Enhanced Oil Recovery by CO_2 Injection in Fractured Reservoirs

Emphasis on Wettability and Water Saturation

Marianne Steinsbø

Dissertation for the degree of philosophiae doctor (PhD)
at the University of Bergen

2016

Dissertation date: March 4th

Table of Contents

Summary

The work presented in this Thesis is part of ongoing research on Enhanced Oil Recovery (EOR) in fractured reservoirs within the reservoir physics research group at the Department of Physics and Technology, University of Bergen. This research group has previously identified chemical EOR to alter wettability, miscible gas injection and mobility control by foam and polymers to be the most promising methods for applications on the Norwegian Continental Shelf.

In this Thesis a series of laboratory scale injection tests have thus been performed to mimic oil recovery in fractured carbonate reservoirs to understand fluid flow dynamics when applying the above mentioned EOR techniques. The objective is to improve the understanding of the governing displacement processes in order to contribute to increased oil recovery. Wettability controls the fluid distribution on pore scale level in porous rock material and is emphasized throughout this Thesis.

The first objective of the experimental work was to establish stable wetting preferences uniformly distributed in core samples cut from strongly water-wet outcrop rock material. In a reservoir a wettability change towards less water-wet preference occurs over geologic time when hydrocarbon components adsorb on the rock surface. A dynamic aging technique, designed to establishing uniform wetting preferences by continuously flowing crude oil through core samples, was used to establish wetting states being typical for partly waterflooded areas in North Sea chalk fields. **Paper 1** reports the results from systematic investigation of wetting stability in aged Rørdal chalk, an analogue to the Ekofisk field. The effect of initial water saturation and aging time was studied and a systematic decrease in endpoint water saturation for spontaneous imbibition was observed with i) a decreasing water saturation during aging and ii) increasing aging time. Repeated cycles of spontaneous imbibition tests, forced waterfloods and drainage were performed in the same core sample to measure the stability of the Amott-Harvey water index, I_w. Typical reservoir conditions for a large transition zone, residual oil zones or partly waterflooded areas were also investigated by varying the initial water saturation before the spontaneous imbibition test. The established I_w (ranging from 0.39 to 0.80), was stable during several flooding cycles.

The aging technique presented in **Paper 1** established a range of stable wetting states on the water-wet side in outcrop analogues of North Sea chalk. Weakly water-wet samples have less potential for spontaneous imbibition of water. EOR can therefore

be achieved by adding chemicals to the injection brine through wettability enhancement: if the matrix becomes more water-wet more water will spontaneously imbibe and more oil will be produced. Previous laboratory studies have shown that injection strategies using seawater as the injection fluid can benefit from potential determining ions. Experiments by sulfate enriched waterfloods with mineral oil as oil phase demonstrated increased oil recovery up to 35 % in Stevns chalk, while no EOR-effect was observed in Rørdal chalk. **Paper 2** presents the wettability altering effects during sulfate enriched waterfloods in aged Rørdal and Stevns chalk core samples saturated with crude oil. The average additional recovery with the presence of sulfate was found to be 43 %OOIP for Stevns chalk and 12 %OOIP for Rørdal chalk. These experiments showed that sulfate increased the potential for spontaneous imbibition during waterfloods and that the effect varied with the oil composition, the chalk mineralogy, reservoir temperature and with solvent properties.

Several of the North Sea oil fields have been waterflooded for decades and in general this has been a great success. However, there is still a great potential for enhanced oil recovery which call for a new generation of EOR techniques. Miscible CO_2 injection for enhanced oil recovery (CO_2-EOR) in mature oil fields has the potential to safely store CO_2 and reduce atmospheric emissions, while at the same time significantly enhance oil production to meet the increasing energy demand. The main part of the work, presented in **Paper 3-6**, reports on CO_2-EOR injection tests in fractured core samples at varying experimental conditions using different injection strategies.

Experimental results obtained in this Thesis exhibited in general that CO_2-EOR in fractured systems was characterized by: 1) a rapid breakthrough of CO_2 where most of the oil was produced after CO_2-breakthrough, 2) a low oil production rate from the onset of CO_2 injection, 3) a long tail production and 4) no apparent differential pressure across the core length, which indicated diffusion dominated recovery process. Secondary CO_2 injections, with no preceding waterflood, was generally very efficient in terms of oil recovery, up to 96 %OOIP was observed recovered. Reduced oil recovery efficiency was observed when CO_2-onset started at higher initial water saturation and after waterfloods i.e. as a tertiary recovery method, likely due to water shielding. Higher initial water saturation may reduce or prevent contact and mixing between the injected gas and matrix oil. In moderately water-wet systems the water shielding effect was less prominent. The effect of wettability in CO_2-EOR recovery strategies is discussed in **Paper 3** and **Paper 6**. **Paper 3** presents results from injection tests in core samples saturated with a pure mineral oil (n-Decane) and crude oil (hydrocarbon composition: 97 % C_{7+}, 28 % C_{30+}). Oil recovery was lower and slower in fractured core samples saturated with crude oil compared to a pure mineral oil (n-Decane), likely due to the development of multi-contact miscibility and a less favorable mobility ratio. The influence of fracture permeability and matrix size (diffusion length) in cylindrical core plugs and larger rectangular blocks are investigated in **Paper 4**. An increasing diffusion length i.e. the distance from the CO_2-filled fracture to the end of porous system resulted in decreased oil recovery efficiency. By reducing the fracture permeability the oil recovery efficiency was improved.

Viscous fingering, gravity override and flow in high permeability fractures or thief zones will reduce the volumetric sweep and lead to early gas breakthrough in the producer and a low oil recovery rate per unit of injected CO_2. CO_2 is typically in its liquid or supercritical state at reservoir conditions with a liquid-like density and gas-like viscosity. Apparent viscosity will be reduced in CO_2-foam, therefore generation of foam will give CO_2 a more favorable mobility ratio relative to oil and water, divert flow to increase sweep and add a viscous component to the oil displacement process. **Paper 5** presents a sequential CO_2 injection strategy: when pure CO_2 injection efficiency decreases, co-injection of CO_2 and surfactant starts. The strategy of switching to foam during pure CO_2 injection accelerated the oil production and increased the end point oil recovery and was observed to most effective in heterogeneous rock material.

Paper 6 presents a conceptual numerical model where foam is simulated by reducing the fracture conductivity. A history match with experimental data obtained during secondary CO_2 and CO_2-foam injections tests in oil and brine saturated cylindrical core plugs was used to validate the model. Foam significantly increased the experimentally measured oil recovery rate compared to pure CO_2 injection by adding a viscous component to the oil recovery process. The increased pressure gradients measured experimentally was a result of the decreased CO_2 mobility by increasing the apparent CO_2 viscosity with foam. The CO_2-foam injection tests all showed an accelerated oil recovery rate compared to pure CO_2 injections, with increased differential pressure across the core due to flow diversion. The numerical model showed a decreasing contribution from diffusion on oil recovery as the matrix size/diffusion length increased.

The main conclusions in this Thesis are:

- A dynamic aging technique using crude oil established a range of uniform, stable wetting preferences in originally strongly water-wet outcrop chalk samples.
- Experimental studies showed that sulfate enriched waterfloods may be an attractive EOR-method to improve the water-wetting state of the rock surface.
- Laboratory evaluations of miscible CO_2 injections for EOR in fractured systems demonstrated a very efficient displacement process in terms of final oil recovery, up to 96 %OOIP was recovered.
- Increased water saturation decreased oil recovery efficiency during CO_2 injections, particularly after efficient preceding waterfloods in strongly water-wet fractured systems.
- Foam as EOR-mobility control in fractured systems improved conformance control and reduced CO_2 channeling in high permeable fractures.

Acknowledgements

I would like to thank my supervisors Professor Arne Graue, Associate Professor Geir Ersland and Associate Professor Martin Fernø. It has been a privilege to work with you and I am very grateful for your excellent guidance!

A very special thank you to Dr. Bergit Brattekås. You are a true inspiration every day in every way!

Thank you Dr. Else B. Johannesen!

Thank you to everyone working at IFT, especially the mechanical workshop and Inez Luiza Buzdugan.

Thank you to all my fellow students and friends at the Reservoir Physics group.

I would like to thank the Norwegian Research Council for financial support.

Finally I would thank my kids Leon and Benjamin and my parents Ingebjørg and Tore!

Marianne Steinsbø

Marianne Steinsbø

List of scientific papers

1. **Steinsbø, M.**, Graue, A., Fernø, M.A., 2014. A systematic investigation of wetting stability in aged chalk. SCA 2014-37. International Symposium of the Society of Core Analysts, Avignon, France.
2. **Steinsbø, M.,** Graue, A., Fernø, M.A., 2015. EOR by sulfate enriched waterfloods in aged outcrop chalk samples. In preparation for being submitted to Journal of Petroleum Science and Engineering.
3. **Steinsbø, M.**, Brattekås, B., Ersland, G., Fernø, M.A., Graue. A., 2014. Supercritical CO_2 injection for enhanced oil recovery in fractured chalk. SCA2014-092. International Symposium of the Society of Core Analysts, Avignon, France.
4. **Steinsbø, M.**, Brattekås, B., Ersland, G., Bø, K., Oppdal, I., Tunli, R., Graue, A., Fernø, M.A., 2015. Foam as Mobility Control for Integrated CO_2-EOR in Fractured Carbonates. IOR 2015 – 18th European Symposium on Improved Oil Recovery, Dresden, Germany.
5. Fernø, M.A., **Steinsbø, M.**, Eide, Ø., Ahmed, A., Ahmed, K., Graue, A., 2015. Parametric study of oil recovery during CO_2 injections in fractured chalk: Influence of fracture permeability, diffusion length and water saturation. Journal of Natural Gas Science & Engineering, doi: 10.1016/j.jngse.2015.09.052.
6. Fernø, M.A., Eide, Ø., **Steinsbø, M.**, Langlo, S.A.W., Christophersen, A., Skibenes, A., Ydstebø, T., Graue, A., 2015. Mobility control during CO_2 EOR in fractured carbonates using foam: Laboratory evaluation and numerical simulations. Journal of petroleum Science and engineering, 135, 442–451.

Additional papers

A. Fernø, M.A., Gauteplass, J., Hauge, L.P., Ersland, G. Abell, G.E., Adamsen, T.C.H., **Steinsbø, M.**, Brattekås, B., Graue, A., 2015. Combined PET-CT for Visualization and Quantification of Fluid Flow in Porous Rock Samples. MedViz Conference, Bergen, Norway.

B. Johannesen, E.B., **Steinsbø, M.,** Howard, J., Graue, A., 2006. Wettability Characterization by NMR T_2 measurements in chalk. SCA2006-39. International Symposium of the Society of Core Analysts, Trondheim, Norway.

Part I
Fluid Flow in Fractured Reservoirs

1 Fractured Reservoirs and Recovery Mechanisms

The recovery mechanisms in fractured reservoirs differ from conventional reservoirs and request Enhanced Oil Recovery strategies where the interaction between fractures and porous rock material is considered. This chapter introduce fractured reservoirs in the context studied in this Thesis.

1.1 Naturally Fractured Reservoirs

Naturally fractured reservoirs are characterized by the presence of two distinct types of porous media with different fluid storage and conductivity characteristics: the matrix and the fractures. A reservoir fracture is a naturally discontinuity in the rock due to deformation or physical diagenesis. Fractures in a reservoir cause fundamental differences in recovery mechanisms compared to unfractured and are mainly due to the capillary pressure difference between matrix and fractures (Firoozabadi, 2000). Geological processes in different rock material cause different types of fractured reservoir and a classification based on porosity and permeability characteristics was made by Nelson (2001):

- Type 1: Fractures provide the essential reservoir porosity and permeability.
- Type 2: Fractures provide the essential reservoir permeability.
- Type 3: Fractures assist permeability in an already producible reservoir.
- Type 4: Fractures provide no additional porosity or permeability but create significant reservoir anisotropy (barriers).

The work in this Thesis emphasizes Type 2 and Type 3 matrix/fracture systems where the main hydrocarbon target is in the matrix while the network of fractures constitutes the main flow for transport. Different types of outcrop chalk material was used as analogue to water-wet North Sea chalk reservoirs and Edwards limestone was aged to reflect oil-wet conditions in carbonates reservoirs. Laboratory fractures were made by cutting the core samples with saw and thereafter reassemble them either without a spacer or with a spacer to maintain the fractures open with a constant fracture aperture.

1.2 Oil Recovery Mechanisms

During oil production in a reservoir the fluid flow is governed by viscous, capillary and gravitational forces. In fractured reservoirs the contribution from viscous forces are generally low due to the highly conductive fractures. During waterfloods, oil displacement from matrix by spontaneous imbibition of injected water from fractures into matrix, is an important recovery mechanism. The potential for spontaneous imbibition is controlled by the wettability preference of the rock and further described in **Chapter 2**. The capillary pressure difference in a water-wet matrix block saturated with oil and water will induce spontaneously imbibition of water from the fracture until capillary equilibrium P_c=0 (see **Figure 1**). The difference in capillary pressure for less water-wet systems will be lower and decrease the potential for spontaneous imbibition. In neutral-wet and oil-wet systems the capillary forces are unfavorable for spontaneous imbibition of water.

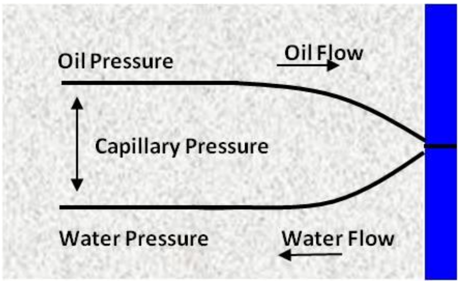

Figure 1. In a water-wet matrix block spontaneous imbibition of water from the fracture into the matrix will displace oil due to a favorable difference in capillary pressure (figure from Ersland, 2008).

Oil recovery in fractured reservoirs can be higher than recovery by spontaneous imbibition if capillary contact between the matrix blocks are present. Graue et al. (2001a; 2000a; 2001b; 2000b) and Aspenes et al., (2002; 2007) investigated fluid transport across open fractures between adjacent matrix blocks using Magnetic Resonance Imaging. In system with strongly water-wet preferences they observed a block-by-block oil displacement, limited by the spontaneous imbibition potential. At less water-wet preference droplets formed on the fracture surface and water bridges between the matrix blocks allowed for fluid transport across the fracture. The bridges reduced the impact of the fractures and added a viscous component to the displacement process and oil recovery was 0.10 PV above the potential for spontaneous imbibition (Aspenes et al., 2007).

In immiscible gas-oil displacement in fractured reservoirs oil recovery rely on capillary forces or gravity drainage. Gravity forces are determined by the density difference between the gas in the fracture network and the matrix oil and also the matrix block height. If the density difference is large or the matrix blocks small, as they can be in heavily fractured reservoirs, and in laboratory core size experiments, the gravitational contribution on oil recovery will be low. The contribution from gravity can be increased if capillary contact is established between matrix blocks and increase the effective height of the matrix block (see **Figure 2**). The interfacial tension between the injected gas and oil can be lowered and reduce the capillary contrast if the injected gas is miscible with the oil. Miscible gas injection is discussed in **Chapter 2**.

