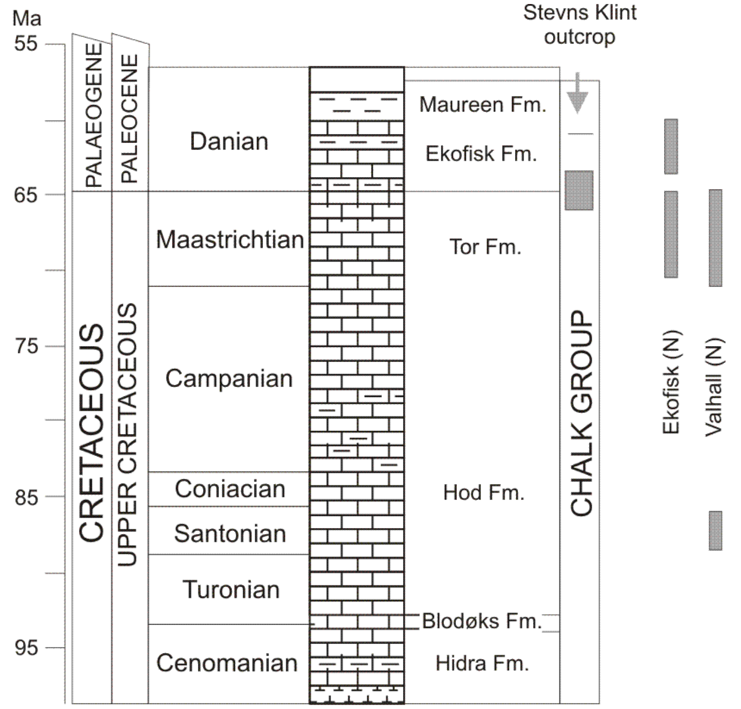
MATERIALS AND METHODS

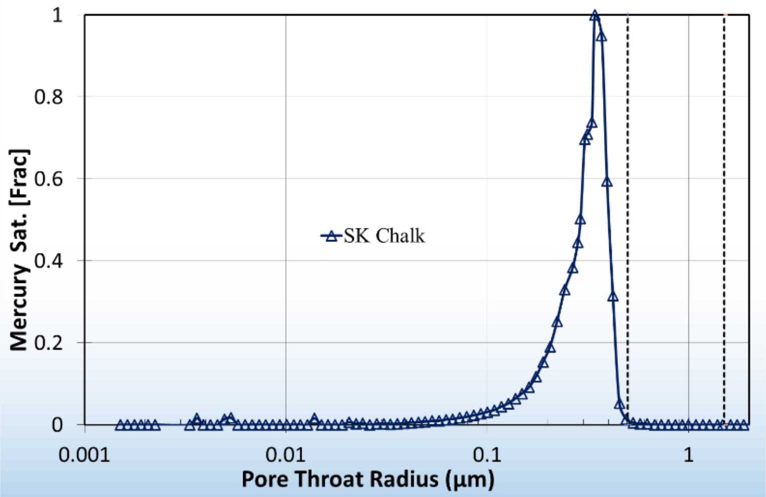
SK CHALK PROPERTIES

Outcrop Stevns Klint chalk cores

Core	SK1	SK2	SK3	SK4	SK5	SK6	SK7	SK8	SK9
Length (cm)	7.1	7.1	7.1	7.2	7.0	6.9	7.1	7.0	7.0
Diameter (cm)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
PV (ml)	38.6	39.1	39.1	40.1	41.3	38.6	37.9	40.0	37.9
Porosity (%)	48.6	48.6	48.8	49.2	49.3	49.2	47.4	50.2	47.2
Permeability (mD)	4.1	4.7	3.8	3.8	4.1	4.7	3.8	3.8	4.0
BET m^2/g	2.0								
Used in experiment	SIFW @90°C	SISW @90°C	SIDW-PS @90°C	SISW-PS @90°C	SIFW @110°C	SISW @110°C	SIDW-PS@110°C	SISW-PS@110°C	CWT @25 & 90 °C



- Stevns Klint (SK) Outcrop chalk
  - Around 65 million years
  - The same chalk deposit as the North Sea chalk reservoirs
  - Analog to both Ekofisk and Valhall chalk reservoirs
  - Heterogeneous pore size distribution



