«Smart Water» EOR in carbonate and sandstone reservoirs, new reservoir screening techniques to evaluate increased oil recovery potential

Joining forces 2016
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«Smart water» EOR in Carbonate

- Spontaneous imbibition in Chalk: $K = 3-5$ mD; $S_{wi}=10\%$, Crude oil $AN=0.5$, $T_{res}=90$ °C;

- Formation water: VB
- Seawater: SW
- Seawater depleted in NaCl
- Seawater depleted in NaCl and spiked with 4x sulfate
«Smart water» EOR, Reservoir Limestone

- Oil recovery by forced displacement at 100°C
  - Composite limestone reservoir core.
    - $\text{Swi} = 10\%$. Reservoir Crude Oil.
  - Brine injection:
    - FW0S - GSW - SW0Na
    - Injection rate: $\approx 0.6 \text{ PV/D (0.01 ml/min)}$

![Graph showing oil recovery vs. PV injected]
«Smart water» EOR in Sandstone

- Outcrop cores
  - Swi = 20%
  - Crude Oil with high BN
- Viscous flooding@40°C:
  HS - LS

<table>
<thead>
<tr>
<th>Ions</th>
<th>HS mM</th>
<th>LS1 - NaCl mM</th>
<th>LS2 - CaCl2 mM</th>
<th>LS3 - KCl mM</th>
<th>LS4 - MgCl2 mM</th>
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<tbody>
<tr>
<td>Na+</td>
<td>1540.0</td>
<td>17.1</td>
<td>3.1</td>
<td>0.0</td>
<td>3.1</td>
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<tr>
<td>K+</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>17.2</td>
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<tr>
<td>Ca²⁺</td>
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<td>0.0</td>
<td>4.7</td>
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<tr>
<td>Mg²⁺</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>4.7</td>
</tr>
<tr>
<td>TDS, g/l</td>
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<td>1</td>
<td>0.7</td>
<td>1.28</td>
<td>0.63</td>
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<tr>
<td>IS</td>
<td>1.810</td>
<td>0.017</td>
<td>0.017</td>
<td>0.017</td>
<td>0.017</td>
</tr>
</tbody>
</table>

- Tertiary LS EOR effects observed for all LS Brines
- Increased pH for all LS brines
What is «Smart Water»?

• «Smart water» improves wetting properties in 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 \( k_{rw} = f(S_w) \)
How does «Smart Water» work?

- Minor changes in O/W IFT
- Same pore distribution, \( r = k \)
- Unfavorable sweep with LS
  - LS viscosity lower than HS
  - Still increased recovery
- Increased Microscopic Sweep

\[
P_c = \frac{2 \sigma \cos \theta}{r}
\]

Wettability alteration towards more Water wet

\( P_c > 0 \rightarrow \) Imbibition

Increased Microscopic sweep efficiency
Reservoir Chemistry

- Chemical reactivity are temperature dependant. Reservoir Chemistry controlled by:

**Crude oil**
- Polar organic acids
- Polar organic bases

**Brine**
- Formation Water salinity and Ion composition
- Injection Water salinity and Ion composition

**Rock**
- Mineral surface reactions
- Carbonate
- Sandstone

- Reservoir Chemistry effects:
  - Initial Reservoir wettability
  - Wettability alterations by "Smart Water"
  - Scaling
Crude Oil chemistry

- Crude oil consists of thousands of different components:
  - Liquid fraction
  - Resins
  - Asphaltenes

  \[
  \text{Contain polar organic molecules}
  \]

  - Polar Organic Bases:
    \[
    R_3NH^+ \leftrightarrow H^+ + R_3N \quad \text{pKa} \sim 4.5-5
    \]

  - Polar organic Acids:
    \[
    RCOOH \leftrightarrow H^+ + RCOO^- \quad \text{pKa} \sim 4.5-5
    \]

- Surface reactivity of Polar organic Acids and Bases are pH dependant
- Polar organic Acids and bases interacts with charged rock surfaces
- serve as anchor molecules for the Oil phase towards Rock surface
Brine chemistry

- Injection water disturbs the chemical equilibrium in the reservoir

Chemical interactions at Ekofisk, 130°C, During SW injection:

- PW contained 73.6 vol% SW and 26.4 vol% FW (based on Na Cl mass balance)

-- Mg$^{2+}$ substitutes Ca$^{2+}$
-- SO$_4^{2-}$ adsorbs (and precipitates CaSO$_4$ (S))

- Field observations = Laboratory observations
Rock chemistry

- Carbonates:
  - positive surface charge
- Sandstones:
  - negative surface charge
  - Different ions and chemistry involved
    - Initial wetting
    - Wettability alteration

Different «Smart Water» EOR chemistry in Sandstone and Carbonate reservoirs!
Systematically worked with the chemical understanding of «Smart Water» EOR effects:
- Sandstone reservoirs
- Carbonate reservoirs

