Technical University of Denmark



Rock physical aspects of CO₂ injection in chalk



Mohammad Monzurul Alam

DTU Environment Department of Environmental Engineering PhD Thesis April 2011

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The thesis will be available as a pdf-file for downloading from the homepage of the department: www.env.dtu.dk

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Preface

This PhD thesis entitled "Rock physical aspects of CO₂ injection in chalk" is based on the research carried out in parallel to the project "Øget olieudvinding gennem CO₂ udnyttelse (Enhanced Oil Recovery through CO₂ utilization)", financed by Danish Advanced Technology Fund (Højteknologifonden). The work was supervised by Associate Professor Ida Lykke Fabricius at the Department of Environmental Engineering, Technical University of Denmark (DTU). This research has been accomplished in collaboration with DONG Energy, Geological Survey of Denmark and Greenland (GEUS), Danish Geotechnical Institute (GEO) and Department of Chemical Engineering, DTU. The laboratory experiments in this thesis were carried out at DTU, GEO, GEUS, Copenhagen University (Life Science), Imperial College, London and University of Stavanger, Norway. Four months external research (theoretical and experimental) was performed at the Colorado School of Mines, USA under the supervision of Associate Professor Dr. Manika Prasad at the department of Petroleum Engineering.

The thesis consists of a synopsis and six papers. Chapter 4 of the synopsis is written as a substitute for a technical report on "work package 1.1: Monitoring changes in pore-structure and fluid properties as a result of CO_2 injection into hydrocarbon reservoirs" under the research project "Enhanced oil recovery through CO_2 utilization". The papers comprise one published paper, one accepted manuscript, two submitted manuscripts and two peer reviewed extended abstracts, which were not converted into a journal paper due to time constraints. They are placed after the synopsis and marked and cited by roman numbers. In addition an appendix with laboratory results is included and referred to by the roman number VII.

- I *Alam, M.M.*, Borre, M.K., Fabricius I.L, Hedegaard, K., Røgen, B, Hossain, Z and Krogsbøll, A.S., 2010, Biot's coefficient as an indicator of strength and porosity reduction: Calcareous sediments from Kerguelen Plateau. Journal of Petroleum Science and Engineering 70 (2010) 282-297.
- **II** *Alam, M.M.*, Prasad, M and Fabricius, I.L., Permeability prediction in Chalks. Accepted manuscript in AAPG Bulletin.

- **III** *Alam, M.M.*, Fabricius, I.L. and Christensen H.F., Static and dynamic effective stress coefficient of chalk. Submitted to Geophysics.
- **IV** *Alam, M.M.*, Hjuler, M.L., Christensen H.F. and Fabricius, I.L., Petrophysical and rock-mechanics effects of CO₂ injection for enhanced oil recovery: chalk from South Arne field, North Sea. Submitted to Geophysical Prospecting.
- V Alam, M.M., Ahsan, R., Shaik, A. K. and Fabricius, I. L., 2010, Surface charge of calcite and its influence on the electrical conductivity in chalk. Presented in the SEG International Exposition and 80th Annual Meeting, 17–22 October 2010, Denver, Colorado, USA.
- **VI** *Alam, M.M.* and Fabricius, I.L., 2010, NMR as a Tool for Estimation of Excess Conductivity in Chalk. Poster presented in 72nd EAGE Conference and Exhibition, Barcelona, Spain 14-17 June 2010.
- **VII** Appendix with detailed experimental results.

Mohammad Monzurul Alam April 2011

Summary

Enhanced oil recovery by CO_2 injection (CO_2 -EOR) is a tertiary oil recovery process which has a great potential for being used at the same time as an effective technique for carbon dioxide capture and storage (CCS). Impact of supercritical CO₂ on the petrophysical and rock-mechanics properties of Ekofisk Formation and Tor Formation chalk from South Arne field, Danish North Sea, chalk was investigated. Chalk is a carbonate rich sedimentary rock. The chalk of the studied field is characterized by high porosity and low permeability. Injection of supercritical CO₂ increases mobility of the oil in these low permeable chalk and at the same time high porosity provides large storage capacity. However, our current knowledge on the interaction between particles of chalk and CO₂ and its influence on the reservoir characteristics for long time storage is limited. A series of laboratory experiments was performed on core material collected from the reservoir zone of the South Arne field in order to reveal the changes with respect to porosity, specific surface, pore stiffness, wettability, mineralogy and mechanical failure. In addition, a theoretical rock physical background was also established in order to be able to make sensible interpretation of laboratory data.

Sound wave velocity was used as the central tool to study any change in petrophysical and rock mechanical properties. The main focus was to achieve a better understanding of effective stress coefficient (also known as Biot's coefficient); by means of which effective stress can be predicted more accurately. Independent theoretical studies were made on diagenesis, surface properties and stiffness of chalk and their relation with sonic velocity (or Boit's coefficient calculated from sonic velocity). The knowledge and experience from these studies was combined to achieve the main research objective of monitoring changes in hydrocarbon reservoirs in chalk due to CO_2 injection.

In order to understand the development of chalk from calcareous ooze and achieving pore stiffness, the diagenesis process of a sedimentary sequence from Kerguelen Plateau in the Indian Ocean was studied. The principal objective of the study was to explore how different porosity reduction mechanisms change the strength of these deep sea carbonate-rich sediments and how these mechanisms can be traced from the change in Biot's coefficient, α . In calcareous ooze, α was found close to one. Mechanical compaction reduces porosity, but only leads to a minor decrease in α . Recrystallization process renders particles smoother, but do

not lead to reduction in α unless it gives rise to pore stiffening cementation. Pore stiffening cementation causes α to fall, even when porosity remains constant.

Fluid flow mechanism in the pores of chalk was studied by means of a widely used concept of flow zone indicator (*FZI*) and a more realistic model for chalk based on specific surface of the grains (S_g). The aim of the study was to use sonic velocity for permeability prediction. It was found that permeability prediction in chalk can be improved significantly by knowing the approximate specific surface of a stratigraphic sequence.

Reservoir compaction is a result of both elastic and plastic deformation (static), while sound velocity only characterizes elastic properties of rocks (dynamic). Studies on Biot's coefficient suggest that the stress dependence of the static effective stress coefficient, n must be established in order to use 4D seismic data for monitoring reservoir compaction and changes in pore pressure. In addition, an investigation on how static effective stress coefficient, n is related to the dynamic effective stress coefficient (Biot's coefficient), α was made in order to be able to estimate n from sonic velocity data.