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BRINES

Ions	FW (mM)	SW (mM)	DW-PS (mM)	SW-PS (mM)	DW0T (mM)	DW1T (mM)
Na^+	997.0	450.1	6.3	466.2	6.3	6.3
K^+	5.0	10.1	17.4	28.2	17.4	17.4
Li^+	-	-	-	-	-	24.0
Ca^+	29.0	13.0	15.2	29.6	15.2	15.2
Mg^{2+}	8.0	44.5	5.8	47.9	5.8	5.8
Cl^-	1066.0	525.1	9.2	528.5	9.2	33.2
HCO_3^-	9.0	2.0	-	-	2.0	2.0
SO_4^{2-}	0.0	24.0	31.5	55.9	-	31.5
TDS (g/L)	62.83	33.38	4.9	38.14	6.5	6.1
Density (g/cm^3)	1.04	1.02	1.0	1.02	1.0	1.0
Bulk-pH	7.3	7.8	7.5	8.1	7.8	7.8

- Brines:
  - FW - Formation water
  - SW – Seawater
  - DW – Distilled water
  - Imbibition brines:
    - FW
    - SW
    - SW-PS: 5000 mg/L polysulfate
    - DW-PS: 5000 mg/L polysulfate
- Surface reactivity by chromatography
  - Li^+ / SCN- as non-reactive tracers
  - SO_4^{2-} as surface reactive tracer
- Oil recovery by spontaneous imbibition
  - 90 °C
  - 110 °C

All cores equally restored for same initial wettability:
- 5 PV DW to remove dissolvable salts (Puntervold et al., 2007)
- S_{wi} = 10 % FW by desiccator (Springer et al. 2003)
- 4 PV crude oil, AN ~0.58 mgKOH/g, 0.81 g/cm^3, 2.4 cP
- Aging at 90 °C for 2 weeks

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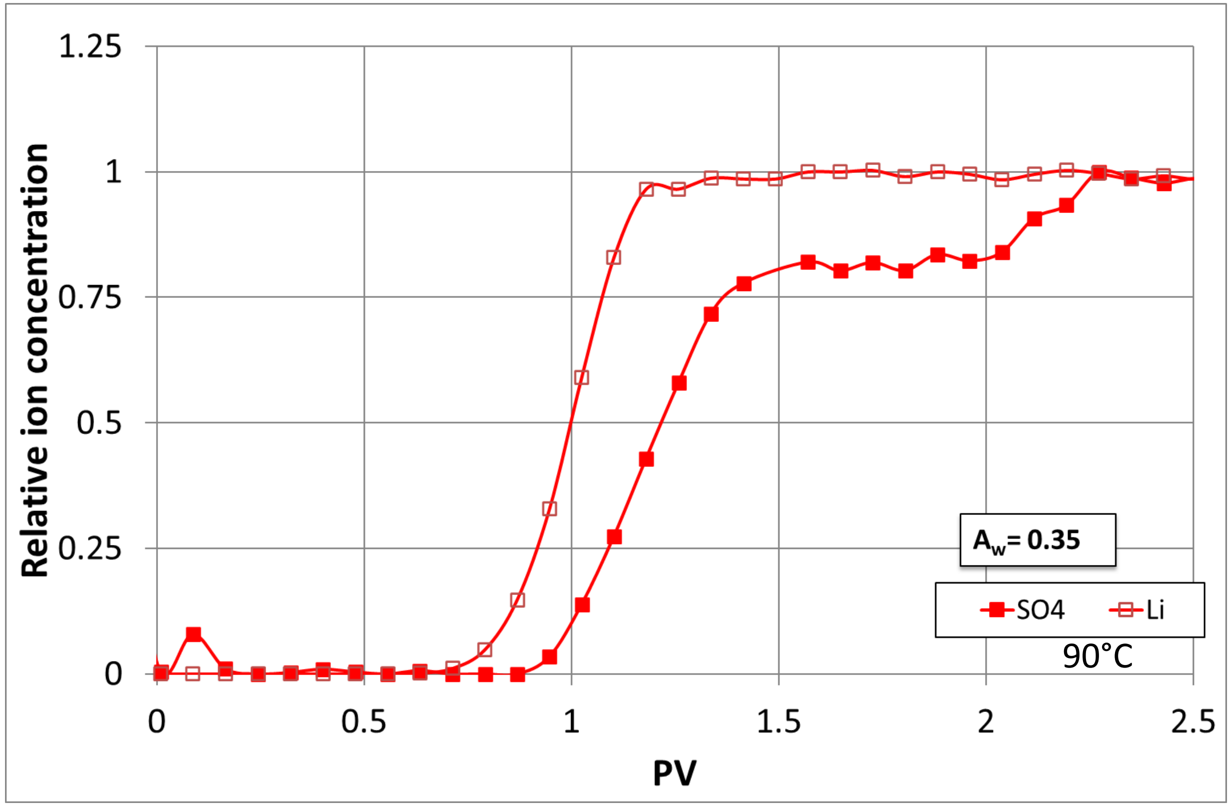
RESULTS