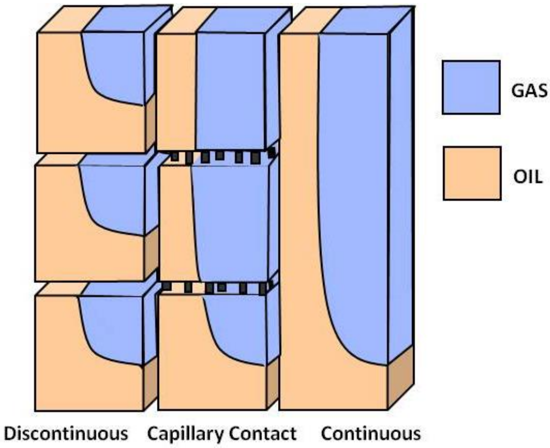

Figure 2. Oil recovery efficiency during gravity drainage depends on the height of the matrix blocks. If capillary contact is established between the blocks this will increase oil recovery considerably in fractured reservoirs (figure from Ersland, 2008).

1.3 Methods for Oil Recovery in Fractured Reservoirs

Oil recovery from a reservoir can be divided into primary, secondary and tertiary recovery. During primary recovery oil is using natural reservoir energy. The oil is mobilized by pressure depletion and sometimes gravity assisted by a natural gas drive from an overlying gas cap or water drive from an underlying aquifer. Typical recovery at this stage is 10-30 % of the original oil in place (OOIP). Secondary recovery methods such as waterfloods and gas injection maintain reservoir pressure and may provide a more efficient oil displacement typically 30-50 %OOIP. Waterfloods in fractured reservoirs may be very efficient if the wetting preference of the rock material is water-wet and favors spontaneous imbibition of water into the matrix from the fractures. If the wetting state is oil-wet or neutral wet, however, the potential for spontaneous imbibition is low and the injected water tend to flow through the fracture network leaving the majority of the oil behind. Tertiary recovery or Enhanced oil recovery (EOR) is the implementation of various techniques to increase the amount of oil that can be produced from a reservoir after or during conventional recovery strategies. EOR methods can be divided into five categories: mobility control (e.g. foam), chemicals (e.g. surfactants), miscible (e.g. CO_2), thermal and others (Green and Willhite, 1998).

2 Wettability and its Impact in Fractured Reservoirs

This chapter introduces wettability, the key parameter to control fluid distribution and fluid flow within a porous media. Wettability is of particular interest in fractured reservoirs as it determines the potential for spontaneous imbibition of water from the fracture network into the matrix and therefore has a large influence on oil recovery.

2.1 Definition of Wettability

Wettability is the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids (Craig, 1971). In a rock/oil/brine system wettability is a property of the rock and determines the rocks preference for oil or brine. The recovery mechanisms in a reservoir is determined by wettability, which governs the microscopic fluid distribution and fluid flow in the porous rock material (Anderson, 1986a). The wetting fluid is located on the pore walls and typically occupies the smallest pores while the non-wetting fluid is located in the pore bodies. Systems with a preference for water are water-wet, oil-wet system has a preference for oil and neutral-wet system has a preference for neither fluids. The system can also have a non-uniform wetting condition, where some areas of the rock surface are oil-wet and some areas are water-wet. The term mixed wettability was introduced by Salathiel (1973), who proposed that the initial draining process in a reservoir, results in oil-wet surfaces in a continuous path for oil through the larger pores leaving the smaller pores water-wet.

2.2 Wettability measurement

Wettability of a porous rock material is usually scaled from strongly water wet to strongly oil wet. There are several methods to measure the wettability. The contact angle method is a quantitative measure of wettability to a specific surface. The contact angle, θ, between a rock surface and two immiscible fluids such as oil and water (see **Figure 3**) is measured through the water phase. The wettability of the surface is strongly water wet if $\theta = 0°$, less water wet if θ = 60-75°, neutral wet if $\theta = 90°$, moderately oil wet if θ = 120-150° and strongly oil wet if $\theta = 180°$ (Anderson, 1986b).

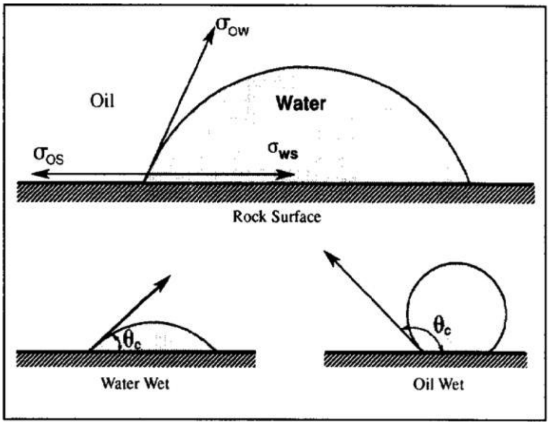

Figure 3. The contact angle measurement of wettability is a quantitative measure of wettability to a specific surface. In a rock/oil/brine system the contact angle θ_c is measured through the water phase. The surface is defined as: water-wet when the contact angle is small (less than 60°), oil-wet when the contact angle is large (more than 120°) and intermediate wet when the contact angle is between 60° and 120° (Anderson, 1986b).

The Amott method (Amott, 1959) combines spontaneous imbibition and forced displacement to measure the average wettability in a core. The wetting fluid of a rock/oil/brine system will spontaneously imbibe into the core, displacing the non-wetting fluid. The Amott Harvey wettability index I_{AH} is defined as:

$$I_{AH} = I_w - I_o$$

where I_w is the displacement-by-water-ratio (the ratio of the oil volume displaced by spontaneous imbibition alone to the total oil volume displaced by water imbibition and forced displacement) and I_o is the displacement-by-oil-ratio (the ratio of the water volume displaced by spontaneous imbibition alone to the total volume displaced by oil imbibition and forced displacement). I_{AH} range between 1 for a strongly water-wet system and -1 for a strongly oil-wet system.

2.3 Relationship between Wettability and Crude Oil Composition

An oil or gas reservoir is formed by hydrocarbon migration into a water saturated reservoir with an impermeable caprock. The reservoir rock surface is originally strongly water-wet, but over geologic time a change towards less water-wet preferences occurs when surface active polar compounds from the crude oil are adsorbed on the rock surface. The heavier fractions of the crude oil generally have a larger influence on wettability compared to the lighter compounds (Anderson, 1986a; Buckley et al., 1998; Cuiec, 1984). Another important property is the solvent environment of the oil, which influences partitioning of the surface active components between bulk oil and oil/brine or oil/brine/solid interfaces (Buckley et al., 1998). Four main interactions influencing wettability alteration in rock/oil/brine systems has been identified as (Buckley and Liu, 1998; Buckley et al., 1998):

- Polar interactions that predominate in the absence of a water film between oil and solid.
- Surface precipitation, dependent mainly on crude oil solvent properties with respect to the asphaltenes.
- Acid/base interactions that control surface charge at oil/water and solid/water interfaces.
- Ion-binding or specific interactions between charged sites and higher valency ions.

In addition to the oil composition, the degree to which the wettability is affected is determined by several other parameters including pressure, temperature, mineral surface, and brine chemistry (ionic composition and PH) (Anderson, 1986a). The net surface charge of a rock surface will influence the adsorption ability of the different polar components (acidic and basic). Carbonate reservoirs are typically more oil-wet compared to sandstone reservoirs (Chilingar and Yen, 1983).

2.4 Brine composition for Enhanced Oil Recovery

Adding surface active potential determining ions, such as sulfate, calcium and magnesium, to the injection brine has shown to improve the water-wetting nature of chalk (Austad et al., 2008; Gomari et al., 2006; Karoussi and Hamouda, 2008; Strand et al., 2006a; Zhang et al., 2007). Several different theories explaining the wettability altering mechanism have been proposed, including ion-exchanging models (Karoussi and Hamouda, 2008; Strand et al., 2006a; Zhang and Austad, 2005b; Zhang et al., 2006) and dissolution of the chalk surface (Hiorth et al., 2010). Temperature is of great importance in this regard. Affinity of sulfate towards the chalk surface is strongly dependent on temperature and there is a large increase of adsorption at 100-130^{o}C (Austad et al., 2008).

3 Injection of Carbon Dioxide for Enhanced Oil Recovery

This chapter will present the background, advantages and challenges using CO_2 as an injection gas for EOR in fractured reservoirs. Foam generation by co-injection of CO_2 and surfactant may improve CO_2 injections with conformance control.

3.1 Implementation of CO_2-EOR

One attractive enhanced oil recovery (EOR) method is the injection of a gas which is miscible with the oil. Depending on reservoir pressure, temperature and oil composition, a range of available gases may develop miscibility with crude oil (Lambert et al., 1996; Skjæveland and Kleppe, 1992). One such gas is carbon dioxide (CO_2). The opposing interests involved with rising world energy demand and anthropogenic CO_2 emissions may be addressed through Carbon Capture, Utilization and Sequestration (CCUS). Implementation of CCUS to reduce greenhouse gas emissions through safe CO_2 injection and storage in mature oil fields will provide incremental oil recovery for energy consumption (Harrison and Falcone, 2013).

It is estimated that more than 60% of the world's oil reserves are stored in carbonate reservoirs, characterized by large heterogeneities and natural fractures with mixed or oil-wet conditions (Roehl and Choquette, 1985), thus a large percentage of remaining oil reserves may be found as residual oil in carbonate reservoirs. This makes carbonates good candidates for CO_2 enhanced oil recovery (EOR), because CO_2 can achieve miscibility with oil at lower pressures compared to other available gases (Skjæveland and Kleppe, 1992). CCUS has been implemented in the United States for 40 years, mainly due to the CO_2 availability (from large natural sources and natural gas plants) and extensive CO_2 pipeline infrastructure (Enick et al., 2012; Lambert et al., 1996; N.E.T.L., 2010). In the North Sea, however, CO_2-EOR is still not realized, although identified as a particularly attractive area because of light crude oil and favorable reservoir geology compared with US fields (Blunt et al., 1993). Two Carbon, Capture and Storage (CCS) projects have so far been implemented on the Norwegian Continental Shelf (Eiken et al., 2011) party realized as a result of Norwegian taxation on CO_2 emissions. The current focus on CO_2 capture and storage, might, however, provide a less expensive source of CO_2. With economic incentives, governments can create a demand for CO_2 and contribute to make it a commodity (Hustad and Austell, 2004) in a CCUS market. A study indicates that the Ekofisk field, a fractured chalk reservoir located in southern part of the North Sea, is a good CCUS candidate (Jensen et al., 2000) but not economically or technically feasible due to high CO_2 prices and limited CO_2 injection sources and infrastructure.

3.2 Challenges using CO_2 in Fractured Reservoirs

The microscopic sweep efficiency during CO_2 injection is potentially very high as a result of miscibility between oil and CO_2, diffusion and oil swelling. The macroscopic sweep efficiency, however, is generally low as a result of the high CO_2 mobility. Naturally fractured reservoirs are very heterogeneous in terms of porosity and permeability (Chilingar and Yen, 1983), and the conductive fracture system, where the contribution from viscous forces is limited, usually leads to rapidly declining production and low total recoveries (Allan and Sun, 2003; Alvarado and Manrique, 2010). Injection of highly mobile CO_2 leads to gravity induced stabilities and/or viscous fingering (Hirasaki and Zhang, 2004; Lescure and Claridge, 1986) resulting in low macroscopic sweep efficiency and early CO_2 breakthrough with the negative consequence of large quantities of CO_2 to be recycled. The poor sweep efficiency in heterogeneous reservoirs remains a severe problem, and typically 10-20 %OOIP incremental recoveries are reported on the field scale during miscible CO_2 injections (Brock and Bryan, 1989). Here, the main production mechanism is gravity drainage, with the additional benefit of diffusion and volume expansion of oil, especially near or at miscible conditions (van Golf-Racht, 1982). Laboratory experiments indicate that miscible displacement/drainage aided by diffusion in fractured reservoirs can be an efficient production mechanism (Firoozabadi, 1994), however, it requires close fracture spacing for the rate of diffusion to significantly contribute to oil recovery (Firoozabadi, 1994; Thompson and Mungan, 1969; Trivedi and Babadagli, 2008). In most fractured reservoirs gas-oil gravity drainage is a slow process, with early breakthrough of injected gas and poor CO_2 utilization (Grigg and Schechter, 1997; Jonas et al., 1990).

3.3 CO_2 Foam for Mobility Control

Reservoir pressures and temperatures typically corresponds to CO_2 being in its liquid or supercritical state with a liquid-like density and gas-like viscosity. The poor macroscopic sweep efficiency associated with the high mobility of the injected CO_2 may be improved with CO_2-foam to produce a more favorable mobility ratio to increase sweep, and thereby improve oil recovery (Talebian et al., 2013). Foam effectively increases the viscosity of the gas phase by mixing gas and surfactant solution, creating a discontinuous gas phase separated by thin water films (lamella) stabilized by the surfactant. Foam as mobility control in fractured reservoirs will add a viscous component and fracture permeability reduction (Sydansk and Romero-Zeron, 2011). There have been several successful foam pilots (Blaker et al., 2002; Li et al., 2009; Mukherjee et al., 2014; Sanders et al., 2012; Yu et al., 2008), but historically very few foam pilots in fractured reservoirs have been performed, and those have largely been deemed unsuccessful (Enick et al., 2012; Smith, 1988). This has been attributed to the lack of foam generation mechanisms in fractures, namely snap-off, film division and leave-behind. Recent research, however, confirms in-situ foam generation in single fractures (Buchgraber et al., 2012; Kovscek et al., 1995), leading to increased sweep (Yan et al., 2006) and flow diversion within a rough-walled carbonate fracture network during co-injection of surfactant and gas (Fernø et al., 2014). Hence, the reported unsuccessful foam pilots in fractured reservoirs may be related to operational issues or lack of optimized, field-specific surfactants (Castanier and Hanssen, 1995; Prieditis and Paulett, 1992), rather than lack of foam generation mechanisms in fractured reservoirs. With the development of better surfactants (Buchanan, 1998; Cui et al., 2014; Elhag et al., 2014; Ryoo et al., 2003), the injection of foam in naturally fractured reservoirs is increasingly recognized as a potential EOR technique in fractured reservoirs (Farajzadeh et al., 2012; Haugen et al., 2012; Lopera Castro et al., 2009; Panahi, 2004; Pancharoen et al., 2012; Zuta and Fjelde, 2010).

Part II
Materials and Experimental Methods

4 Materials

This chapter presents a brief description of the rock material and fluids used in the laboratory tests investigating EOR-efforts and the influence of wettability.