Due to supercritical CO_2 injection 2-3% increase in porosity, minor smoothening of particle surface and consequent small increase in permeability and a decrease in elastic stiffness (as indicated by Biot's coefficient) was observed. However, no significant change in wettability was noticed. It was found that the effect of CO_2 injection on both petrophysical and mechanical properties of chalk depend on carbonate content. Pure chalk with high carbonate content is relatively prone to mechanical weakening due to CO_2 injection, while no significant effect was observed in relatively impure chalk of Ekofisk Formation during the span of the experimental study. It was noted that, in spite of mechanical weakening only minor compaction is expected because effective stress is decreased due to an increase in effective stress coefficient.

Extensive time-lapse monitoring strategies are required during a CO_2 -EOR process for the measurement of changes in reservoir properties that may cause deformation of and leakage from a reservoir. Results of this study will provide data for designing future monitoring strategies based on 4D seismic.

Dansk resume

 (CO_2-EOR) olieindvinding ved CO₂ injektion Øget er en tertiær indvindingsteknik, som kan bruges samtidig med CO₂-lagring. I afhandlingen undersøges, hvordan injektion af superkritisk CO₂ påvirker de petrofysiske og bjergartsmekaniske egenskaber af kridt fra Ekofisk og Tor Formationen i Syd Arne feltet i Nordsøen. Kridt er en sedimentær bjergart, der overvejende består af karbonat. I det undersøgte oliefelt har kalken høj porøsitet, men lav permeabilitet. Når superkritisk CO₂ injiceres, øges oliens mobilitet i den lavpermeable bjergart, og samtidig betinger den høje porøsitet stor lagerkapacitet. Imidlertid har vi kun begrænset viden om vekselvirkningen mellem kalkens partikler og CO₂, og om hvordan denne påvirker reservoiregenskaberne i lageret. Derfor blev der udført laboratorieeksperimenter på kernemateriale fra reservoirintervallet i Syd Arne feltet for at måle ændringerne i porøsitet, specifik overflade, porestivhed, fugtpræference, mineralogi og mekanisk styrke. Derudover blev den teoretiske bjerartsfysiske baggrund uddybet som udgangspunkt for tolkningen af laboratorieeksperimenterne.

Hastigheden af elastiske bølger blev anvendt som det centrale redskab til at undersøge ændringer i petrofysiske og bjergartsmekaniske egenskaber. Der blev lagt vægt på at opnå en bedre forståelse af den effektive spændingskoefficient (Biot's koefficient): ved hjælp af denne kan den effektive spænding estimeres med større nøjagtighed. Der blev udført uafhængige teoretiske undersøgelser af diagenese, overfladeegenskaber og stivhed af kalk, og af hvordan disse relaterer til hastigheden af elastiske bølger (eller af Biot's koefficient, som kan beregnes ud fra bølgehastighederne). Resultaterne fra disse undersøgelser blev integreret for at belyse mulighederne for monitering af ændringer af kulbrintereservoirer på grund af CO_2 injektion.

For at kunne forstå udviklingen fra kalkslam til kalk og dermed etableringen af porestivhed undersøgtes diagenesen i en sedimentær lagsøjle i Kerguelen Plateauet i Det indiske Ocean. Hovedformålet var at se, hvordan forskellige porøsitetsreduktionsmekanismer ændrer styrken af disse karbonatrige dybhavssedimenter, og at se, hvordan disse mekanismer kan afsløres ud fra ændringer i Biot's koefficient, α . I kalkslam er α nær en. Mekanisk kompaktion reducerer porøsiteten, men fører kun til en mindre reduktion af α . Rekrystallisering gør sedimentpartiklerne glattere, men fører ikke til reduktion af

 α , med mindre den giver anledning til kontaktcementering. Kontaktcement øger porestivheden og får α til at falde, også selvom porøsiteten forbliver uændret.

Væskestrømning i kalkens porer blev undersøgt ud fra det velkendte "flow zone indicator" (FZI) koncept, der blev sammenlignet med en mere realistisk model for kalk, der bygger på partiklernes specifikke overflade (S_g). Hovedformålet med denne undersøgelse var at introducere brugen af elastisk bølgehastighed til at forudsige permeabiliteten. Resultatet blev, at forudsigelsen af permeabiliten kan forbedres væsentligt, hvis den specifikke overflade af en given stratigrafisk enhed kendes.

Reservoirkompaktion skyldes både elastisk og plastisk deformation (statisk deformation), mens elastiske bølger kun giver elastisk deformation (dynamisk deformation). Undersøgelser af Biot's koefficient tyder på, at det er den statiske effektive spændingskoefficient, n, der skal kendes, for at man kan bruge 4D seismiske data til at monitere reservoirkompaktion og ændringer i poretryk. Derfor undersøgtes det, hvordan den statiske effektive spændingskoefficient, n, afhænger af den dynamiske effektive spædingskoefficient (Biot's koefficient), α , så at n kan estimeres ud fra hastigheden af elastiske bølger.

Injektion af superkritisk CO_2 gav anledning til en porøsitetsstigning på 2-3% samt en mindre udglatning af partikeloverflader. Derfor sås også en mindre permeabilitetesforøgelse og et fald i porestivheden som afspejlet i Biot's koefficient. Derimod sås der ingen ændring i fugtpræference. Virkningen af CO_2 på petrofysiske og mekaniske egenskaber ser ud til at afhænge af kalkens karbonatindhold. Ren kalk med højt karbonatindhold svækkes forholdsvis meget af CO_2 injektion, mens der, i det tidsrum eksperimentet strakte over, kun blev fundet en ubetydelig svækkelse af den relativt urene kalk fra Ekofisk Formationen. Det blev observeret, at der på trods af den mekaniske svækkelse kun blev observeret ubetydelig mekanisk kompaktion ved de geotekniske forsøg. Dette kan skyldes, at den effektive spænding mindskes, når den effektive spændingskoefficient øges.

Det anbefales at bruge 4D seismisk monitering af øget olieudvinding med CO_2 , for at ændringer i reservoiregenskaberne kan opdages, før de fører til deformation af reservoiret og mulig lækage. Resultater fra nærværende undersøgelse giver data til fremtidige moniteringsstrategier baseret på 4D seismik.

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1 Introduction

1.1 Statement of problem

Enhanced oil recovery by injecting supercritical CO₂ (CO₂-EOR) in depleted hydrocarbon reservoirs addresses two global issues at the same time: reducing CO₂ in the atmosphere and increasing oil production. Chalk reservoirs in the Danish North Sea are of particular interest for applying this method. Because of high porosity the storage capacity in these chalk reservoirs are high. On the other hand, conventional oil recovery processes, as waterflooding is less effective in North Sea chalk, especially in Ekofisk Formation chalk, due to the low (<0.5mD) matrix permeability (Blunt et al., 1993; Austad et al., 1998). By injecting supercritical CO₂ in these low permeable reservoirs, a miscible flow of low kinematic viscosity fluid (CO₂ dissolved in oil) is achieved and recovery of oil can be increased by up to 15% (Gozalpour et al., 2005; Darvish et al., 2006; Ferguson et al., 2009; Shaffer, 2010).