SURFACE REACTIVITY



Ions	DW0T (mM)	DW1T (mM)
Na^+	6.3	6.3
K^+	17.4	17.4
Li^+	-	24.0
Ca^+	15.2	15.2
Mg^{2+}	5.8	5.8
Cl^-	9.2	33.2
HCO_3^-	2.0	2.0
SO_4^{2-}	-	31.5
TDS (g/L)	6.5	6.1
Density (g/cm^3)	1.0	1.0
Bulk-pH	7.8	7.8

- Sulphate from polysulphate salt has affinity toward chalk mineral surfaces
- The affinity increases with an increase in temperature

➢ **Polysulphate reactivity toward chalk surfaces – promising for wettability alteration!**

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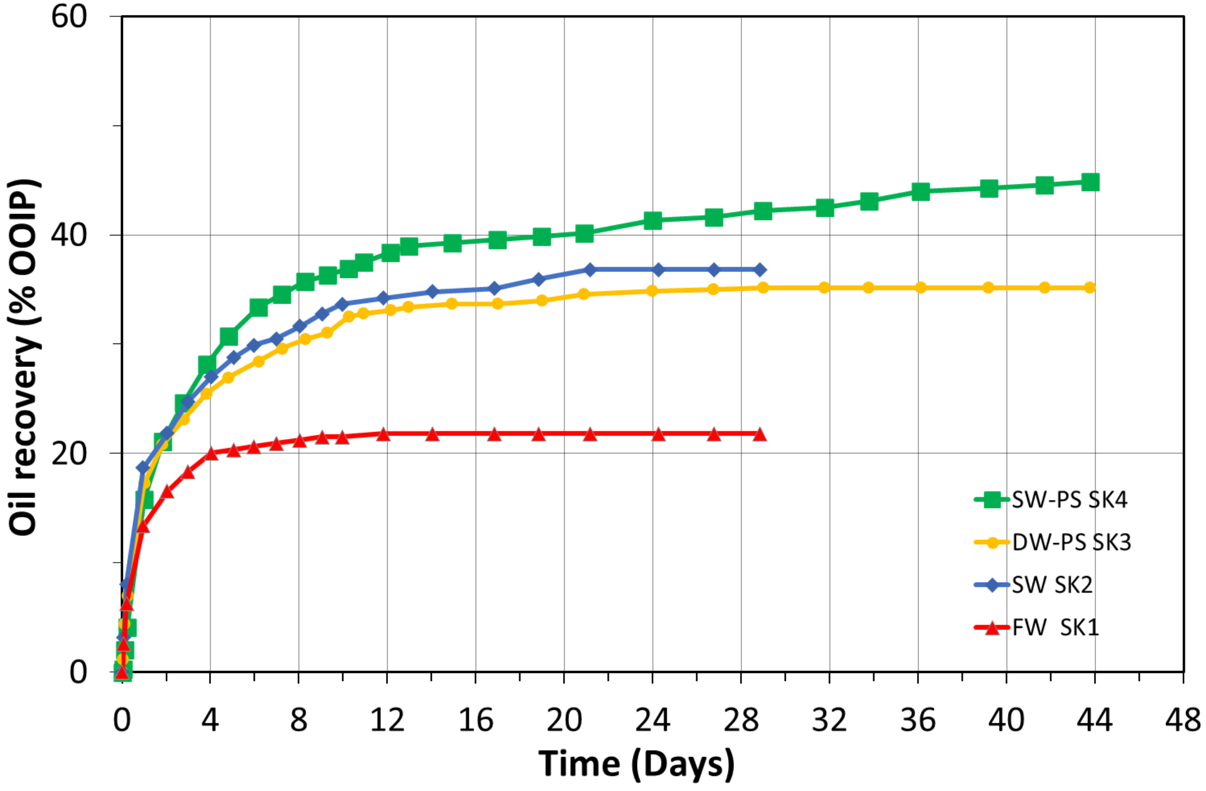
POLYSULFATE BRINES AS SMART WATER AT 90°C