4.1 Rock types

Cylindrical core plugs and rectangular blocks were cut from larger slabs of outcrop rock material, obtained from four different outcrop quarries:

- Rørdal chalk was obtained from the Portland cement factory at Ålborg, Denmark. The rock formation is of Maastrichtian age and consists mainly of coccolith deposits, and the composition is calcite (99 %) with some quartz (1 %). The rock is homogeneous on the Darcy scale, porosity and permeability range from 45-47 % and 3-8 mD, respectively. Details of deposition and diagenetic history may be found in (Ekdale and Bromley, 1993; Hjuler, 2007). The outcrop core material is assumed strongly water-wet based on MRI measurements of wettability and imbibition tests (Johannesen, 2008).
- Stevns chalk was obtained from Stevns Klint near Copenhagen Denmark. The chalk is of Maastrichtian age and generally very homogeneous with >96 % fine graded coccolith matrix. The rock is soft with BET surface area of 2 m^2/g. Porosity and permeability range from 45-50 % and 2-5 mD, respectively. Further geological characterization may be found in (Milter, 1996; Strand et al., 2007; Zhang and Austad, 2005a).
- Niobrara chalk was obtained from an outcrop in Kansas. The chalk is fine grained micrite representing a mixture of calcareous, organic, and terrigenous components (70-80 % carbonate). The carbonate constitute macrofossils and nanofossils (60-90 %) including coccoliths (golden-brown algae) and lesser Foraminifera and calcispheres. Local diagenetic reactions lead to authigenic minerals such as pyrite and kaolinite. Porosity and permeability ranges from 40-50 % and 0.1-3 mD, respectively (Lockridge and Scholle, 1978; Pollastro and Scholle, 1986).
- Edwards limestone was collected from a quarry in West Texas and is considered heterogeneous, with porosity ranging between 16-24 %, and absolute permeability of 3-28 mD (Haugen et al., 2012). Mercury injections, thin sections and NMR T_2 relaxation experiments have been used to characterize this rock type consisting of a trimodal pore size distribution with the majority of pores about

150 µm diameter, some pores with pore diameter at about 40 µm and some micro pores (~ 1 µm) (Johannesen, 2008). The pore throat size of most pores in Edward limestone core material is in the range of 0.1 to 10 µm, and frequently in the 1 to 10 µm range. An aspect ratio in the range of 50 to 60 is documented, which is a result of huge difference between the size of the pore bodies and throats (Morrow and Burkley, 2006; Seth and Morrow, 2007).

4.2 Fluids

Crude oil and mineral oil was used as oil phase in separately laboratory core experiments. The crude oil was used in high temperature experiments > 60 °C (prior to use the oil was filtered through a porous media and stored above 60 °C due to wax precipitation at lower temperatures). Three batches of a crude oil produced from the same North Sea reservoir was used. The mineral oil n-Decane was used as oil phase in experiments at lower temperature and in experiments where reproducibility in terms of wetting state was of importance. The surfactant solution to generate foam during co-injection with CO_2 was Alpha Olefin Sulfonate (AOS) surfactant. The composition and properties of oils and selected brines are listed in **Table 1**.

Table 1. Fluid components and properties.

Fluid	Components	Properties
North Sea Crude Oil, Barrel 1 NSCO#B1	Acid Number: 0.41 mgKOH/g Base Number: 1.4 mgKOH/g Saturates: 61 wt% Aromates: 20 wt% Resins: 19 wt% Asphaltenes: 0.6 wt%	ρ(20°C): 0.85 g/cm^3 ρ(80°C): 0.85 g/cm^3 μ(20°C): 14.3 cP μ(80°C): 2.7 cP
North Sea Crude Oil, Barrel 2 NSCO#B2	Acid Number: 0.09 mgKOH/g Base Number: 1.2 mgKOH/g Saturates: 53 wt% Aromates: 35 wt% Resins: 12 wt% Asphaltenes: 0.9 wt%	ρ(20°C): 0.85 g/cm^3 ρ(80°C): 0.85 g/cm^3 μ(20°C): 14.3 cP μ(80°C): 2.7 cP
North Sea Crude Oil, Barrel 3 NSCO#B3	Not measured	Not measured
n-Decane	$C_{10}H_{12}$	ρ(20°C): 0.73 g/cm^3 ρ(80°C): 0.68 g/cm^3 μ(20°C): 0.92 cP μ(80°C): 0.40 cP
Synthetic Seawater, 0xSulfate SSW-0S	NaCl: 26.8 g/l $CaCl_2$: 1.91 g/l $MgCl_2$: 9.05 g/l $NaHCO_3$: 0.17 g/l KCl: 0.75 g/l	ρ(20°C): 1.02 g/cm^3 μ(20°C): 1.09 cP
Synthetic Seawater, 4xSulfate SSW-4S	NaCl: 13.2 g/l $CaCl_2$: 1.91 g/l $MgCl_2$: 9.05 g/l $NaHCO_3$: 0.17 g/l KCl: 0.75 g/l Na_2SO_4: 13.4 g/l	ρ(20°C): 1.02 g/cm^3 μ(20°C): 1.09 cP
Synthetic Formation Brine SFB	NaCl: 40 g/l $CaCl_2$: 34 g/l $MgCl_2$: 5 g/l	ρ(20°C): 1.05 g/cm^3 μ(20°C): 1.09 cP
Surfactant solution	Brine 1 wt% AOS	

5 Experimental Methods

The laboratory work presented in this Thesis was performed using a number of methods, strategies and experimental set-ups. This chapter presents the key elements of techniques and methods used during laboratory experiments.

5.1 Dynamic Aging Technique

A dynamic aging technique in crude oil at elevated temperature (80 °C) was used to establish uniform wetting states ranging from strongly-water wet to oil-wet in the core samples (Aspenes et al., 2003; Fernø et al., 2010; Graue et al., 2002; Graue et al., 1999). The core samples were drained with North Sea crude oil to different initial water saturation. After primary drainage the flow of crude oil was reduced to a low injection rate, continuously injecting crude oil through the core during an aging period of varying length. The direction of flow was reversed midway. In experiments with following injection tests requiring stable wetting states, the crude oil was displaced from the core by injecting 5 PV decahydronaphthalene followed by 5 PV n-Decane to avoid asphaltene precipitation, to stop the aging and to establish more reproducible experimental conditions by using the mineral oil n-Decane as the oil phase during the subsequent steps of the experiments. The experimental aging set-up is shown in **Figure 4**. More details about the aging procedure and results may be found in **Paper 1-3** and **Paper 6**.

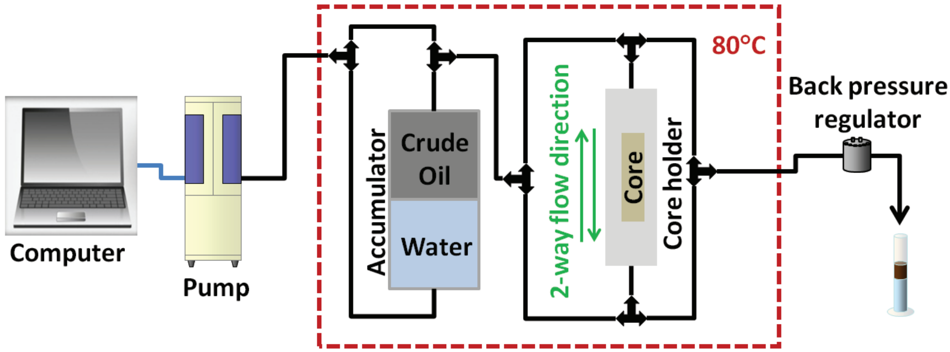

Figure 4. The aging set-up was used to continuously inject crude oil through a core sample at 80 °C. The flow direction was reversed midway of the aging period to establish uniform wetting conditions. The dynamic aging technique enabled a range of laboratory induced wetting preferences by varying the length of the aging period and the initial water saturation in the core samples.

5.2 Sulfate Enriched Waterfloods

Spontaneous imbibition and waterflood tests were performed at elevated temperatures (130 °C) to investigate the wettability altering effect using sulfate enriched brine. Prior to the sulfate enriched waterfloods less water-wet and near neutral-wet conditions were established in originally strongly water-wet chalk cores using the dynamic aging technique. Synthetic formation brine (SFB) was the initial water phase saturating the core samples during the aging period. Synthetic seawater was the imbibing fluid during the spontaneous imbibition test and subsequent waterflood. Two sulfate concentrations were used: synthetic seawater without sulfate (SSW-0S) and synthetic seawater added four times the sulfate concentration found in seawater (SSW-4S). The spontaneous imbibition tests were performed in high pressure imbibition glass cells with custom made titanium bottoms (see **Figure 5**). The imbibing brine was pressurized to 3.4 bar to avoid boiling. The produced oil by capillary imbibition versus time was measured by visual inspection of the imbibition cell. More details about the sulfate enriched waterfloods may be found in **Paper 2**.

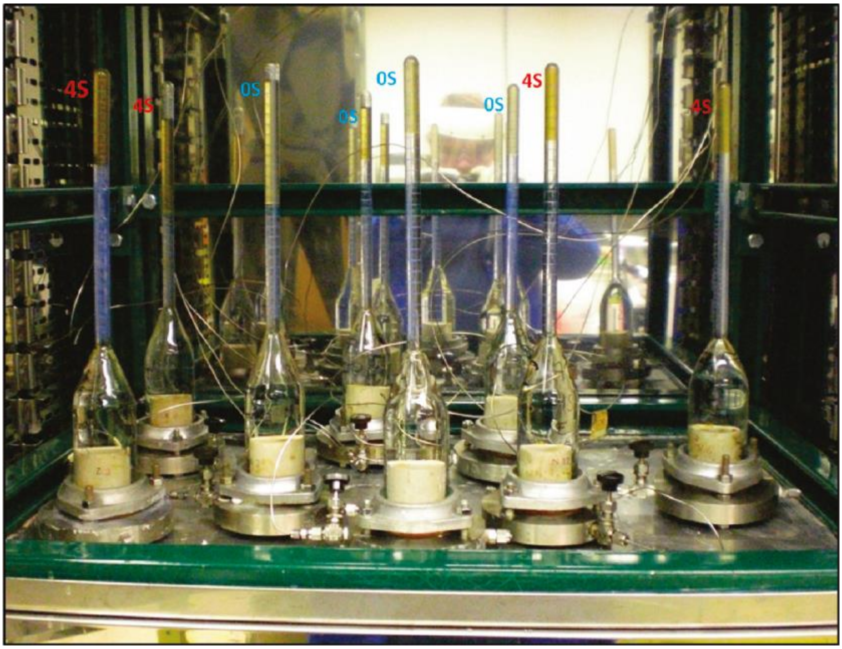

Figure 5. The picture shows core samples spontaneously imbibing synthetic seawater with and without sulfate in high pressure and high temperature custom made imbibition cells (Fernø et al., 2011).

5.3 The Wetting Test Cycle - a modified Amott-Harvey Method

The wetting preference of the core samples was measured experimentally using a modified Amott-Harvey method to find I_w (and I_o for Edwards limestone). **Figure 6** shows the four steps of the wettability test cycle:

1. Spontaneous imbibition of water - the core was placed in an imbibition cell and spontaneously produced oil was measured
2. Forced imbibition of water - the core was subjected to forced waterflood in a core holder (2 bar/cm) and oil production was measured
3. Spontaneous imbibition (drainage) of oil - the core was placed in an imbibition cell and spontaneously produced water was measured
   (this step was only used for limestone core samples)
4. Forced imbibition (drainage) of oil - the core was subjected to forced oilflood in a core holder (2 bar/cm) and water production was measured

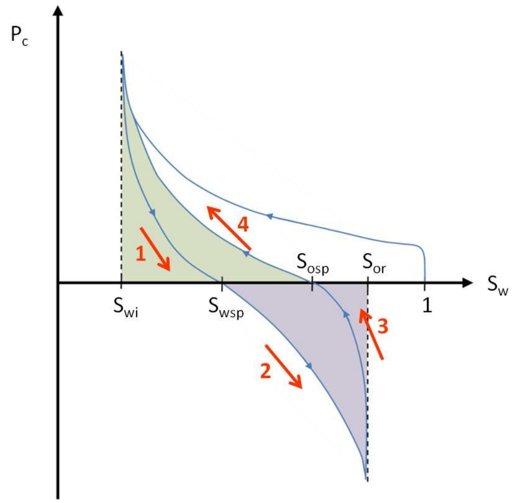

Figure 6. The wettability test cycle was used to measure the laboratory induced wetting preference after dynamic aging with crude oil. Several cycles was performed to investigate wetting stability in the core samples and also how different EOR injection strategies influenced the potential for spontaneous imbibition and the Amott water index I_w.

The wettability test cycle was repeated several times to investigate i) the stability of the laboratory induced wetting preference and the potential for spontaneous imbibition and also ii) the wettability altering effects during different EOR injection strategies. The dynamic aging technique using the North Sea crude oil did not establish conditions for spontaneous production of water at S_{or} in the outcrop chalk material used in this Thesis: Rørdal, Stevns and Niobrara. An extra step in the wettability test cycle, measuring the spontaneous imbibition of oil at $S_{or,}$ was performed for Edwards limestone. More details about experimental procedures and results from the wettability analysis may be found in **Paper 1-3** and **Paper** 6.

5.4 Injection of CO_2 and CO_2-foam for EOR

CO_2 and CO_2-foam injection tests were performed in core samples at different initial states and with a range of experimental variables to investigate different mechanisms for Enhanced Oil Recovery (see **Table 2**.)

Table 2. Experimental variables and investigated mechanisms in CO_2 injection tests.

Experimental variables	Mechanisms
Fracture permeability	Sweep efficiency
Rock type	Miscibility
System size/shape	Diffusion
Oil composition	Foam mobility control
Wettability	
Initial water saturation	
Injection strategy	
Pressure/Temperature	

Before CO_2 injections, the core samples were prepared with a given initial states and tightly wrapped in aluminum foil and/or aluminum tape to prevent contact between the core confining material and injected CO_2, which was detrimental to the rubber sleeve/epoxy during the experiments performed at typical reservoir conditions. Foam injection was performed by co-injection of CO_2 and surfactant solution. In short core samples (core length < 10 cm) a small sand-pack system upstream of the core was used to mix the injecting fluids. Constant volumetric injection rates corresponding to front velocities between 5 cm/day and 12 cm/day was used. Oil production was measured downstream a back pressure regulator (BPR) at ambient pressure in a graded cylinder. The BPR maintained a constant core outlet pressure throughout each experiment. Duration of injection tests was generally until no additional oil was recovered. The initial oil production from the fracture network was not included in the reported oil recoveries, which only included oil production from the porous matrix blocks adjacent to the fracture network. The typical experimental set-up for a CO_2 injection test is shown in **Figure 7**. All CO_2 injection tests are described in detail in **Paper 4-7**.