However, there is a concern that CO_2 can dissolve in the aqueous phase and produce weak acids which could be a threat for the carbonate frame in chalks and compaction or failure in the reservoir. If this happens there is a possibility to change the reservoir characteristics with respect to porosity, permeability, wettability, stiffness and strength (Plummer and Busenberg, 1982; Wolcott et al., 1989; Wellman et al., 2003; Hawkes et al., 2005; Madland et al., 2006; Xu et al., 2007; Zuta and Fjelde, 2008). These changes may influence the overall productivity from the reservoir and the stability of the reservoir rock, sealing rock and wellbore.

North Sea chalks are composed of nanometer to a few micrometer sized fossils (coccolith fragments or aggregates of coccolith platelets) which is developed from the diagenesis of pelagic calcareous ooze (Scholle, 1977). Due to small particle size, chalk has a homogeneous structure with high specific surface area. A high specific surface of particles means that the solid has large exposure to the fluid. Therefore, the degree of change in the reservoir properties will be high if any reactive fluid is produced due to CO_2 injection.

Hydrocarbon reservoirs in the North Sea chalk are well known for its susceptibility under changed effective stress. Due to a high porosity and low induration, compaction in the reservoir and subsidence at the surface as result of

production induced decrease in pore pressure in the North Sea chalk fields has been reported by several authors (e.g. Hermansson and Gudmundsson, 1990; Kristiansen, 1998; Barkved and Kristiansen, 2005; Tjetland et al., 2007). Effective stress in a reservoir alters both by the change in pore pressure and degree of cementation as indicated by effective stress coefficient (Biot, 1941). Change in kinematic viscosity of pore fluid also affects the stiffness of chalk (Andreassen and Fabricius, 2010).

Geomechanics modeling related to stress and strain associated with reservoir compaction and surface subsidence is required for estimating the stability of a reservoir during CO₂-EOR and for long time storage of CO₂. In addition, permanent monitoring techniques as 4D seismic are required to be applied in a CO_2 injected field. Theoretical background on fluid-chalk interaction as well as laboratory-determined petrophysical and rock-mechanics properties are required for both modeling and monitoring purposes.

Physical properties that are responsible for reservoir stability has been addressed in this project by conducting supercritical CO_2 injection in core plugs collected from the reservoir zone of the South Arne field, North Sea. In addition a theoretical study was made on the relation of these properties with velocity of elastic wave propagation in chalk. The aim of this project is to provide data for rock physical models to describe changes after CO_2 storage and to assess which geophysical method would be suitable for the monitoring purposes.

1.2 Scope of study

Velocity of elastic waves is the primary data available for acquiring information about subsurface characteristics. Therefore, sound wave velocity has been used as the central tool to study any change in petrophysical and rock mechanical properties. In this thesis Gassmann (1951) fluid substitution, Biot (1941) effective stress law, Biot theory of fluid flow in porous medium (Biot, 1956a, b), effective medium model theories (Fabricius, 2003) and modified Mohr-Coulomb (p'-q) failure criteria was applied.

This study can be divided into four parts: 1.) diagenesis and development of pore stiffness (Paper I), 2.) characteristics of the surface properties of the particles in chalk (Paper II, V and VI), 3.) static and dynamic behaviour (Paper III) and 4.) effect of supercritical CO_2 (Paper IV). Both petrophysical and rock-mechanics

effect of CO_2 injection were studied. However, experimental work only related to petrophysical properties were done under this project. For rock-mechanics properties (pore collapse, shear failure, static elastic moduli and creep) experimental data of Hjuler et al. (2010) were used in this study.

In the study on diagenesis and development of pore stiffness (Paper I), calcareous sediments of Kerguelen plateau were used as reference chalk. The primary objective was to understand the pore structure and grain size and shape of chalk and how it changes during burial diagenesis. Biot's coefficient was calculated from sonic velocity and density for water-saturated chalk samples. The change in Biot's coefficient was investigated with respect to the diagenetic processes: mechanical compaction, recrystallization, grain-contact cementation and pore-filling cementation. Furthermore, an experimental study was made on the relation between Biot's coefficient and the stress of pore collapse and creep. How Biot's coefficient influences the rapid porosity reduction during mechanical testing was examined to mimic the rapid compaction of high porosity hydrocarbon-producing reservoirs. This may point to a route for prediction pore collapse in porous North Sea chalk from data on porosity and seismic velocity.

The calcite surface was studied for its influence on fluid flow and electrical current flow (Paper II). Earlier studies of chalk indicate that specific surface of the grains (S_g) tends to be closer to constant for a given stratigraphic unit (Fabricius et al., 2007a). Changes in specific surface affect both permeability and sonic velocity (Alam et al., 2010). The variation of permeability and compressional velocity of sound waves in chalk with the variation in S_g was examined. In addition the applicability of the Flow Zone Indicator (*FZI*) method in chalk that Prasad (2003) had successfully applied in sandstones and limestones was examined. The main objective of this study was to understand the controls on permeability in the high-specific surface area chalks as opposed to the low-specific surface area sandstones and limestones.

The exchangeability property of Ca^{2+} ions from calcite surface was studied for its relation to excess electrical conductivity (Paper V). Nuclear Magnetic Resonance (*NMR*) technique was used to quantify the contribution from the non-calcite and from the calcite fraction to the overall specific surface of chalk (Paper VI). Moreover specific surface of the individual components were compared with the excess conductivity of the chalk in order to identify the component which

contribute most to the overall excess conductivity. Ahsan and Fabricius's (2010) experimental data on synthetic calcite was utilized in this study.

An important aspect of this thesis is to investigate the relationship between static and dynamic properties of rock (Paper III). Variation of physical properties with the change in stress was studied. Dynamic effective stress coefficient calculated form sonic velocity was compared with the static effective stress coefficient measured from the rock mechanical compaction test. An investigation was made to find the effective stress coefficient relevant for rapid change in effective stress state.