4 equally restored SK chalk cores

- S_{wi}= 10% FW
- Exposed to 4 PV oil (AN = 0.58 mgKOH/g)
  - 2 week aging at 90°C

- Spontaneous imbibition at 90 °C
  - FW
  - SW
  - DW-PS
  - SW-PS

Ions	FW (mM)	SW (mM)	DW-PS (mM)	SW-PS (mM)
Ca^{+}	29.0	13.0	15.2	29.6
Mg^{2+}	8.0	44.5	5.8	47.9
SO_4^{2-}	0.0	24.0	31.5	55.9

- ➢ FW does not disturb chemical equilibrium
  - ➢ Baseline recovery without wettability alteration
- ➢ Polysulfate added to the imbibition brine leads to increased oil mobilization
  - SW-PS > SW ≈ DW-PS

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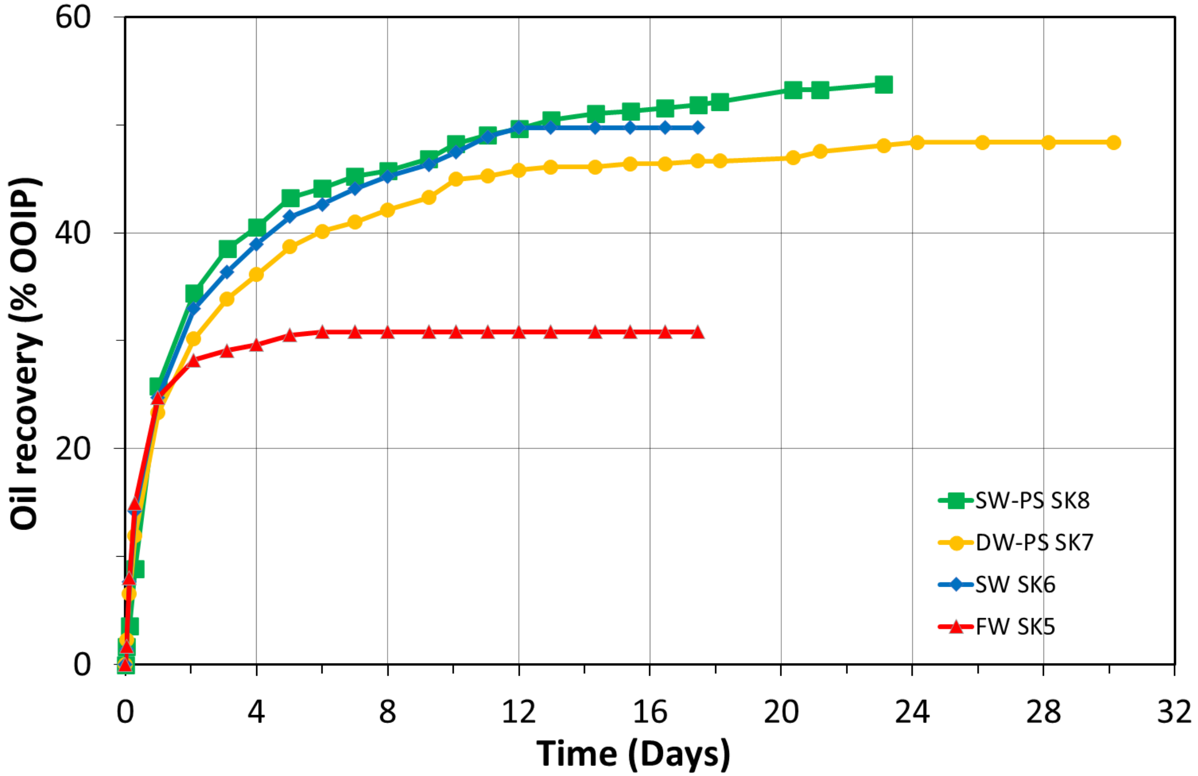
EFFECT OF POLYSULFATE AT 110°C