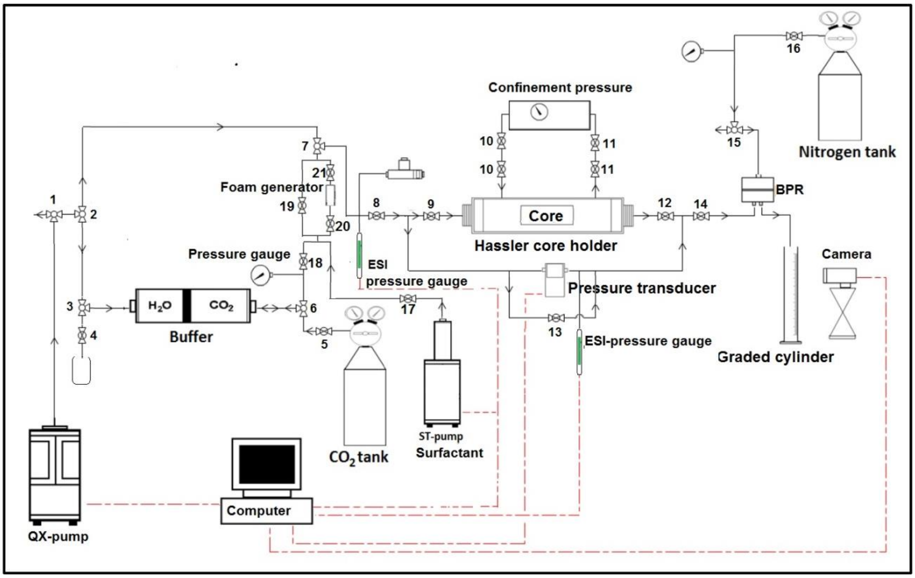

Figure 7. Experimental set-up for CO_2 injection tests. The core sample was placed in a core holder. Fluid injections were controlled with pumps and a back pressure regulator maintained a constant outlet pressure. Differential pressure was measured across the core length with pressure transducers.

Part III
Results and Discussion

6 Laboratory Wettability Alteration

This chapter will summarize the results of two important objectives in this Thesis: 1) Establish a range of stable, uniform wetting preferences in core samples using a dynamic aging technique and 2) Increase the spontaneous imbibition potential by sulfate enriched waterfloods by inducing a more water-wet state of the rock surface.

6.1 Stability of Laboratory Induced Wetting Preference

The dynamic aging technique (**Section 5.1**) with North Sea crude oil (NSCO#B1) was used to establish a range of wetting states in Rørdal chalk. The core samples were aged at different initial water saturations (*low, medium and high*) and the measured Amott water index, I_w, was between 0.39-0.80, as detailed in **Paper 1**. I_w decreased systematically with increasing aging time and decreasing initial water saturation during aging. **Figure 8** show development in oil recovery by spontaneous imbibition of water in cores aged at different initial water saturation and with varying length of the aging period.

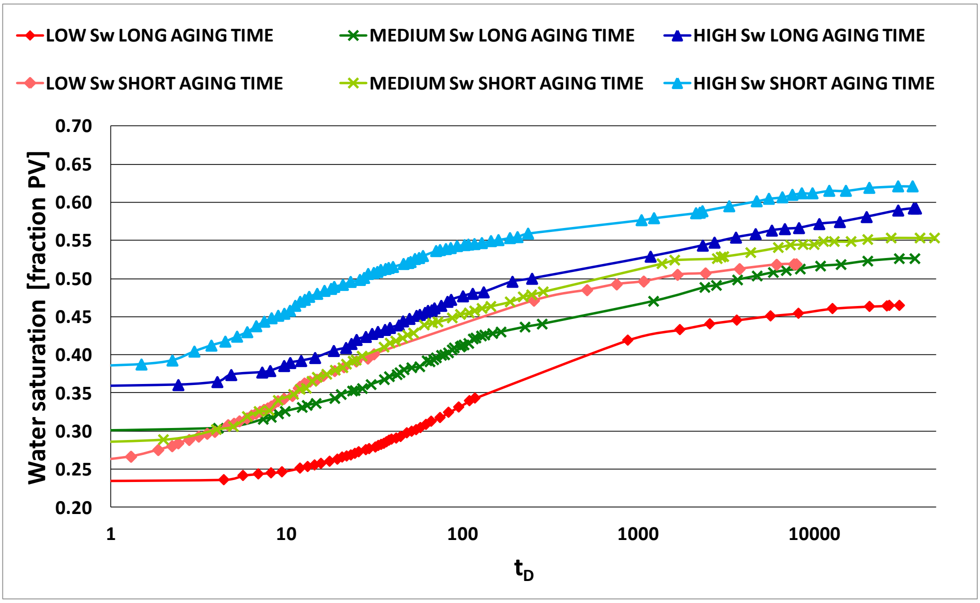

Figure 8. A range of wetting preferences was established in originally strongly water-wet Rørdal chalk core samples by the dynamic aging technique. The Amott water index and endpoint saturation for spontaneous imbibition decreased systematically with increased aging time and decreased initial water saturation during aging.

The wetting test cycle (see **section 5.3**) confirmed that the laboratory established wetting preference was stable within I_w ± 0.04 during two cycles. The spontaneous imbibition endpoint water saturation, in the same core i.e. at a given wettability, was not affected by varying the initial water saturation before each wetting test cycle. **Figure 9** show spontaneous imbibition of water in core samples during two wetting test cycles.

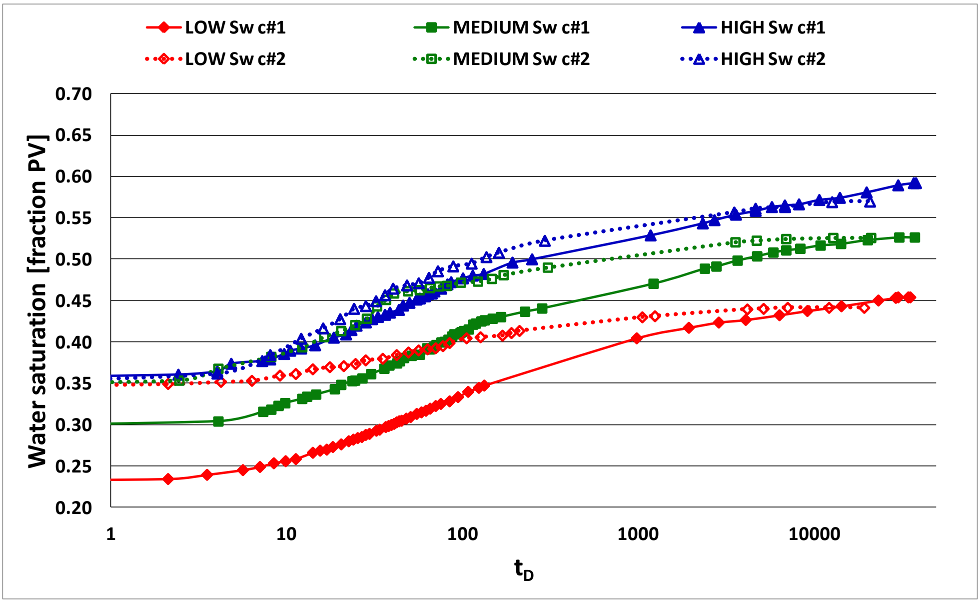

Figure 9. The laboratory induced wetting preferences in Rørdal chalk core samples were stable: the end point saturation for spontaneous imbibition did not change during two cycles of spontaneous imbibition tests.

Fernø et al. (2011) measured repeated Amott water indices in association with high temperature (HT) spontaneous imbibition in Rørdal, Stevns and Niobrara core samples. They established moderately water-wet preferences using the dynamic aging technique with crude oil NSCO#B2 (see **Table 1**). The first cycle (C1) was performed at low temperature (20 °C), the second cycle (C2) at high temperature (130 °C), and finally, the third cycle (C3) at low temperature (20 °C). The I_w for Rørdal and Stevns chalk was relatively stable between cycles 1 and 3 (Rørdal: I_w = 0.24±0.02; Stevns: I_w = 0.23±0.01), before and after the high temperature spontaneous imbibition test performed at 130 °C. The high temperature test altered the wetting preference in the Niobrara core sample considerably from I_w = 0.32 to I_w = 0.81.

Moderately water-wet conditions with I_w ranging from 0.2-0.8 was established in the systematic wetting stability test in Rørdal chalk using NSCO#1 (**Paper 1**) and during high temperature tests in Stevns and Niobrara using NSCO#2 (Fernø et al., 2011). A systematic wetting stability test, similar to the one presented in **Paper 1**, was also performed in Stevns and Niobrara, using NSCO#B3 (see **Table 1**). After aging the measured wetting preference in the Niobrara core samples ranged from I_w = 0.03 to

I_w = 0.10 and the oil recovered by spontaneous imbibition of water was typically less than 5 %OOIP. The Stevns cores did not spontaneously imbibe any water and I_w was 0 for all cores. **Figure 10** shows development in oil recovery for Rørdal (aged with NSCO#B1), Niobrara and Stevns (aged with NSCO#B2) and Niobrara and Stevns (aged with NSCO#B3). The measured I_w, both in Stevns and Niobrara, was considerably lower when NSCO#3 was used during aging compared to NSCO#2 with otherwise identical experimental conditions and method. Although oil composition was not measured for NSCO#B3 it was expected to contain more heavy components and/or have a higher acidic number compared to the other two batches. The Amott Harvey method can be insensitive at near neutral-wet conditions (Morrow, 1990) and may predict neutral wetting conditions even though a very small fraction of the surface area is coated with organic material, especially if the oil-wet areas are located at the pore throats (Strand et al., 2006b). Each rock/oil/brine system is unique and initial wetting tests should be performed to evaluate I_w for each system. If a lower or higher I_w is required in subsequent tests, the initial water saturation during aging or the aging period should be adjusted. At near-neutral conditions other methods e.g. use of NMR (**Paper B**) should be considered for wettability measurment.

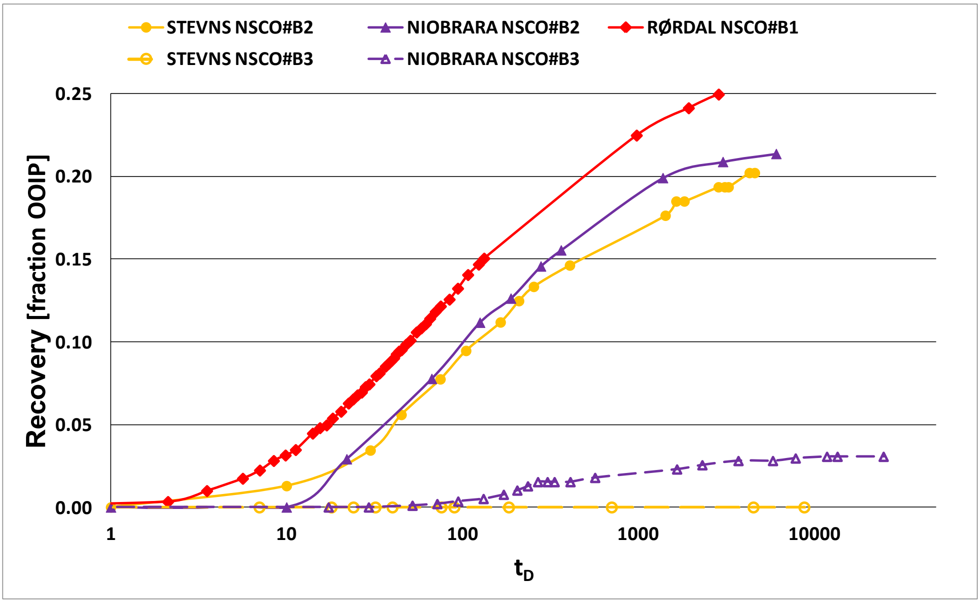

Figure 10. Spontaneous imbibition at elevated temperature (130 °C) demonstrated that crude oil composition strongly influenced the laboratory induced wetting preferences in the rock types Stevns, Niobrara and Rørdal. Crude oil from the same batch established coinciding wetting preferences in each rock type. Crude oil from a different batch established different, but coinciding wetting preferences.

6.2 Sulfate Enriched Waterfloods for Enhanced Oil Recovery

Fernø et al., (2011) found that the EOR-effect of adding sulfate to injection brine depended on rock type and the Amott water index. After the dynamic aging technique they replaced the crude oil with n-Decane. Waterfloods with sulfate enriched brine increased oil recovery with 10-35 % (with initial I_w<0.2) and 6-8 % (with initial I_w>0.2) compared to brines without sulfate. The produced n-Decane was light brown when no sulfate was present and darker brown when sulfate was present, indicating dissolution of organic components from the rock surface. They observed no EOR-effect in Rørdal chalk and in Niobrara chalk the high temperature brine altered the wettability towards more water-wet conditions regardless if sulfate was present or not (Fernø et al., 2011).

With crude oil as the oil phase in otherwise identical experimental conditions and core plugs cut from the same batch of rock, the average additional recovery with the presence of sulfate was 43 %OOIP for Stevns core plugs (**Figure 11**) and 12 %OOIP for

Rørdal core plugs (**Figure 12**). For Stevns chalk I_w increased from 0.46 to 0.98 when sulfate was added to injection and from 0.81 to 0.92 for Rørdal chalk. These experiments showed that sulfate increased the effect on I_w, S_{wsp} and R_f when using crude oil as oil phase compared to n-Decane.

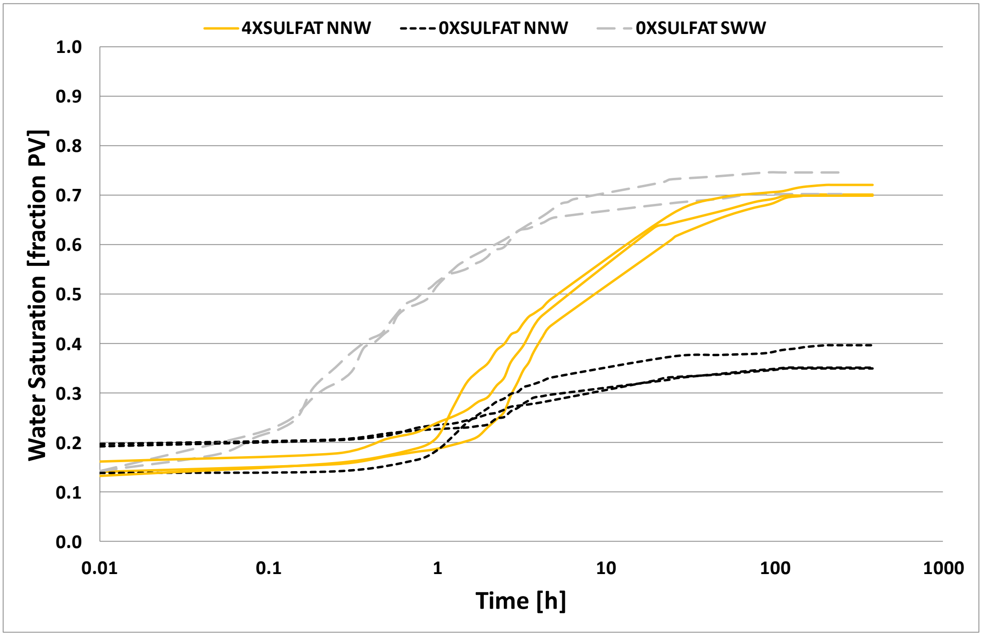

Figure 11. Oil recovery by spontaneous imbibition in near neutral-wet Stevns core samples was on average 43% OOIP with sulfate enriched brine (yellow lines) compared to brine without sulfate (dotted black lines). Strongly water-wet core samples without sulfate present in the brine are indicated in grey.