Investigating the impact of supercritical CO₂ injection on petrophysical and rockmechanics properties of chalk was the main objective of this project (Paper IV). In order to address this issue, a series of laboratory experiments were performed to gather data to be used for reservoir modeling and provide a better understanding of the interaction between chalk and CO₂ for future monitoring purposes. Porosity, permeability, carbonate content, specific surface, wettability, compressional and shear wave velocity, NMR T_2 relaxation and electrical resistivity. All parameters were measured before and after the CO₂ injection. Experimental data of triaxial compression experiments (Hjuler et al., 2010) on waterflooded (reference) and water/CO₂ injected cylindrical chalk cores were compiled in terms of strength envelopes to detect the effect of CO₂ on the mechanical properties of chalk. Changes in porosity, permeability, stiffness, wettability and strength have been discussed from combined petrophysical and rock-mechanics perspective. Furthermore, moduli calculated from sonic velocity have been compared with two static moduli calculated 1.) from Linear Voltage Deformation Transducer (LVDT) measurement and 2.) strain gauge measurement.

2 Pore stiffness and effective stress

Chalk reservoirs in the North Sea are characterized by high porosity, which could be as high as 50% (Munns, 1985; Andersen, 1995). High porosity of chalk makes it mechanically weak (Teufel and Warpinski, 1990; Ruddy et al., 1989). For instance, chalk from the North Sea reservoir zone demonstrates a significant impact on pore stiffness under changed effective stress state (Ruddy et al., 1989; Hermansson and Gudmundsson, 1990; Pattillo et al., 1998; Kristiansen et al., 2005; Tjetland et al., 2007). Decrease in stiffness causes porosity reduction, reservoir compaction, subsidence at the seafloor as well as increased pressure at the pore space which acts as compaction drive for increased oil production. Thus, pore space stiffness is an important parameter for reservoir simulation to model stability of reservoir under altered condition of pore fluid, overburden stress and pore pressure. Change in pore stiffness and effective stress due to CO_2 injection could be a crucial factor and should be considered in assessing reservoirs in chalk as a CO_2 storage site and for enhanced oil recovery by CO_2 injection (CO_2 EOR).

2.1 Petrography

Chalk is a firm pelagic sediment composed predominantly of CaCO₃ particles, which develops as a result of diagenesis of calcareous ooze. Mazzullo et al. (1988) defined ooze as an unconsolidated calcareous and/or siliceous pelagic sediment. Particles in calcareous ooze are primarily the skeletons of algae called coccospheres. The spherical shaped coccospheres are between 10 and 30 μ m in diameter and composed of 7-20 wheel shaped coccolith platelets of 2 to 20 μ m diameter and 0.5 to 2.5 μ m across (Scholle, 1977; D'Heur, 1984) (Figure 2.1). North Sea chalk is predominantly composed of coccolith fragments or aggregates of coccolith platelets: entire coccospheres are relatively rare (Scholle, 1977) (Figure 2.1c).

Due to the mineralogical and textural similarity with North Sea chalk, in order to understand the diagenetic process and its relation to the development of chalk from calcareous ooze and achieving pore stiffness, a sedimentary sequence from Kerguelen Plateau in the Indian Ocean was studied (Paper I). In Kerguelen Plateau, the upper 660 m of sediments are carbonate-rich, mostly carbonate mudstone with occasional wakestone texture (according to Dunham, 1962 classification) and the porosity ranges from 75% at the top to 25% at the bottom (Figure 2.2). Some intervals are rich in amorphous silica (Opal A), indeed the

amount of non-carbonate fraction exceeds 60% in the top 120 meters (Late Pliocene and Late Miocene). More than 15% non carbonate fraction (mainly amorphous silica) was also found in samples near 340 mbsf (Late Eocene to Early Oligocene) and below 625 mbsf (Santonian to Turonian). High specific surface was found in intervals where the amount of non carbonate fraction is high. This may be due to the high specific surface of amorphous silica and clay.



Figure 2.1: Backscatter micrographs (BSE) of epoxy-impregnated and polished chalk samples from three different places of the world, (a) Kerguelen plateau (Paper I), (b) Ontong Java plateau (Fabricius, 2003), (c) North Sea (Paper IV). The North Sea samples are from oil bearing zone and deeper burial depth (higher temperature). The deep sea samples are normally brine saturated and come from shallower depth. North Sea chalk contains high degree of recrystallization (grain smoothening) as seen in large magnification image (30 μ m×30 μ m).



Amorphorus silica and clay

Large calcite matrix grains (316-3.16 sq. micron) □ Large calcite grains (>316 sq. micron)

Figure 2.2: Backscattered Electron (BSE) images of chalk from Kerguelen Plateau shows variation in porosity and grain size distribution according to depth.

2.2 Porosity

Reservoir compaction is associated with the reduction of porosity due to changed stress state. Diagenetic porosity reduction and preservation were studied in order to determine which kind of porosity reduction is likely to occur during hydrocarbon production and CO_2 storage in chalk.



Figure 2.3: Distribution of grains and porosity and a schematic of the phases of a chalk sample. Intraparticle or large pores, ϕ_l and inter particle or matrix pores, ϕ_s constitute the pores. The solid is composed of large calcitic grains, G_l , small calcitic grains, G_s , other solid minerals, G_{ir} as clay, silica etc. (modified after Røgen et al., 2001).

Porosity is defined as the total void space in the rock relative to the bulk volume. However, the volumetric composition of a chalk sample can be divided into solid phase *G* and porosity, ϕ . The solid phase is composed of large grains, *G_l*, smaller matrix grains, *G_s*, and fine grained insoluble residue, *G_{ir}* (Figure 2.3). The large grains include calcareous microfossils whereas clay minerals, pyrite and silica constitute the insoluble residue. The porosity can be subdivided into large porosity, ϕ_l and small porosity, ϕ_s . Matrix porosity, ϕ_m is the pore space between the small grains, expressed as:

$$\phi_m = \frac{\phi_s}{\phi_s + G_s + G_{ir}}$$
 Eq. 2.1

2.2.1 Porosity change during diagenesis

Several studies were also done on the porosity reduction mechanisms in deep sea carbonate rich sediment: ooze, chalk and limestone (Schlanger and Douglas, 1974; Hamilton, 1976, Scholle; 1977, Wetzel, 1989; Lind, 1993; Bassinot et al., 1993; Borre and Fabricius, 1998; Grützner and Mienert, 1999; Fabricius, 2003). Based on material from Magellan Rise, Schlanger and Douglas (1974) proposed that during the burial diagenesis of carbonate ooze, mechanical compaction reduces the porosity form 80% near the seafloor to 60% at 200 meter below the sea floor (mbsf) transforming the ooze into chalk. Hamilton (1976) indeed found that calcareous ooze of porosity close to 80% compact by mechanical loading, reducing the porosity to 60%. Lind (1993) found that deep sea chalk with matrix porosity down to around 40% may compact by mechanical loading. Schlanger and Douglas (1974) incurred recrystallization as a porosity reducing mechanism, whereas Borre and Fabricius (1998) found that recrystallization only changes the shape of the particles. By recrystallization, irregular and small calcite crystals dissolve and reprecipitate on larger and smoother crystals. Fabricius (2003) found that recrystallization may lead to the formation of contact cement, which counteracts mechanical compaction and thus tends to preserve porosity. Porosity reduction due to chemical action probably takes place by pressure dissolution. Pressure dissolution between calcite crystals in chalk was proposed, but not documented by Scholle (1977), whereas sign of pressure dissolution is observed at stylolites, indicting that pressure dissolution more likely takes place at silicatecalcite contacts as discussed by Fabricius and Borre (2007).