- 4 similarly prepared chalk cores
- S_{wi}= 10% with FW
- Exposed to 4 PV oil (AN = 0.58 mgKOH/g)
- Aged 2 weeks at 90°C

- Spontaneous imbibition at 110 °C
  - FW
  - SW
  - DW-PS
  - SW-PS

Ions	FW (mM)	SW (mM)	DW-PS (mM)	SW-PS (mM)
Ca^{+}	29.0	13.0	15.2	29.6
Mg^{2+}	8.0	44.5	5.8	47.9
SO_4^{2-}	0.0	24.0	31.5	55.9

- ➢ FW does not alter wettability
- ➢ Sulphate in the imbibition brine leads to wettability alteration!
  - SW-PS ≈ SW > DW-PS

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SUMMARY

Imbibition fluid	OOIP % T = 90°C	Δ OOIP % related to FW T = 90°C	OOIP % T = 110°C	Δ OOIP % related to FW T = 110°C
FW	22	-	31	-
SW	37	15	50	19
DW-PS	35	13	48	17
SW-PS	45	23	54	23

- Sulphate dissolved from polysulphate can react with the chalk minerals aiding wettability alteration.
- Increased oil mobilization was observed with brines containing sulphate.
- SW-PS was the most effective brine, thus effectiveness of SW can be further increased by adding PS.
- DW-PS was able to alter wettability similar to SW.

Onshore, where seawater is not readily available:
Smart Water can be prepared by mixing polysulphate with surface water

In areas where produced water is required re-injected:
Polysulphate can be added to produced water and become Smart Water

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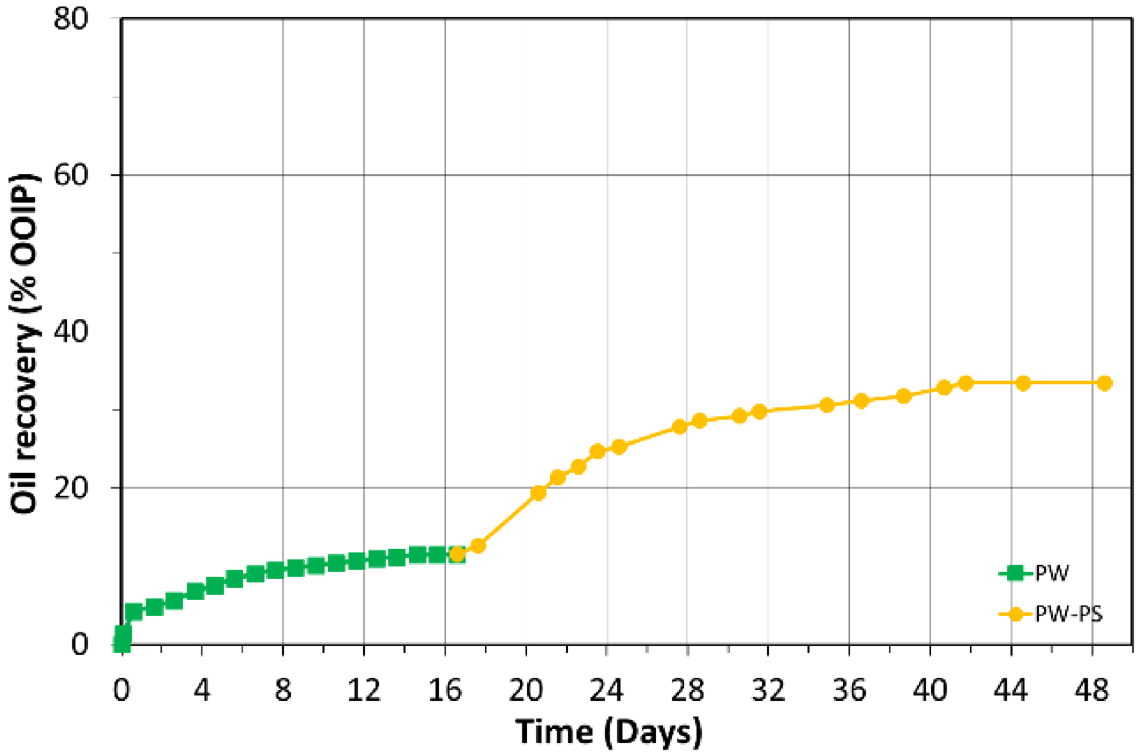
Polysulphate as an additive to produced water for re-injection?