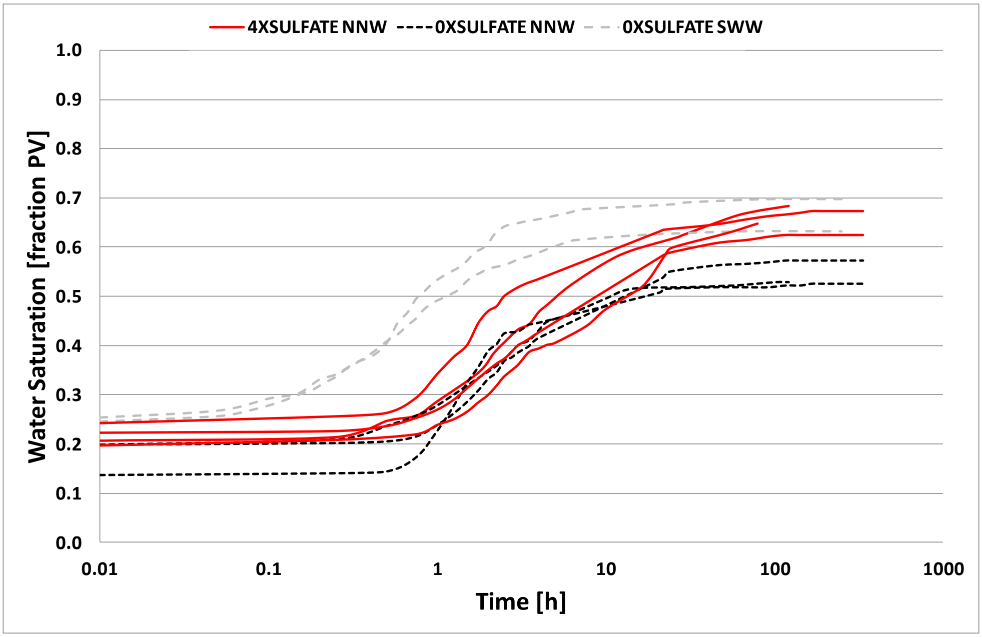

Figure 12. Oil recovery by spontaneous imbibition in near neutral-wet Rørdal core samples was on average 12% OOIP with sulfate enriched brine (red lines) compared to brine without sulfate (dotted black lines). Strongly water-wet core samples without sulfate present in the brine are indicated in grey.

6.3 Observations from Laboratory Induced Wettability Alteration

The following key observations were made during laboratory wettability altering test in different outcrop rock using crude oil and brine with varying composition:

- ✓ The dynamic aging technique with North Sea crude oil was used to establish a range of less water-wet preferences in originally strongly water wet outcrop chalk material.
- ✓ By varying the initial water saturation and/or the length of the aging period, the potential for spontaneous imbibition and I_w was increased or decreased.
- ✓ The wetting preference was stable during several flooding cycles.
- ✓ Temperature and EOR-efforts altered the wetting preference and the degree of alteration depended on rock type, wettability preference and oil composition.
- ✓ The composition of the crude oil affected the degree of wettability alteration.

7 Experimental Investigation of CO_2 Enhanced Oil Recovery

This chapter will discuss the main objective of the Thesis: Laboratory CO_2 injections for Enhanced Oil Recovery and the influence of wettability in fractured systems. The experimental conditions were varied to investigate recovery mechanisms such as degree of CO_2-oil miscibility, diffusion and conformance control using foam.

7.1 The Influence of Fractures during CO_2 Injections

Injection of CO_2 may be an attractive EOR method depending on the reservoir quality and crude oil, and may favorably change the physical properties of the oil phase to increase flow through 1) oil swelling, 2) reduction of oil viscosity, 3) increased oil density, 4) vaporization and extraction of hydrocarbon components up to C_{30}, 5) reduction of interfacial tension, and, 6) the ability to achieve miscibility with crude oil at relatively low pressure (Ahmed, 1994; Holm and Josendal, 1974; Lambert et al., 1996; Skjæveland and Kleppe, 1992).

The macroscopic sweep efficiency during field scale CO_2 injections is often low due to heterogeneities, naturally occurring fractures and unfavorable mobility ratio in the displacement process. Theoretically, however, first-contact miscible (FCM) CO_2 floods may produce all oil from a reservoir, allocated sufficient time for diffusion to take part and enough volume of CO_2 injected. In laboratory injection tests it was observed a very efficient oil recovery, typically 96-100 %OOIP within 2-5 PV injected, during secondary CO_2 injection in unfractured core samples at FCM conditions with the oil. In general, oil recovery in unfractured systems was identified by: 1) a late CO_2-breakthrough, where most of the oil was produced before the breakthrough, 2) a high oil production rate from the onset of CO_2 injection, 3) a short tail production and 4) differential pressure across the core sample indicating a piston displacement of oil (with viscous drive and little degree of CO_2 fingering). High end point oil recovery was also observed in fractured core samples, but the recovery process was much less efficient in terms of PV injected and the CO_2-breakthrough was typically observed before 0.05 PV injected. In general, oil recovery from fractured systems was identified by: 1) a rapid breakthrough of CO_2, where most of the oil was produced after CO_2-breakthrough, 2) a low production rate from the onset of CO_2 injection, 3) a long tail production and 4) no differential pressure across the core length, which indicated diffusion dominated recovery process.

7.2 Recovery Mechanisms by Miscible CO_2-EOR

Oil recovery during CO_2 injection at first contact miscible conditions in fractured reservoirs depends on molecular diffusion and mechanical dispersion, driving CO_2 from the fracture to the matrix. Dispersion by convection (mechanical mixing) is the prevailing mechanism in the fracture network, while dispersion by diffusion will influence matrix flow. Dispersion may occur due to differences in concentration (molecular diffusion), temperature or pressure between two areas. Molecular diffusion is especially important in miscible gas flooding in fractured reservoirs (da Silva and Belery, 1989; Hu et al., 1991; Jamili et al., 2011). The contribution from molecular diffusion to oil recovery is increased when the flow rate in the matrix is low or when the contact area between injected gas and reservoir oil is high, e.g. in fractured reservoirs. Generally, diffusion depends on diffusion length, rock type, crude oil composition, temperature and pressure (Alavian and Whitson, 2010; Ghedan, 2009; Skjæveland and Kleppe, 1992).

The controlling factor for the oil recovery efficiency in laboratory tests was the distance the CO_2 diffused from the fracture to the oil saturated matrix. This was investigated in **Paper 5** and development in oil recovery versus time for core samples with different diffusion lengths is shown in **Figure 13**. The contribution of diffusion on the oil recovery process was larger than in most fractured reservoirs, and may be explained by i) the large surface area between the fracture and the matrix, ii) the high CO_2 concentration in the fracture, iii) the small matrix size and short diffusion length and iv) the low front velocity.

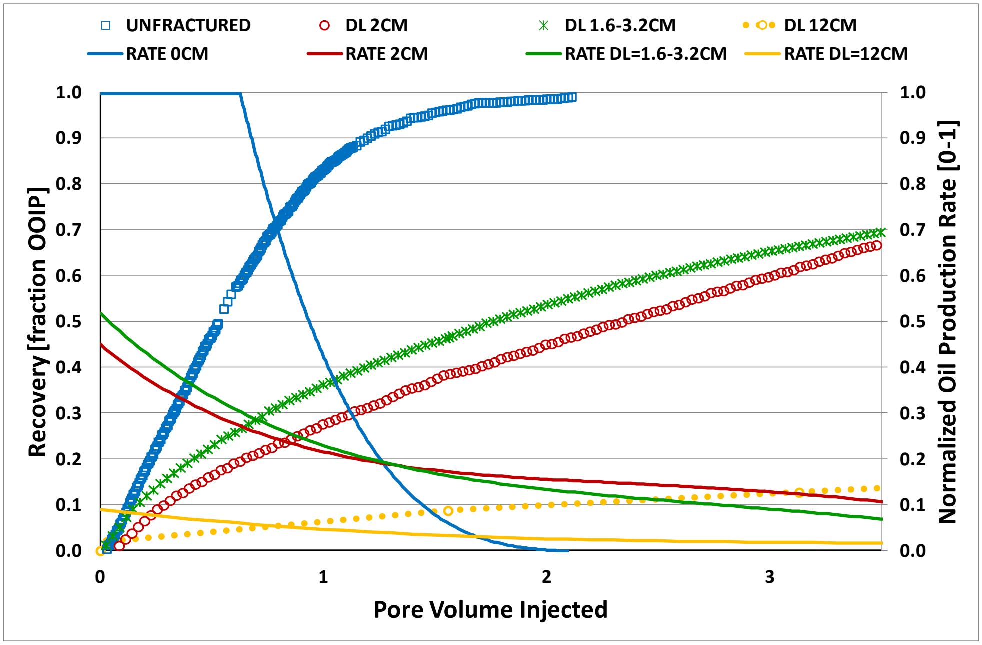

Figure 13. Diffusion as a recovery mechanism is controlled by the diffusion length in a fractured system: increased diffusion length decreased oil recovery efficiency. In the unfractured system the initial oil production rate was high and endpoint oil recovery was reached within 2 pore volumes injected. The oil production rate in fractured systems was low from onset of CO_2 injection and long tail production was observed.

During CO_2 injections in fractured systems the highly mobile gas tends to channel through the fractures without contacting the matrix oil. The influence of fracture permeability was also investigated in **Paper 5** and **Figure 14** shows development in oil recovery versus PV injected in systems with varying fracture permeability. The high permeable fracture system limited the viscous contribution, and oil was produced mainly by diffusion, dispersion and oil swelling. The lower permeable fracture system produced almost twice as much oil during the first PV injected compared to the high permeable system and shows that a reduction of fracture conductivity by use of e.g. foam would increase oil recovery efficiency considerably. Reduction of fracture conductivity by mobility control is discussed further in **Section 7.5**.

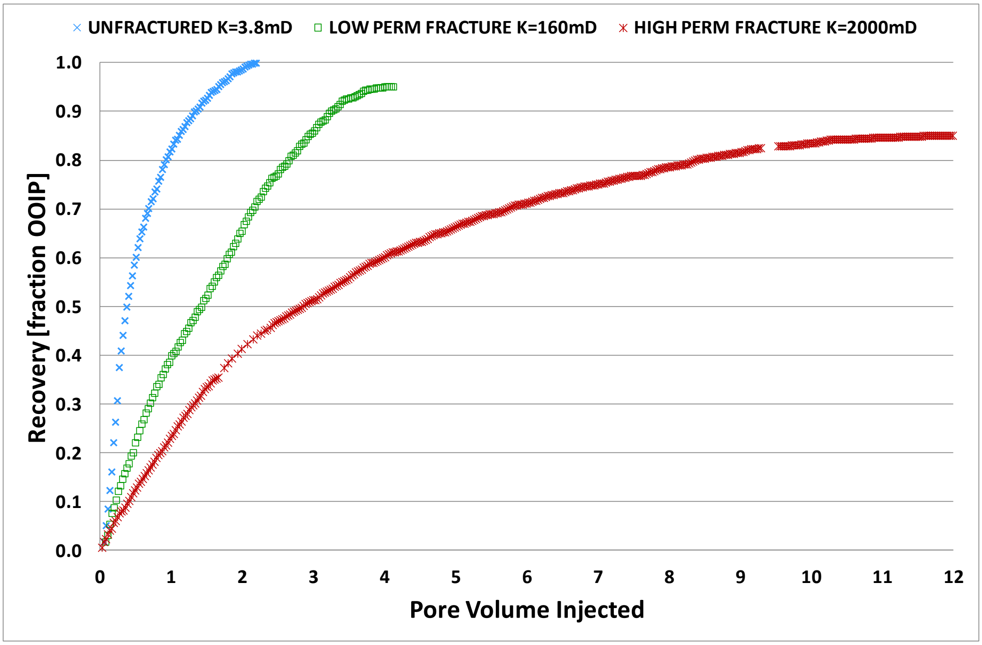

Figure 14. The recovery efficiency in terms of pore volumes CO_2 injected and final end point recovery was strongly influenced by the fracture permeability. A high permeable fracture compared to a low permeable fracture increased the amount of CO_2 injected to reach endpoint oil recovery from 4 to 12 pore volumes.

7.3 The Influence of Rock type and Oil Composition on CO_2-EOR

Rock type with different pore size distribution and degree of heterogeneity will influence CO_2-oil interaction in the matrix. A higher tortuosity will increase the path length each CO_2-moelcule must travel, and hence decrease the efficiency of CO_2-oil diffusion. **Paper 6** investigated secondary miscible supercritical CO_2 injections for Rørdal chalk and Edwards limestone, see **Section 4.1.** A larger degree of variation in oil recovery was observed in limestone core samples and oil recovery was generally lower compared to chalk, which can be explained by the high permeable zones increasing the degree of CO_2 fingering and the higher tortuosity i.e. longer diffusion length in limestone. As tortuosity goes down the diffusion length approaches bulk diffusion length (Eide et al., 2015). The smaller pore size in chalk may also contribute to more surface area and less water shielding. Development in oil recovery versus PV injected for unfractured and fractured Rørdal chalk and Edwards limestone core samples are shown in **Figure 15**.

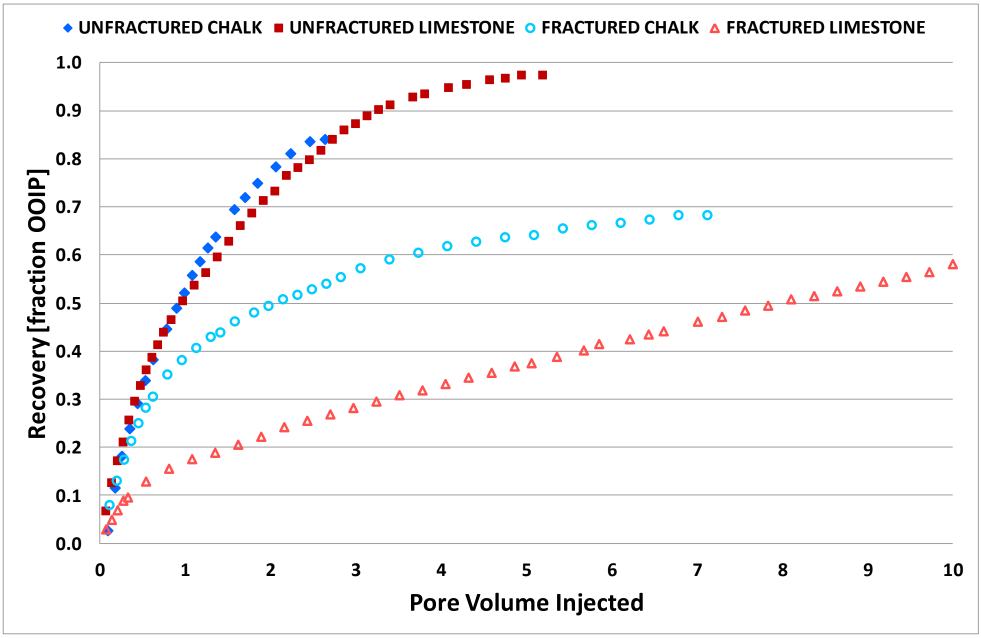

Figure 15. The oil recovery efficiency was similar in terms of pore volumes injected for two different rock types, Rørdal chalk and Edwards limestone, when the core samples were unfractured. In fractured core samples the different rock properties influenced the efficiency and oil recovery was slower in the more heterogeneous limestone with a higher tortuosity, compared to chalk.