2.2.2 Production induced porosity change

The effective stress of a hydrocarbon reservoir typically increases during primary production of oil and gas or may decrease due to water-flooding. In both cases the stress changes as a result of altering the pore fluid pressure. A high porosity and low induration makes the hydrocarbon reservoirs in chalk relatively susceptible to deformation when subjected to increasing effective stress. Compaction in the reservoir and subsidence at the surface may occur due to this deformation. For example, due to production of oil from Valhall Field of the North Sea, a part of the reservoir has compacted and subsidence of the sea floor has reached more than 5 m and increases by 0.25 m/year (Kristiansen et al., 2005).

The study on chalk from Kerguelen plateau (Paper I) indicates that porosity reduction in chalk subjected to mechanical load is more likely due to the volume change of the small pores (inter-particle porosity). It is in accordance with other geotechnical studies (Valent et al., 1982; Lind, 1993). In the deep sea pelagic carbonates in the Kerguelen Plateau, porosity reduction by compaction and creep takes place by the reduction of the matrix porosity, whereas the large (intra-particle) porosity does not change significantly. However, in geological time scale, the majority of the porosity loss with depth at Kerguelen Plateau was found to be due to the time dependent creep which is a very slow process. Porosity reduction due to the depletion of pore fluid pressure in hydrocarbon reservoir is a fast process. Porosity reduces mainly due to the increase of effective stress in this case. Therefore, results from compaction test should be used to predict compaction in a hydrocarbon reservoir.



2.2.3 Use of sonic velocity for monitoring porosity change

Figure 2.4: Relationship between porosity and compressional wave velocity (V_p) as measured in brine saturated North Sea chalk and a few other sedimentary rocks.

Porosity is considered to be the major controlling factor of the velocity of elastic waves in rocks (Figure 2.4). However, the velocity-porosity relationship is made complicated by the geometric distribution of pores and cements (Prasad, 2003). Based on data from ODP Leg 130, site 807, Fabricius (2003) showed that the porosity-velocity trend changes during the diagenetic process depending on the changes in pore space, grain surface and contact cement between the grains. The study on Kerguelen chalk (Paper I) confirms the finding of Fabricius (2003).

Compressional wave velocity remains almost constant until the ooze starts to transform into chalk. Velocity increases with depth in the chalk interval indicating the growth of grain contact cement. Limestone develops as a result of pore filling cementation. Decrease in porosity and increase of velocity over a short depth interval occurs at the transition between chalk and limestone. Therefore, it may be possible to separate chemical effects from mechanical effects on porosity reduction during CO_2 -EOR from velocity porosity trends.

2.3 Effective stress

Effective stress defines the actual stress the sediment undergoes in a subsurface condition. Stresses arise from the weight of the overlying sediments, σ_{ov} which works downwards due to gravity. On the other hand, in a simple subsurface condition hydrostatic pressure P_p develops in the fluid inside the pore space due to the weight of the fluid. Pore fluid can also be overpressured if it fails to escape when overburden stress increases during the diagenetic process, e.g. due to the presence of a low permeable overlying sediments (seal), as in most hydrocarbon reservoirs. Effective stress in a reservoir is determined by a combination of these two stresses. In the simplest formulation effective stress can be defined as the difference between the overburden stress, σ_{ov} and pore pressure, P_p (Terzaghi, 1923). Biot (1941) gave a robust definition of an effective stress by introducing effective stress coefficient (Biot's coefficient), α :

$$\sigma_{eff} = \sigma_{ov} - \alpha P_p \qquad \qquad \text{Eq. 2.2}$$

2.3.1 Effective stress coefficient (Biot's coefficient)

From a rock mechanics view, pressure in the wetting phase works on the internal surface of the rock. The more the horizontal projection of surface of grains are in contact with the wetting fluid, the more resistance the fluid can offer against the overburden stress. A reduction of the pore pressure effect on the effective stress is caused by an increase in surface contact between the rock grains (Figure 2.5). Biot (1941) characterized this reduction by a effective stress coefficient, α . Terzaghi (1923) studied loose granular sediments, where the contact area among the grain surfaces is negligible and consequently α is close to unity. Therefore the differential overburden stress ($\sigma_{ov} - P_p$) is equal to the effective stress for these sediments. However, most rocks are cemented to some extent and therefore have more stable grain to grain contacts. It makes α less than unity.



Figure 2.5: Conceptual state of stresses in subsurface. Pore fluid works against a fraction, α of the horizontal projection of the grains, when grains are partially connected by contact cement (modified after Fabricius, 2010).

Due to deformation in a rock-mechanics and/or chemical process due to CO_2 injection, there is a possibility of increased or decreased grain contact (softening or hardening behaviour). If this happens, the value of α as well as effective stress will change. In addition, change in effective stress causes deformation of the rock, the degree of which is a function of the stiffness on the porous structure. Thus the mechanical behavior of a rock can be related to α and α may be used as a deciding parameter in reservoir monitoring strategies.