- Produced water is not a Smart Water in Chalk or Limestone

➢ ~20 %OOIP extra oil produced by adding polysulphate to produced water!

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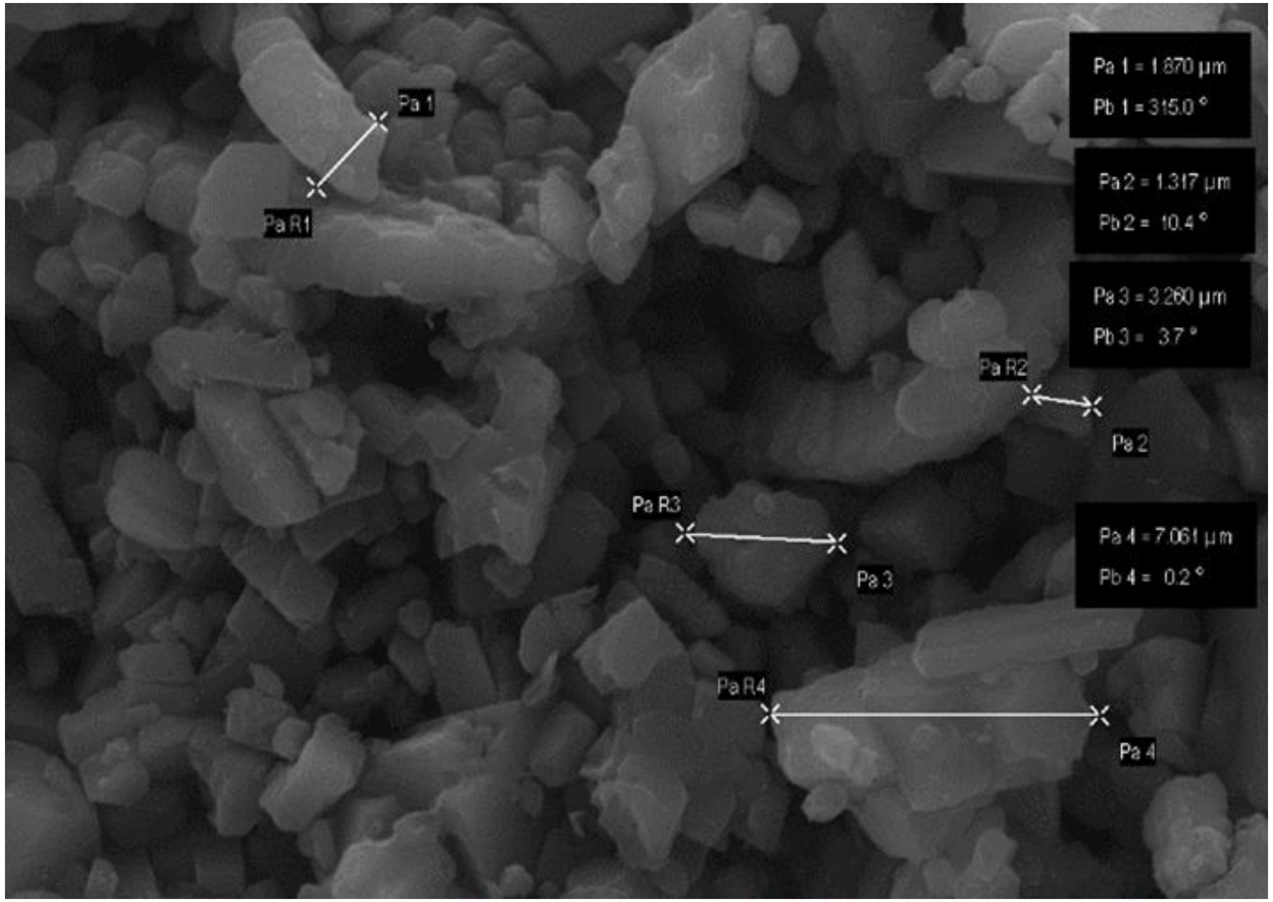
The University of Stavanger
and ICL Group LTD
for financial support
and permission
to publish the work



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