Outcrop core systems:
- systems for Sandstone
- Systems for Carbonate
- Contributed Fundamental understanding of
  - Crude Oil effects
  - Mineral effects
  - FW effects
  - Wettability alteration effects by «Smart Water»
«Smart Water» EOR industry projects

- Reservoir systems screened for EOR effects:
  - More than 30 Carbonate reservoirs/formations
  - More than 10 Sandstone reservoirs/formations

Special thanks to:
- BP, UK
- Total, France & Total, Norway
  - Talisman, Norway
  - Talisman Synoptics, UK
  - Lundin, Norway
- Saudi Aramco, Saudi Arabia
  - Petoro, Norway
- TaQa, UK
- Maersk, Qatar
- Shell, Netherlands
- Wintershall Holding GmbH, Germany
- Wintershall Noordzee B.V. Northsee, Netherlands
  - DNO, UAE
- JSC "Zarubezhneft, Russia
«Smart water» EOR in Carbonate

- Chemical wettability alteration Mechanism

- Wettability alteration mechanism in Carbonates
  - Acidic components strongly attached to surface
  - Need to be chemically reacted away
    - Wettability alteration catalysed by $\text{SO}_4^{2-}$
    - $\text{Ca}^{2+}$ interacts with the R-COO$^-$ and releases it from surface
      - R-COO$^-$ --- Ca$^{2+}$ bonding ~10 times stronger than
      - R-COO$^-$ - - Mg$^{2+}$
  - Reactivity increases with reduced salinity
«Smart water» EOR in Sandstone - Chemical wettability alteration Mechanism

- Wettability alteration Mechanism in Sandstone
  - Clays are the main wetting mineral in Sandstone
  - Wettability alteration linked to pH increase, FW vs. «Smart water»

Model for Basic polar organic material:

- Desorption of Cations by low salinity water (Rate determining step)
  \[ \text{Clay-} \text{Ca}^{2+} + \text{H}_2\text{O} = \text{Clay-H}^+ + \text{Ca}^{2+} + \text{OH}^- + \text{HEAT} \]
- Wettability alteration induced by pH increase, Basic material
  \[ \text{Clay-R}_3\text{NH}^+ + \text{OH}^- = \text{Clay} + \text{R}_3\text{N} + \text{H}_2\text{O} \]

«Smart Water» EOR potential
- Reservoir screening procedure

- 3 stage «Smart water» EOR Screening of Reservoirs:
  1. Desk evaluation on available reservoir data
     - Reservoir history
     - FW salinity and composition
     - Rock properties, Mineralogy
     - Pore distribution/heterogenity
     - Crude Oil properties
     - Reservoir temperature
     - Evaluating if the reservoir are a «Smart Water» Candidate
  2. Experimental Screening with reservoir cores and FW + inj. Brines
     - Surface reactivity tests on reservoir rock/core
       - Chemically induced Brine – Rock interactions
       - Possible Wettability effects
     - Evaluating potential for wettability alteration by «Smart Water»
  3. Oil Recovery tests on preserved reservoir cores
     - Compare recoveries with Smart Water and other brines
       - Spontaneous imbibition
       - Viscous flooding
       - Secondary /Tertiary mode
     - Conclude/evaluate «Smart Water» EOR Potential
Ongoing/planned Research activities:
- «Smart Water» EOR Group

- «Smart Water» EOR activities:
  - Type of Reservoirs
    - Dolomitic reservoirs
    - Limestone/Chalk reservoirs
    - Sandstone Reservoirs
    - Shale Oil Reservoirs
  - Reservoir heterogeneity
    - Pore distribution / tracer tests on cores
  - Minerals
    - Chemical reactivity of minerals
    - QuemScan project together with Drilling and GeoScience group at UiS
      - Type of minerals and distribution at pore surfaces
  - Crude Oil properties
    - Polar components/Asphaltenes
    - Crude Oil/brine IFT at reservoir conditions
  - Reservoir wettability
    - Crude Oil species with high surface affinity
    - Chemical Reactivity / Surface Charge of reservoir minerals
    - FW ion composition and salinity
    - Temperature effects
Ongoing/planned Research activities:
- «Smart Water» EOR Group

- Core cleaning / core restoration procedures
  - Cleaning solvents / fluids
  - Crude Oil sat. /readsoption of polar components
- «Smart Water» EOR
  - Reactivity of pore wall Minerals
  - Wettability and wettability alteration mechanisms
  - Optimizing Smart Water EOR Brine compositions
  - Design of new «Smart Water» EOR fluids
- PennState University Collaboration (Group of Prof. Russel Johns)
  - Modelling of Chemical Wettability alteration processes

- Combined techniques with «Smart Water»:
  - EOR chemicals will influence Reservoir Chemistry:
    - Polymers
    - Nano-particles
    - Surfactants
    - New

- We are open for Industry Knowledge building projects:
  - Reservoir Evaluation of «Smart Water» EOR potential
  - in combination with Fundamental «Smart Water» EOR studies