Effective stress coefficient, α can be calculated from the dry bulk modulus, K_{dry} and bulk modulus of the mineral frame, K_o (Biot, 1941; Biot and Willis, 1957):

$$\alpha = 1 - \frac{K_{dry}}{K_0}$$
 Eq. 2.3

Biot's (1941) theory was developed on the basis of linear elasticity and reversible strain. In a linear-elastic isotropic sediment α may ideally be calculated from the density and velocity of ultrasonic sound wave propagation in dry rocks; which produces very small linear elastic strain (Banthia et al., 1965, Todd and Simmons, 1972; Christensen and Wang, 1985; Mavko and Jizba, 1991; Prasad and Manghnani, 1997; Frempong et al., 2007; Mavko and Vanorio, 2010). K_{dry} is calculated from the compressional velocity, V_p and shear velocity, V_s as measured on the dry rock, as well as dry density, ρ_{dry} :

$$K_{dry} = \rho_{dry} V_p^2 - \frac{4}{3} \rho_{dry} V_s^2$$
 Eq. 2.4



Figure 2.6: (a) Thoritical bound for (a) dry bulk moduls and (b) Biot's coefficient. Calcite (bulk modulus K=75 GPa; Mavko et al., (1998)) and air (bulk modulus K= 14.2×10^{-6} GPa) mixed in a rock by assuming a part (*IF*) of the solid to be in the solid frame and the remaining solid to be in suspension. Voigt (1910) defines the stiffest mixing. Critical porosity is considered as 0.7 (Fabricius, 2003) for the plot. If critical porosity is 1, the *IF*=1 line coincide with the modified upper Hashin-Shtrikman bound (Hashin and Shtrikman, 1963; Mavko et al., 2009), and *IF*=0 is equal to the Reuss (1929) bound. (b) Theoretical bounds for effective stress coefficient for the system described in (a). Degree of cementation is indicated by the isoframe curves (IF) (Fabricius, 2003).

2.3.2 Bounds for Biot's coefficient for chalk

The amount of resistance a pore fluid can offer against the overburden stress in a cemented rock frame can be quantified by an effective medium model called isoframe modelling (Fabricius, 2003). By isoframe modelling the solid content of the rock is separate into a suspended portion and a skeleton of cemented grains. The suspended solid portion has no ability to bear load and is treated like a fluid. For porosities lower than critical porosity, ϕ_c the mineral grains start to bear mechanical load (Mavko et al., 1998). If a rock with 100% porosity can still bear a mechanical load, its critical porosity will be 100%. Critical porosity is rarely 100% (Nur et al., 1998) and for North Sea 70% is a reasonable assumption (Alam, 2007). Isoframe modeling allows the determination of theoretical modulus of a rock, using a modified upper Hashin-Strikman bound (Hashin and Shtrikman, 1963) for mixing of a solid frame and a suspension. If compressional wave velocity and bulk density is known, by changing the isoframe value (IF) the theoretical compressional modulus is set equal to the actual compressional modulus. The higher the IF value the higher the grain contact cement and likewise the load bearing capacity of the grains. When large amounts of the

surface area of the grains are in contact, pore fluids get less surface to react against the overburden stress. It makes the effective stress coefficient lower.

The variation of α can be illustrated by means of isoframe model (Figure 2.6) (Fabricius, 2003). For chalk of constant porosity, α decreases as the cementation increases (Olsen et al., 2008a). For poorly cemented chalks (low isoframe value), α does not change significantly with porosity and remains close to unity, whereas for strongly cemented rocks, α decreases rapidly with decreasing porosity (Figure 2.6). Any chemical interaction of chalk with supercritical CO₂ will change the degree of cementation and α will move from one IF curve to another (Figure 2.6). On the other hand if supercritical CO₂ reacts only with the particle surface and increase the porosity α will move along the same IF curve as long as the degree of cementation remains unchanged.

2.4 Static and dynamic effective stress coefficient

Reservoir compaction is monitored by 4D seismic utilizing changes in sonic velocity and changing thickness of reservoir layers. Changing thickness in reservoir (static) is due to both elastic and plastic deformations. In contrast, sound wave propagation (dynamic) characterizes purely elastic behaviour. So the question arises, how accurately deformations in reservoirs due to changes in pore pressure can be predicted by using the dynamic effective stress coefficient (Biot's coefficient). Therefore, a study was made to investigate the relationship between static and dynamic effective stress coefficient (Paper III)

2.4.1 Background study of static and dynamic behaviour

Elastic moduli can be obtained from acoustic measurements often called dynamic moduli and from rock mechanics loading experiments often called static moduli. Numerous studies of elastic rock properties as Young's modulus, Poisson's ratio, bulk modulus and shear modulus, show significant difference between static and dynamic elastic properties (Simmons and Brace, 1965; King, 1969; Cheng and Johnston, 1981; Montmayeur and Graves, 1985; Jizba and Nur, 1990; Tutuncu and Sharma, 1992; Tutuncu et al., 1994; Plona and Cook, 1995; Yale et al., 1995; Wang, 2000; Olsen et al., 2008b; Fjær, 2009). Most authors point to micro-cracks as a major cause of the discrepancy. Other inferred causes include strain amplitude (Simmons and Brace, 1965; Cheng and Johnston, 1981; Plona and Cook, 1995), frequency (Simmons and Brace, 1965; Tutuncu and Sharma, 1992),

viscoelasticity (Tutuncu and Sharma, 1992), inelasticity (Cheng and Johnston, 1981; Jizba and Nur, 1990) and stress path (Montmayeur and Graves, 1985; Yale et al., 1995; Fjær, 2009). Polna and Cook (1995) suggested that crack formation at grain contacts during mechanical loading could significantly deviate the static Young's modulus from the dynamic Young's modulus. Olsen et al. (2008b) suggested that the difference in drainage condition between a static and a dynamic experiment is a major source of difference between measured static and dynamic properties. They pointed out that the correct way of comparing dynamic and static Young's modulus for saturated samples is to compare dynamic Young's modulus to the undrained static Young's modulus.

2.4.2 Stress dependent behavior of Biot's coefficient

Theoretically the effective stress coefficient is well studied (e.g. Geertsma, 1957; Nur and Byerlee, 1971; Todd and Simmons, 1972; Carroll and Katsube, 1983; Mavko and Jizba, 1991; Berryman, 1992; Dvorkin and Nur, 1993; Gurevich, 2004; Ciz et al., 2008). The pressure dependent dynamic effective stress coefficient α is measured by several authors (e. g. Banthia et al., 1965; Todd and Simmons, 1972; Christensen and Wang, 1985; Mavko and Jizba, 1991, Hornby 1996, Prasad and Manghnani, 1997; Frempong et al., 2007; Mavko and Vanorio 2010). In addition Geertsma (1957), Nur and Byerlee (1971), Frempong et al. (2007), Omdal et al. (2009) design an experimental setup and conducted mechanical tests to measure the effective stress coefficient. Although, most studies are made on sandstones, Banthia et al. (1965) studied Austin chalk and Omdal et al., (2009) studied chalk from the Stevns outcrop, Denmark.