Two fluids that are miscible at a given pressure and temperature form a single phase when mixed in any proportion when first brought into contact. In reservoir gasflooding, the injected gas composition, oil composition, temperature and the injection pressure determine the condition of first-contact miscibility (FCM). In contrast, fluids that develop miscibility after exchanging components have multiple-contact miscibility (MCM). When CO_2 is injected in a crude oil/rock/brine system, multi-contact miscibility develops through several exchange processes if the injection pressure at a given temperature is above the minimum miscibility pressure (MMP). Hydrocarbon-components from the oil vaporize into the CO_2, which in turn condense into the oil phase until they may be considered one phase (Ghomian et al., 2008). Lighter components vaporize more easily into the gas phase than heavier (Holm and Josendal, 1974).

The influence of oil composition was investigated in **Paper 4** comparing oil recovery efficiency in crude oil systems (MCM) to pure mineral oil systems (FCM). Supercritical CO_2 injections were performed at reservoir temperature and pressure conditions above MMP (n-Decane: 40°C/90 bar, crude oil: 75°C/208 bar), using the setup described in section **5.4**.

Oil recovery was slower in the fractured core samples compared to unfractured, observed by low production rates and long tail production after CO_2 breakthrough, both for crude oil and n-Decane saturated core samples. Oil recovery was more efficient in systems saturated with n-Decane compared to crude oil, most likely because CO_2 and n-Decane were first-contact miscible above MMP and the crude oil hydrocarbon composition (97 % C_{7+}, 28 % C_{30+}) resulted in multiple-contact miscibility with CO_2. After breakthrough of CO_2 in crude oil saturated systems, visual observations indicated that the lighter components in the crude oil, which developed miscibility first, were also produced first. Other experiments confirm that crude oil composition changes at different production stages during CO_2 injections: oil with composition similar to the original crude oil in place is viscously produced first, followed by the light end components and finally the heavy end components (Darvish et al., 2006). Development in oil recovery versus PV injected for unfractured and fractured crude oil and n-Decane saturated core plugs are shown in **Figure 16**.

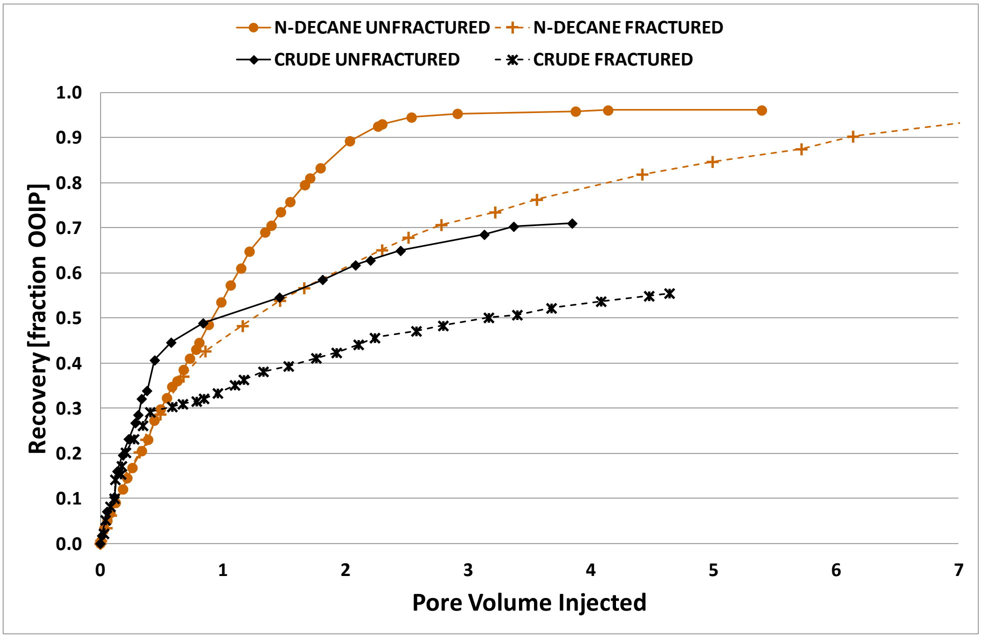

Figure 16. Oil composition influenced oil recovery efficiency in fractured core samples during CO_2 injections. A higher efficiency was observed in systems saturated with a pure mineral oil (C_{10}) at FCM conditions compared to crude oil (97% C_{7+}, 28% C_{30+}) at MCM.

7.4 How Wettability and Water Shielding affects CO_2-EOR

A water shielding effect occurs in the rock/oil/brine system when initial water saturation prevents or reduces contact and mixing between the injected gas and oil residing in the pore space. CO_2 is also soluble in water and may diffuse through the water layers to mix with the oil for swelling and mobilization and increase oil recovery during tertiary injection schemes (Martin and Taber, 1992). High water saturations as a result of an efficient preceding waterflood at the onset of CO_2 injection may leave high residual oil saturations due to bypassing of oil in dead end/dendritic pores or clusters (Campbell and Orr, 1985). Wettability controls the distribution of fluids in the pore space and may therefore influence the location and presence of water films. A strongly water-wet rock has strong water films and the oil is trapped in the pores. More neutral-wet conditions with some oil-wet surfaces may allow for mixing and diffusion.

The effect of initial water saturation at CO_2 injection onset is investigated experimentally in this Thesis and the results are presented in **Paper 3-6**. The main observations regarding initial water saturation and the influence of wettability are shown in **Figure 17**. Wettability is a key parameter during waterfloods of fractured reservoir as it controls the spontaneous imbibition potential of water from fractures into matrix. Waterflooding as a secondary recovery method is usually very efficient in strongly water-wet (SWW) fractured system, but may be inefficient in near neutral-wet (NNW) systems due to the low potential for spontaneous imbibition. A significant reduction in oil recovery by tertiary CO_2 was observed in fractured systems after efficient preceding waterfloods at SWW compared to NNW conditions. In general, total oil recovery after waterfloods and subsequent CO_2 injection was higher in NNW systems compared to SWW. The oil production rate was also reduced during secondary CO_2 injections with residual water saturation in place. In unfractured systems oil recovery was not observed to be influenced by the irreducible water saturation, likely due to contribution from viscous forces.

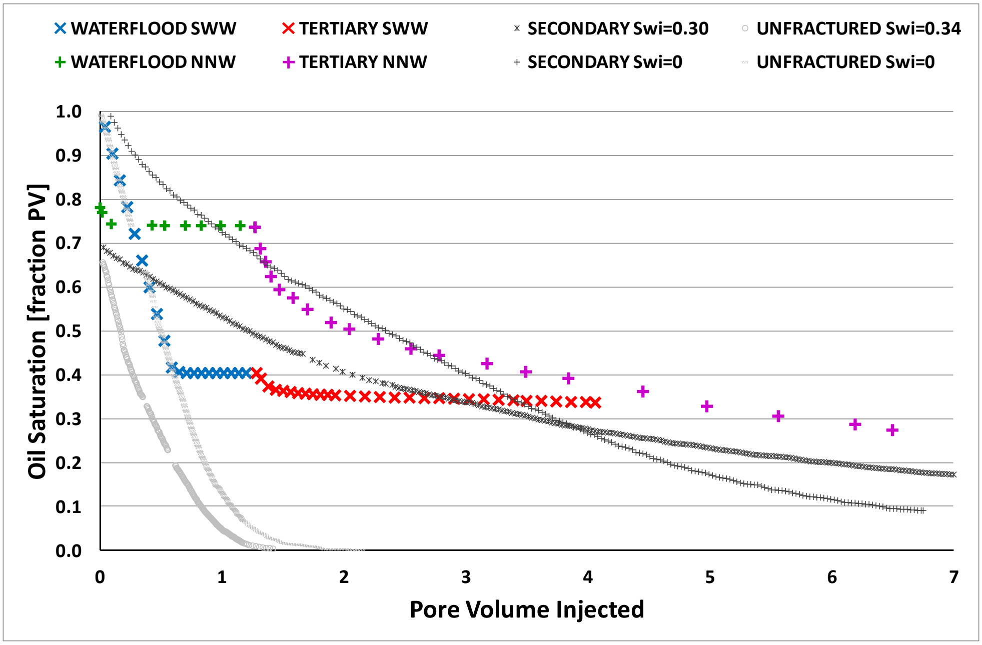

Figure 17. A water shielding effect, reducing the oil recovery efficiency, was observed with increasing water saturation at onset of CO_2 injections. Water shielding was particularly pronounced in tertiary CO_2 injections after efficient waterfloods in strongly water-wet systems.

7.5 Foam-EOR for Mobility Control

Foam can be generated by adding a surfactant solution to the injected gas, the gas phase can be made discontinuous and separated into bubbles by thin liquid films called lamella. The apparent viscosity of CO_2-foam will be larger than pure CO_2, therefore generation of foam will give CO_2 a more favorable mobility ratio relative to oil and water, divert flow to increase sweep and add a viscous component to the oil displacement process. Foam as mobility control may improve conformance control and reduce channeling in high-permeability porous media.

As the experimental data in **Figure 16** clearly demonstrates, CO_2-foam significantly increased the oil recovery rate compared to pure CO_2 in terms of PV injected. The final recovery, however, was not increased in the studied systems because foam does not increase the microscopic displacement efficiency compared with pure CO_2. The mechanism resulting in the accelerated oil recovery during CO_2-foam was the reduction in fracture conductivity that generated a significant differential pressure across the system and added a viscous component to the oil recovery process, in addition to diffusion. A conceptual numerical model, used to simulate foam by decreasing the fracture conductivity, reproduced the experimental data shown in **Figure 18,** and is discussed in more detail in **Paper 6**.

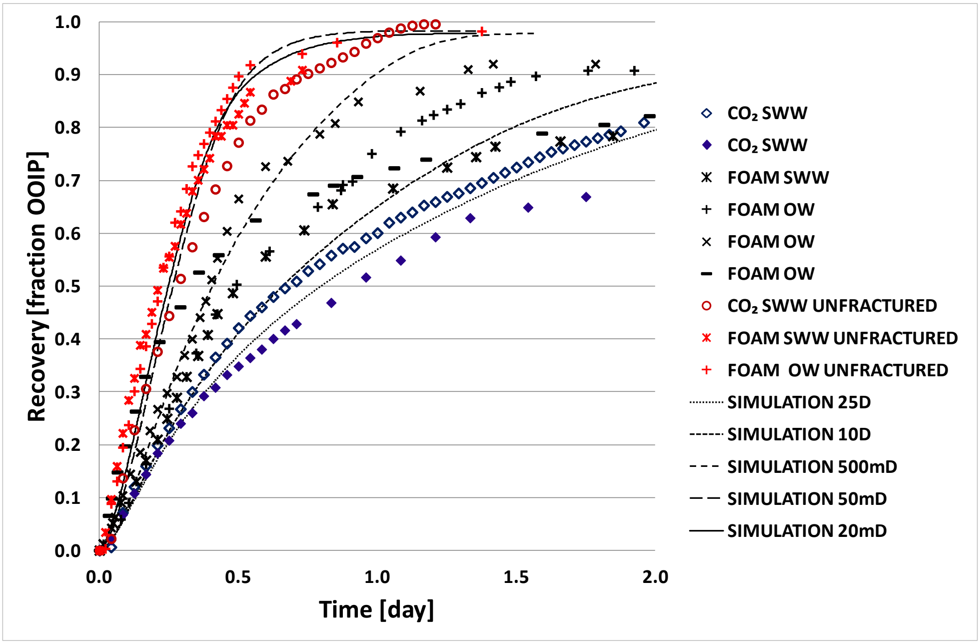

Figure 18. CO_2-foam injections accelerated oil recovery compared to pure CO_2 injections in fractured systems. CO_2-foam injections in fractured systems (black indicators) was more efficient than pure CO_2 injections in fractured systems (blue). Most efficient was CO_2 injections in unfractured systems (red). The simulation data showed an increasing oil recovery efficiency as fracture permeability decreased.

A sequential CO_2 injection strategy was adopted in **Paper 5** with injection of pure CO_2 before CO_2-foam injection. The initial oil production rate decreased rapidly in fractured systems during pure CO_2 injections, and the injection was switched to CO_2-foam injection after 1-2 PV of pure CO_2. The CO_2-foam added a viscous component to the oil displacement process that increased oil recovery rates and final recoveries in all experiments. The increased oil recovery efficiency with foam injections in core samples (Rørdal chalk and Edwards limestone) compared to pure CO_2 is shown in **Figure 19**. An accelerated oil recovery during CO_2-foam was observed in both chalk and limestone, but was more pronounced in limestone. Larger pores and less permeability contrast between fracture and matrix in limestone reduced the entry pressure needed for viscous diversion and invasion of pores and may explain the more pronounced effect observed from CO_2-foam injection in limestone compared to chalk.

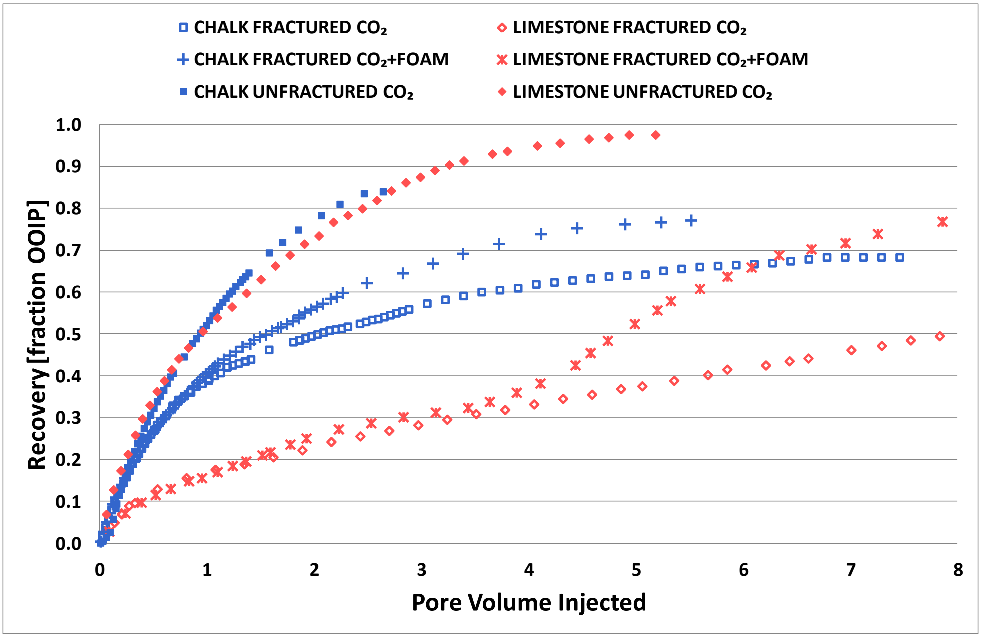

Figure 19. A sequential CO_2 injection strategy, where co-injection of CO_2 and surfactant generating CO_2-foam was initiated after 1-2 pore volumes of pure CO_2 injection, accelerated oil recovery in chalk and limestone rock material. The EOR-effect was higher in limestone, which was likely due to the properties of the rock material.