Based on laboratory measurements of stress dependent sonic velocity, several authors have noted that α is a function of stress (e.g. Banthia et al., 1965; Todd and Simmons, 1972; Christensen and Wang, 1985; Engstrøm, 1992; Frempong et al., 2007) although in the ideal case α should be constant. Failure to satisfy the assumptions of Biot's (1941) theory, such as, drainage condition, linear elasticity and reversibility could be reasons for non-constant α . Several authors have found that α may be different for different physical properties. Teufel and Warpinski (1990) found different effective stress coefficient for velocity and for permeability. Berryman (1992) derived a set of effective stress coefficients for different physical properties of rocks, such as porosity, permeability, electrical conductivity, pore volume compressibility and bulk compressibility. However, the effective stress that is relevant for compaction and subsidence is the effective

stress coefficient for strain. This static effective stress coefficient n ideally should be determined from rock mechanics tests designed on the basis of the theoretical definition of Biot (1941).

For the 20% porous Austin chalk, Banthia et al. (1965) find that the dynamic effective stress coefficient varies from 0.70 to 0.60 in the differential stress range from 3.5 MPa to 14 MPa. Omdal et al. (2009) defined two different static effective stress coefficients from hydrostatic loading tests; the elastic and the plastic. For the >40% porosity water saturated Stevns chalk, they found that the elastic static effective stress coefficient varies from 0.60 to 0.80 in the differential stress range between 0 MPa and 30 MPa. The plastic effective stress coefficient for the same calk ranges between 0.75 and 0.60 in the same stress range. The most important aspect of their finding is the opposite trend of elastic and plastic effective stress coefficient. While the elastic effective stress coefficient decreases with increasing effective stress the plastic effective stress coefficient decreases (Omdal et al., 2009).



Figure 2.7: Dynamic effective stress coefficient α calculated from velocity data measured in dry chalk core plugs from Valhall field. Porosity of the samples varies between 10% and 40% as indicated by colours. α shows dependency on the confining stress. For the same porosity, α decreases with increasing stress. Variation of α with stress is higher in the high porosity samples .The rate of decrease of α decrease for differential hydrostatic stress above 20 MPa.

A large dataset from the Valhall field (Paper III), North Sea also show a significant variation in dynamic effective stress coefficient in a broad stress interval (Figure 2.7).

2.4.3 Static effective stress coefficient

Studies on Biot's coefficient suggest that the stress dependence of the static effective stress coefficient, n must be established in order to use 4D seismic data for monitoring reservoir compaction and changes in pore pressure. In addition, an investigation on how this stress dependent n is related to α would allow estimation of n from sonic velocity data (wireline logging). If it is possible to establish the relationship between α and n, the prediction of pore pressure will become easier and more accurate. In a related study (Paper III) n was measured from mechanical loading tests and compared with α measured from elastic wave velocities. During mechanical loading n is determined based on Biot's (1941) general theory of three-dimensional consolidation. A relation was derived from Biot's (1941) equations in order to measure n under uniaxial stress conditions (Paper III) as:

$$n=1-\frac{\left(\frac{\partial e_{a}}{\partial P_{p}}\right)_{\sigma_{d}}}{\left(\frac{\partial e_{a}}{\partial \sigma_{d}}\right)_{P_{p}}}$$
Eq. 2.5

where e_a is the axial strain in a one dimensional deformation, P_p is the pore pressure and σ_d is the differential stress.

Laboratory (static) measurements of n indicate that n may change more than 10% for a probably insignificant porosity change of 0.5% (Figure 2.8) (Alam et al., 2009). Their test results show that n increases significantly during an unloading cycle and increases during the loading cycle.

2.4.4 Relationship between dynamic and static effective stress coefficient

Details of the study on dynamic and static effective stress coefficient are presented in Paper III. Mechanical measurement of α indicate that α predicts the effective stress coefficient, *n*, well for chalk with porosity near 30%, and acceptably for chalk with porosity near 40%. However, for rapid change in stress it may be more relevant to use the effective stress coefficient, *n*, derived from mechanical tests rather than α .

2.5 Fluid effect on stiffness

The stiffness of a sedimentary rock can be influenced by the pore fluid. Andreassen and Fabricius (2010) showed that failure in rocks occurs at lower stresses if it is saturated with fluid having lower kinematic viscosity. The fluid effect on the stiffness of rocks can be characterized by Biot's (1956a, b) critical frequency:

$$f_c = \frac{\phi \eta}{2\pi \rho_{\eta} k}$$
 Eq. 2.6

which is calculated from porosity, ϕ , liquid permeability, k, fluid density, ρ_{fl} and viscosity, η . The higher the critical frequency the stiffer is the rock (Andreassen and Fabricius, 2010). The effect is more prominent in low permeability rocks as chalk, as fluid flow is highly controlled by the specific surface due to smaller effective pore radius (Fabricius et al., 2010).



Figure 2.8: Critical frequency (Eq. 2.6) as an indicator of stiffness. Symbols indicate that the rock is saturated with air (dry) (triangles), oil (squares with cross), brine (diamonds) and 30 percent (volume) CO₂ dissolved in oil (circles). Grey data points are Ekofisk Formation samples (permeability <0.5 mD) and black data points are Tor Formation samples (permeability >1 mD). Fluid properties and sample description is given in Paper IV.

Figure 2.8 shows that chalk becomes less stiff at fluid saturated condition compared to dry condition. Due to lower permeability, Ekofisk Formation samples show less fluid effect compared to Tor Formation samples. Samples saturated with live oil with 30% dissolved CO₂ show least stiffness at reservoir condition among the fluid (brine and live oil) saturated samples due to lower kinematic viscosity (η/ρ_{fl}). This suggests that possible decrease in stiffness in chalk due to CO₂ injection may not only be due to chemical interaction but also due to fluid effects resulting from altered viscosity and density.

3 Chalk surface and fluid flow

Due to a smaller particle size (nanometre to a few micrometer), specific surface (surface per volume) of chalk is high (typically $1 \text{ m}^2/\text{g}$ to $10 \text{ m}^2/\text{g}$). As a result, despite high porosity as described in chapter 2, matrix permeability of North Sea chalk is low (a fraction of mD to a few mD). For porosity over 20%, permeability of chalk may be several orders of magnitude lower than that in sandstones (Figure 3.1). The porosity-permeability relationship in North Sea chalk is highly influenced by the non-carbonate fraction (clay and silica) that sometimes determines the specific surface area of chalk (Røgen and Fabricius, 2002). Despite having similar porosity, permeability of North Sea chalk varies up to two orders of magnitude (Figure 3.1). Chalk with high carbonate content (pure chalk) and a porosity above 20% has around 1 mD (10^{-15} m²) permeability. In contrast, permeability of chalk having same porosity but having more than 10% non-carbonate fraction is typically 0.01 mD (10^{-13} m²).