Tertiary CO_2 and CO_2-foam injections were performed in strongly water-wet Rørdal chalk samples investigated in **Paper 4**. Additional oil recovery by tertiary CO_2 and CO_2-foam injections after waterfloods was up to 15 %OOIP, depending on the efficiency of the preceding waterflood. **Figure 20** shows a comparison of development in oil recovery during tertiary CO_2 and CO_2-foam injection in two core samples with similar waterflood oil recovery of 60 %OOIP. Mobility control by foam accelerated the oil production rate considerably: all additional oil was produced within 0.3 PV injected and reduced the amount of CO_2 needed during CO_2-EOR by more than 1 magnitude compared to pure CO_2 injection.

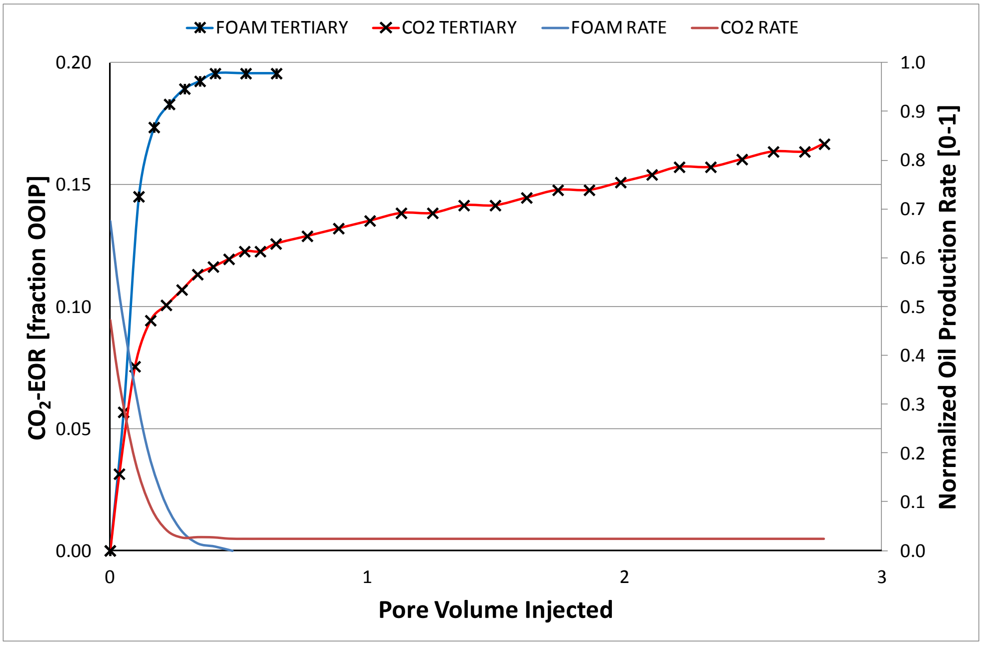

Figure 20. Tertiary CO_2-foam injection and tertiary pure CO_2 injection was performed in two fractured strongly-water-wet core samples with similar waterflood oil recovery of 60%OOIP. Oil recovery was accelerated and reduced the amount of CO_2 injected by more than 1 magnitude to reach final end point oil recovery with CO_2-foam compared to pure CO_2 during the tertiary injection.

8 Conclusions

This Thesis focused on two main objectives: 1) Establish uniform and stable wetting preferences in outcrop core material, and, 2) Investigate CO_2-EOR in fractured reservoirs and evaluate the influence of wettability. The main conclusions are listed below.

- ❖ Laboratory core size experiments may provide useful information regarding EOR-efforts to improve the water-wetting state of the rock surface to increase the potential for spontaneous imbibition of water from fractures into matrix. A wetting preference with a given end point saturation for spontaneous imbibition was established in a rock/oil/brine system with the following method:
  1. A dynamic aging technique using crude oil established uniform, less water-wet preferences in originally strongly water-wet outcrop chalk samples.
  2. By varying the initial water saturation and the length of the aging period a range of different wetting preferences, shown to be stable over several flooding cycles, was established.
  3. A wetting test cycle should be performed to evaluate the wetting preference in terms of wetting index and stability. The aging parameters can be adjusted to induce different wetting preference, which are strongly influenced by rock type, crude oil composition and brine composition.

- ❖ Implementation of EOR-strategies to increase the potential for spontaneous imbibition of water from fractures to matrix are of particular importance in fractured reservoirs with low waterflood recovery. Experimental studies showed that sulfate enriched waterfloods may be an attractive EOR-method to improve the water-wetting state of the rock surface. Key observations from sulfate enriched waterfloods were:
  - ✓ Sulfate enriched brine increased spontaneous imbibition and concomitant oil recovery.
  - ✓ The EOR-efficiency depended on rock type, fluid composition, wettability index and temperature.
  - ✓ The oil composition affected the degree of wettability alteration.

- Laboratory evaluation of secondary, miscible CO_2 injections for EOR in fractured systems demonstrated a very efficient displacement process in terms of final oil recovery, up to 96 %OOIP was recovered. The amount of additional oil recovery during tertiary CO_2 injection after waterfloods depended on the efficiency of the preceding waterflood. The oil recovery process was diffusion dominated with low production rates from the onset of CO_2 injection, rapid breakthrough of CO_2 and a long tail production. The following parameters and conditions were observed to decrease the oil recovery efficiency:
  - ✓ Increasing water saturation.
  - ✓ Increasing diffusion length.
  - ✓ Increasing fracture permeability.
  - ✓ More heterogeneous rock material and higher tortuosity systems.
  - ✓ Oils with heavier hydrocarbon components.

- Foam as EOR-mobility control in fractured systems improves conformance control and reduce CO_2 channeling in high permeable fractures in porous media. The following observations were made:
  - ✓ Low oil recovery in fractured systems was significantly improved with foam injection, which added a viscous component diverting CO_2 from the fractures into the matrix.
  - ✓ Experimental EOR-Foam injection have the following important characteristics compared to pure CO_2 injection: i) accelerated oil production, ii) increased total oil recovery, iii) a more effective displacement (less CO_2 needed), and, iv) enhanced concomitant storage of CO_2.

9 Future Perspectives

The Reservoir Physics Research Group at the Department of Physics and Technology, University of Bergen is currently managing an up-scaling project that uses laboratory data and field pilot tests to prepare for a full-scale CO_2-foam field test. Reservoir cores was cleaned and restored to reservoir conditions. Preliminary results show that tertiary flooding by pure CO_2 was less efficient than expected: CO_2 breakthrough from the cores occurred early and significant volumes of supercritical CO_2 were required to reach the residual oil saturation. Poor macroscopic sweep in the core plugs was caused by large heterogeneities, e.g. micro fractures and vugs, present in the carbonate core material and identified by CT imaging. CO_2-foam floods were implemented as a strategy to reduce the volume of CO_2 injected, and to increase the rate of hydrocarbon recovery. Co-injections of CO_2 and surfactant solution to create foam were performed as a tertiary EOR method directly after waterflooding or after pure CO_2 floods in an integrated recovery strategy. Foam flooding increased tertiary oil recovery and maintained high hydrocarbon production rates for a longer duration of time than pure CO_2. The current focus is to develop a strategy to maximize oil recovery in laboratory experiments in reservoir cores at reservoir conditions with the following objectives: 1. Develop an efficient injection strategy to accelerate oil production and minimize pore volumes of CO_2 injected. 2. Screening of surfactants in reservoir rock/oil/brine system to maximize production and minimise cost.

In-situ imaging by use of X-ray computed tomography (CT), magnetic resonance imaging (MRI), Nuclear Tracer Imaging (NTI) and positron emission tomography (PET) can provide additional information about dynamic fluid flow in porous media that may not be obtained from pressure measurements and material balance only. **Paper A** presents a combined PET-CT imaging of flow processes within porous rocks to quantify the development in local fluid saturations. The same technique could be used to obtain information about in-situ foam generation in fractures by tracing the surfactant water phase and monitor local saturation changes.

Nuclear Magnetic Imaging (NMR) can be used to measure the wettability preference in porous media based on surface relaxation time. The volume of a pore can be divided into a bulk area and a thin surface area. The molecules in the thin surface layer will have a faster relaxation time compared to the molecules in the bulk area. The different relaxation time for oil and water in porous media can provide information about wetting conditions (**Paper B**). A further development of this method to use during EOR-efforts to induce more water-wet states would add valuable information about the laboratory induced wettability, especially at near-neutral wet preferences where the Amott-Harvey method is insensitive.

History match of experimental core data should be performed when building numerical models. These models can be used to simulate EOR injection strategies in up-scaled system to reduce time consuming and expensive laboratory work. A conceptual model is described in **Paper 6** and could be further developed to investigate the influence of different recovery mechanisms such as diffusion and gravity in larger matrix block size.

Nomenclature

EOR	enhanced oil recovery
FCM	first contact miscibility
MCM	multi contact miscibility
MMP	minimum miscibility pressure
NSCO	north sea crude oil
PV	pore volume
OOIP	original oil in place
CO_2	carbon dioxide
f_g	gas fraction
S_{wi}	residual water saturation
S_{or}	residual oil saturation
S_w	water saturation
S_{wsp}	end point water saturation for spontaneous imbibition of water
S_{wsp}	end point water saturation for spontaneous imbibition of oil
S_g	gas saturation
S_o	oil saturation
I_w	Amott water index
I_o	Amott oil index
I_{AH}	Amott-Harvey index
HT	high temperature
T	temperature
SWW	strongly water-wet
NNW	near neutral-wet
OW	oil-wet
SFB	synthetic formation brine
SSW	synthetic seawater
SSW-0S	synthetic seawater added no sulfate
SSW-4S	synthetic seawater added four times the sulfate concentration found in seawater

Bibliography

Ahmed, T.H., 1994. Prediction of CO2 Minimum Miscibility Pressures, SPE Latin America/Caribbean Petroleum Engineering Conference. Society of Petroleum Engineers, Buenos Aires, Argentina

Alavian, S.A. and Whitson, C.H., 2010. Scale Dependence of Diffusion in Naturally Fractured Reservoirs for CO2 Injection, SPE Improved Oil Recovery Symposium. Society of Petroleum Engineers, Tulsa, Oklahoma, USA.

Allan, J. and Sun, S.Q., 2003. Controls on Recovery Factor in Fractured Reservoirs: Lessons Learned from 100 Fractured Fields, SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, Denver, Colorado, USA.

Alvarado, V. and Manrique, E., 2010. Enhanced Oil Recovery: An Update Review. Energies, 3(9): 1529.

Amott, E., 1959. Observations Relating to the Wettability of Porous Rock. Petroleum Transactions, AIME, 216: 156-162.

Anderson, W.G., 1986a. Wettability Literature Survey- Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability J Petrol Technol, 38(10): 1125-1144.

Anderson, W.G., 1986b. Wettability Literature Survey- Part 2: Wettability Measurement. J Petrol Technol, 38(11).

Aspenes, E., Ersland, G., Graue, A., Stevens, J. and Baldwin, B.A., 2007. Wetting Phase Bridges Establish Capillary Continuity Across Open Fractures and Increase Oil Recovery in Mixed-Wet Fractured Chalk. Transport Porous Med, Online First.

Aspenes, E. et al., 2002. Fluid Flow in Fractures Visualized by MRI During Waterfloods at Various Wettability Conditions - Emphasis on Fracture Width and Flow Rate, SPE ATCE, San Antonio, TX, USA.

Aspenes, E., Graue, A. and Ramsdal, J., 2003. In situ wettability distribution and wetting stability in outcrop chalk aged in crude oil. J Petrol Sci Eng, 39(3-4): 337-350.

Austad, T., Strand, S., Madland, M.V., Puntervold, T. and Korsnes, R.I., 2008. Seawater in chalk: An EOR and compaction fluid. Spe Reserv Eval Eng, 11(4): 648-654.

Blaker, T. et al., 2002. Foam for Gas Mobility Control in the Snorre Field: The FAWAG Project.

Blunt, M.J., Fayers, F.J. and Orr, F.M., 1993. Carbon dioxide in enhanced oil recovery. Energ Convers Manage, 34(9-11): 1197-1204.

Brock, W.R. and Bryan, L.A., 1989. Summary Results of CO2 EOR Field Tests, 1972-1987, Low Permeability Reservoirs Symposium. Society of Petroleum Engineers, Denver, Colorado, USA.

Buchanan, J.G., 1998. The exploration history and controls on hydrocarbon prospectivity in the Wessex basins, southern England, UK. Geological Society, London, Special Publications, 133(1): 19-37.

Buchgraber, M., Castanier, L.M. and Kovscek, A.R., 2012. Microvisual Investigation of Foam Flow in Ideal Fractures: Role of Fracture Aperture and Surface Roughness, SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, San Antonio, Texas, USA

Buckley, J.S. and Liu, Y., 1998. Some mechanisms of crude oil/brine/solid interactions. J Petrol Sci Eng, 20(3–4): 155-160.

Buckley, J.S., Liu, Y. and Monsterleet, S., 1998. Mechanisms of Wetting Alteration by Crude Oils SPE Journal, 3(1): 54-61.

Campbell, B.T. and Orr, F.M., Jr., 1985. Flow Visualization for CO2/Crude-Oil Displacements. Society of Petroleum Engineers Journal, 25(05): 665-678.

Castanier, L.M. and Hanssen, J.E., 1995. Foam Field Tests: State of the Art and Critical Review, 8th European IOR Symposium, Vienna, Austria.

Chilingar, G.V. and Yen, T.F., 1983. Some Notes on Wettability and Relative Permeabilities of Carbonate Reservoir Rocks, II. Energy Sources, 7(1): 67-75.

Craig, F.F., 1971. The Reservoir Engineering Aspects of Waterflooding. Monograph Series, SPE, 3, Richardson, Texas.

Cui, L. et al., 2014. Adsorption of a Switchable Cationic Surfactant on Natural Carbonate Minerals. Society of Petroleum Engineers.

Cuiec, L., 1984. Rock/Crude-Oil Interactions and Wettability: An Attempt To Understand Their Interrelation, SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, Houston, Texas, USA.

da Silva, F.V. and Belery, P., 1989. Molecular Diffusion in Naturally Fractured Reservoirs: A Decisive Recovery Mechanism, SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, San Antonio, TX, USA.

Darvish, G.R., Lindeberg, E.G.B., Holt, T., Kleppe, J. and Utne, S.A., 2006. Reservoir Conditions Laboratory Experiments of CO2 Injection Into Fractured Cores. Society of Petroleum Engineers.

Eide, O. et al., 2015. CO2 EOR by Diffusive Mixing in Fractured Reservoirs. Petrophysics, 56(1): 23-31.

Eiken, O. et al., 2011. Lessons learned from 14 years of CCS operations: Sleipner, In Salah and Snøhvit. Energy Procedia, 4: 5541-5548.

Ekdale, A.A. and Bromley, R.G., 1993. Trace Fossils and Ichnofabric in the Kjølby Gaard Marl, Uppermost Creataceous, Denmark. Bull Geol. Soc. Denmark, 31: 107-119.

Elhag, A.S. et al., 2014. Switchable Amine Surfactants for Stable CO2/Brine Foams in High Temperature, High Salinity Reservoirs. Society of Petroleum Engineers.

Enick, R.M., Olsen, D.K., Ammer, J.R. and Schuller, W., 2012. Mobility and Conformance Control for CO2 EOR via Thickeners, Foams, and Gels -- A Literature Review of 40 Years of Research and Pilot Tests, SPE Improved Oil Recovery Symposium. Society of Petroleum Engineers Tulsa, Oklahoma, USA.

Ersland, G., 2008. Studies of flow mechanisms and hydrate phase transitions in fractured rock, Bergen.

Farajzadeh, R., Wassing, B.M. and Boerrigter, P.M., 2012. Foam assisted gas–oil gravity drainage in naturally-fractured reservoirs. J Petrol Sci Eng, 94–95(0): 112-122.

Fernø, M.A. et al., 2014. Experimental Study of Foam Generation, Sweep Efficiency and Flow in a Fracture Network, SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, Amsterdam, The Netherlands.

Fernø, M.A. et al., 2011. Use of Sulfate for Water Based Enhanced Oil Recovery during Spontaneous Imbibition in Chalk. Energ Fuel, 25(4): 1697-1706.

Fernø, M.A., Torsvik, M., Haugland, S. and Graue, A., 2010. Dynamic Laboratory Wettability Alteration. Energ Fuel, 24: 3950-3958.

Firoozabadi, A., 1994. Miscible Displacement in Fractured Porous Media: Part I--Experiments. Society of Petroleum Engineers.

Firoozabadi, A., 2000. Recovery Mechanisms in Fractured Reservoirs and Field Performance. J. Can. Pet. Tech., 39(11): 13-17.

Ghedan, S.G., 2009. Global Laboratory Experience of CO2-EOR Flooding, SPE/EAGE Reservoir Characterization and Simulation Conference, 19-21 October. Society of Petroleum Engineers, Abu Dhabi, UAE

Ghomian, Y., Pope, G.A. and Sepehrnoori, K., 2008. Development of a Response Surface Based Model for Minimum Miscibility Pressure (MMP) Correlation of CO2 Flooding, SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, Denver, CO.

Gomari, K.A.R., Hamouda, A.A. and Denoyel, R., 2006. Influence of sulfate ions on the interaction between fatty acids and calcite surface. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 287(1-3): 29-35.

Graue, A., Aspenes, E., Bogno, T., Moe, R.W. and Ramsdal, J., 2002. Alteration of wettability and wettability heterogeneity. J Petrol Sci Eng, 33(1-3): 3-17.

Graue, A. et al., 2001a. MRI Tomography of Saturation Development in Fractures During Waterfloods at Various Wettability Conditions, SPE ATCE, New Orleans, LA, USA.

Graue, A. et al., 2000a. Complementary imaging techniques applying NTI and MRI determined wettability effects on oil recovery mechanisms in fractured reservoirs International Symposium of the Society of Core Analysts, Pau, France.

Graue, A., Bognø, T., Baldwin, B.A. and Spinler, E.A., 2001b. Wettability Effects on Oil Recovery Mechanisms in Fractured Reservoirs. SPE Reservoir Eval. & Eng., 4(6): 455-466.

Graue, A., Moe, R.W. and Baldwin, B.A., 2000b. Comparison of Numerical Simulations and Laboratory Waterfloods with In-Situ Saturation Imaging of Fractured Blocks of Reservoir Rocks at Different Wettabilities, SPE International Petroleum Conference and Exhibition in Mexico, Villahermosa, Mexico.

Graue, A., Viksund, B.G. and Baldwin, B.A., 1999. Reproducible Wettability Alteration of Low-Permeable Outcrop Chalk. SPE Reservoir Evaluation & Engineering, 2(2): 134-140.

Green, D.W. and Willhite, G.P., 1998. Enhanced Oil Recovery. SPE Textbook Series, 6.

Grigg, R.B. and Schechter, D.S., 1997. State of the Industry in CO2 Floods. Society of Petroleum Engineers.

Harrison, R. and Falcone, G., 2013. Deciding Whether to Fund Either CCS or CCUS Offshore Projects: Are We Comparing Apples and Pears in the North Sea?, SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, New Orleans, Louisiana, USA

Haugen, Å., Fernø, M.A., Graue, A. and Bertin, H.J., 2012. Experimental Study of Foam Flow in Fractured Oil-Wet Limestone for Enhanced Oil Recovery. SPE Reservoir Evaluation & Engineering, 15(2): pp. 218-228.

Hiorth, A., Cathles, L.M. and Madland, M.V., 2010. The Impact of Pore Water Chemistry on Carbonate Surface Charge and Oil Wettability. Transport Porous Med, 85(1): 1-21.

Hirasaki, G. and Zhang, D.L., 2004. Surface Chemistry of Oil Recovery From Fractured. Oil-wet, Carbonate Formations. SPE Journal, 9(2): 151-162.

Hjuler, M.L., 2007. Diagenesis of Upper Cretaceous onshore and offshore chalk from the North Sea area, Technical University of Denmark, Copenhagen, Denmark.

Holm, L.W. and Josendal, V.A., 1974. Mechanisms of Oil Displacement By Carbon Dioxide. Journal of Petroleum Technology, 26(12): 1472-1438.

Hu, H., Whitson, C.H. and Qi, Y., 1991. A Study of Recovery Mechanisms in a Nitrogen Diffusion Experiment, 6th European Symposium on Improved Oil Recovery. Society of Petroleum Engineers.

Hustad, C.W. and Austell, J.M., 2004. Mechanisms and incentives to promote the use and storage of CO2 in the North Sea. European Energy Law Report I: 355-380.

Jamili, A., Willhite, G.P. and Green, D., 2011. Modeling Gas-Phase Mass Transfer Between Fracture and Matrix in Naturally Fractured Reservoirs. SPE Journal, 16(04): 795-811.

Jensen, T.B., Harpole, K.J. and Østhus, A., 2000. EOR Screening for Ekofisk, SPE European Petroleum Conference. Society of Petroleum Engineers, Paris, France

Johannesen, E.B., 2008. NMR characterization of wettability and how it impacts oil recovery in chalk, University of Bergen, Bergen, 1 b. (flere pag.) pp.

Jonas, T.M., Chou, S.I. and Vasicek, S.L., 1990. Evaluation of a C02 Foam Field Trial: Rangely Weber Sand Unit. Society of Petroleum Engineers.

Karoussi, O. and Hamouda, A.A., 2008. Macroscopic and nanoscale study of wettability alteration of oil-wet calcite surface in presence of magnesium and sulfate ions. J Colloid Interf Sci, 317(1): 26-34.

Kovscek, A.R., Tretheway, D.C., Persoff, P. and Radke, C.J., 1995. Foam flow through a transparent rough-walled fracture. J Petrol Sci Eng, 17: 75-86.

Lambert, M.R. et al., 1996. Implementing CO2 Floods: No More Delays!, Permian Basin Oil and Gas Recovery Conference. Society of Petroleum Engineers, Midland, Texas

Lescure, B.M. and Claridge, E.L., 1986. CO2 Foam Flooding Performance vs. Rock Wettability, SPE Annual Technical Conference and Exhibition. 1986 Copyright 1986, Society of Petroleum Engineers, New Orleans, Louisiana.

Li, Z. et al., 2009. Enhance Foam Flooding Pilot Test in Chengdong Of Shengli Oilfield: Laboratory Experiment And Field Performance. International Petroleum Technology Conference.

Lockridge, J.P. and Scholle, P.A., 1978. Niobrara gas in eastern Colorado and northwestern Kansas, Energy Resources of the Denver Basin. Rocky Mountain Association of Geologists, Denver, CO, pp. 35-49.

Lopera Castro, S.H., Restrepo, A. and Ocampo, A., 2009. Use of Divergent Fluids as an Alternative For Enhanced Recovery in Naturally Fractured Cores. Society of Petroleum Engineers.

Martin, D.F. and Taber, J.J., 1992. Carbon Dioxide Flooding. Journal of Petroleum Technology, 44(04): 396-400.

Milter, J., 1996. Ph.D. Dissertation, University of Bergen.

Morrow, N.R., 1990. Wettability and Its Effect on Oil Recovery. J Petrol Technol, 42(12): 1476-1484.

Morrow, N.R. and Burkley, J., 2006. Wettability and Oil Recovery by Imbibition and Viscous Displacement from Fractured and Heterogeneous Carbonates.

Mukherjee, J. et al., 2014. CO2 Foam Pilot in Salt Creek Field, Natrona County, WY: Phase I: Laboratory Work, Reservoir Simulation, and Initial Design, SPE Improved Oil Recovery Symposium. Society of Petroleum Engineers, Tulsa, Oklahoma, USA.

N.E.T.L., 2010. Carbon Dioxide Enhanced Oil Recovery - Untapped Domestic Energy Supply and Long Term Carbon Storage Solution. The Energy Lab.

Nelson, R., 2001. Geologic Analysis of Naturally Fractured Reservoirs. Gulf Professional Publ., Boston.

Panahi, H., 2004. Improving the Recovery Factor of Heavy Crude Reservoirs by Co-injecting CO2 and Other Conventional Gaseous Injecting Materials at Immiscibility Condition with Foam. Society of Petroleum Engineers.

Pancharoen, M., Ferno, M.A. and Kovscek, A.R., 2012. Modeling foam displacement in fractures. Journal of Petroleum Science and Engineering, 100: 50-58.

Pollastro, R.M. and Scholle, P.A., 1986. Diagenetic relationships in a hydrocarbon-productive chalk - The Cretaceous Niobrara Formation, Studies in Diagenesis. Geological Survey Bulletin, pp. 219-236.

Prieditis, J. and Paulett, G.S., 1992. CO2-Foam Mobility Tests at Reservoir Conditions in San Andres Cores. Society of Petroleum Engineers.

Roehl, P.O. and Choquette, P.W., 1985. Carbonate Petroleum Reservoirs. Springer-Verlag, New York.

Ryoo, W., Webber, S.E. and Johnston, K.P., 2003. Water-in-Carbon Dioxide Microemulsions with Methylated Branched Hydrocarbon Surfactants. Industrial & Engineering Chemistry Research, 42(25): 6348-6358.

Salathiel, R.A., 1973. Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks. J. Pet. Tech., 255(10): 1216-1224.

Sanders, A. et al., 2012. Implementation of a CO2 Foam Pilot Study in the SACROC Field: Performance Evaluation, SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, San Antonio, Texas, USA

Seth, S. and Morrow, N.R., 2007. Efficiency of the Conversion of Work of Drainage to Surface Energy for Sandstone and Carbonate. SPE Reservoir Eval. & Eng., 10(4): 338-347.

Skjæveland, S.M. and Kleppe, J., 1992. SPOR - Recent Advances in Improved Oil Recovery Methods For North Sea Sandstone Reservoirs. Norwegian Petroleum Directorate, Chapter 9: 207-250.

Smith, D.H., 1988. Injectivity and Surfactant-Based Mobility Control, Surfactant-Based Mobility Control. ACS Symposium Series. American Chemical Society, pp. 429-438.

Strand, S. et al., 2007. Wettability of chalk: impact of silica, clay content and mechanical properties. Petrol Geosci, 13(1): 69-80.

Strand, S., Høgnesen, E.J. and Austad, T., 2006a. Wettability alteration of carbonates-Effects of potential determining ions (Ca2+ and SO42-) and temperature. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 275(1-3): 1-10.

Strand, S., Standnes, D.C. and Austad, T., 2006b. New wettability test for chalk based on chromatographic separation of SCN- and SO42-. J Petrol Sci Eng, 52(1-4): 187-197.

Talebian, S.H., Masoudi, R., Tan, I.M. and Zitha, P.L.J., 2013. Foam assisted CO2-EOR; Concepts, Challenges and Applications, SPE Enhanced Oil Recovery Conference. Society of Petroleum Engineers, Kuala Lumpur, Malaysia.

Thompson, J.L. and Mungan, N., 1969. A Laboratory Study of Gravity Drainage in Fractured Systems Under Miscible Conditions.

Trivedi, J.J. and Babadagli, T., 2008. Efficiency of diffusion controlled miscible displacement in fractured porous media. Transp Porous Med, 71(3): 379-394.

van Golf-Racht, T.D., 1982. Fundementals of Fractured Reservoir Engineering. Developments in Petroleum Science 12. Elsevier, New York.

Yan, W., Miller, C.A. and Hirasaki, G.J., 2006. Foam sweep in fractures for enhanced oil recovery. Colloids and Surfaces A: Physicochem. Eng. Aspects

Yu, H. et al., 2008. Air Foam Injection for IOR: from Laboratory to Field Implementation in Zhongyuan Oilfield China. Society of Petroleum Engineers.

Zhang, P. and Austad, T., 2005a. The Relative Effects of Acid Number and Temperature on Chalk Wettability, SPE International Symposium on Oilfield Chemistry, Houston, Texas, USA.

Zhang, P.M. and Austad, T., 2005b. Waterflooding in Chalk: Relationship Between Oil recovery, New Wettability Index, Brine Composition and Cationic Wettability Modifier, SPE Europec/EAGE Annual Conference, Madrid, Spain.

Zhang, P.M., Tweheyo, M.T. and Austad, T., 2006. Wettability alteration and improved oil recovery in chalk: The effect of calcium in the presence of sulfate. Energ Fuel, 20(5): 2056-2062.

Zhang, P.M., Tweheyo, M.T. and Austad, T., 2007. Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions Ca2+, Mg2+, and SO42. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 301(1-3): 199-208.

Zuta, J. and Fjelde, I., 2010. Transport of CO2-Foaming Agents During CO2-Foam Processes in Fractured Chalk Rock.

Scientific Papers