Figure 3.1: Porosity-permeability trends for chalk published in literature. Dark closed and dark open data points are chalk from Tor Formation and Ekofisk Formation of North Sea respectively. Grey closed points represent North Sea chalk, from unknown formations. Limestone and sandstone (samples of Prasad, 2003) are indicated respectively by grey and black dashes with a circle in the middle. Trends for North Sea chalk can be primarily divided into two segments. Sandstone and limestone as studied by Prasad (2003) have significantly higher permeability for a given porosity than North Sea Chalk.

A high specific surface of particles means that the solid has large exposure to the fluid. Alteration in the pore fluids due to CO_2 injection may cause dissolution of the solid phase and/or precipitation of solids, so that the reservoir rock may change with respect to porosity, pore-geometry, permeability, wettability,

stiffness and compaction behaviour (Plummer and Busenberg, 1982; Wolcott et al., 1989; Wellman et al., 2003; Hawkes et al., 2005; Madland et al., 2006; Xu et al., 2007; Zuta and Fjelde, 2008). These changes may influence the overall productivity from the reservoir and the stability of the reservoir rock, sealing rock and wellbore.

A manuscript has been prepared on the studies on permeability and fluid flow (Paper II). Influence of surface charge on calcite surface in aqueous environment is published in conference proceedings as extended abstracts (Paper V; Paper VI).

3.1 Fluid flow in chalk

Due to the unique pore structure of chalk, models of fluid flow in other rocks, as sandstone, may be inappropriate to define fluid flow in chalk. Tortuosity is extensively described in literature to model fluid flow in porous media. Mortensen et al. (1998) found that air permeability in chalk is independent of the type of porosity (e.g. intra-particle, inter-particle) and they suggested a porosity-permeability relationship avoiding the tortuosity.

3.1.1 Conventional concept of flow in porous media

It is widely defined in literature that fluid flow in porous media occurs in a tortuous path (Kozeny, 1927; Carman, 1937; Amaefule et al., 1993), where the length of actual equivalent channel for fluid flow is longer than the physical length of a porous medium (Figure 3.2a). On the more simple assumption that a granular bed is analogous to a group of capillaries parallel to the direction of flow, Darcy (1856) developed a fluid flow equation through porous media:

$$Q = k \frac{A}{\mu} \frac{\Delta P}{l}$$
 Eq. 3.1

where k is permeability, ΔP is the pressure difference over length, l, with cross sectional area A. μ is the dynamic viscosity of the flowing fluid. Darcy's equation is based on Poiseuille's law for the flow of a viscous fluid through a capillary tube:

$$Q = \frac{\pi d_e^4}{128\mu} \frac{\Delta P}{l}$$
 Eq. 3.2

where, d_e is the equivalent diameter of the capillary tube.



Figure 3.2: Conceptual flow through a porous rock. All porosity shown in grey shade. (a) Flow in a tortuous path. Actual equivalent flow length (l_e) is longer than the net travelled distance, due to the curved flow path. (b) Concept of flow path in pore space with high connectivity (adapted form the concept of Mortensen et al., 1998). Branches with dark grey shade are aligned in the direction of flow.

3.1.2 Effective Specific Surface concept of fluid flow in chalk Based on laminar flow of fluid in porous media, Kozeny (1927) derived:

$$k = c \frac{\phi^3}{S^2}$$
 Eq. 3.3
 $k = c \frac{1}{S_g^2} \frac{\phi^3}{(1-\phi)^2}$ Eq. 3.4

where k is liquid permeability (Klinkenberg, 1941), ϕ is porosity and c is Kozeny's constant. Kozeny (1927) found that the value of c is around 0.25. S and S_g are grain surface per unit bulk volume and grain surface per volume of grains, respectively.

For homogeneous, fine-grained sediments like chalk, pores are likely to have high connectivity, so the concept of a torturous flow path is difficult to perceive. In such rocks, in addition to the capillaries parallel to the direction of flow (as defined by Darcy, 1856), there should be capillaries in the directions perpendicular to the flow (Figure 3.2b). Even though the resultant flow occurs only in one direction, fluid flows in all capillaries. Major loss of pressure (according to Poiseuille's law) occurs in the direction of resultant flow. In the direction normal to the direction of pressure drop, fluid flow may be seen as practically instantaneous pressure transfer (Røgen and Fabricius, 2002). This perception could be compared with the process of climbing a hill, where work required for the movement parallel to the horizon is negligible compared to the work required for vertical movement.

Mortensen et al. (1998) used this concept by projecting the pore space into the form of orthogonal interpenetrating tubes. Rocks with high connectivity in pore space could be imagined as a system of such tubes (Figure 3.2a). A part of the porosity in such a system is thus insignificant in the resultant flow due to shielding by solid. Mortensen et al. (1998) quantified the porosity that is active to the flow in a given direction where Poiseuille's law is valid by introducing a porosity dependent $c(\phi)$ (to distinguish from Kozeny's constant c in Eq. 3.3):

$$c(\phi) = \left[4\cos\left\{\frac{1}{3}\arccos(2\phi - 1) + \frac{4}{3}\pi\right\} + 4 \right]^{-1}$$
 Eq. 3.5

Theoretically value of c is 0.5 when all the pores are aligned as parallel tubes in the direction of flow and is 0 when aligned as perpendicular tubes to the flow. This porosity dependent $c(\phi)$ replaces the term c of Kozeny's equation (Eq. 3.3). $c(\phi)$ increases with increasing porosity as visualized by the volume of perpendicular interpenetrating tubes in Figure 3.2b. The point is that this volume increases as porosity increases. Decreasing $c(\phi)$ results in higher shielding effect and will have the same effect in the equation as a conceptual tortuous path with higher actual equivalent travel length (l_e) . The advantage of using the concept of $c(\phi)$ is that it can be predicted directly from ϕ , and does not affect the specific surface term. With porosity dependent c, Kozeny's equation becomes:
$$k = c(\phi) \frac{\phi^3}{S^2} \qquad \qquad \text{Eq. 3.6}$$

Specific surface with respect to the bulk, S and specific surface with respect to pore, S_{ϕ} is calculated as (Borre and Fabricius, 1998):

$$S = (1 - \phi)S_g$$
 Eq. 3.7

$$S_{\phi} = \frac{S}{\phi}$$
 Eq. 3.8

Therefore:

$$k = c(\phi) \frac{1}{S_{g-eff}^2} \frac{\phi^3}{(1-\phi)^2}$$
 Eq. 3.9

where S_{g-eff} is the effective specific surface, which in chalk is similar to or only slightly lower than S_g measured by BET (Mortensen et al., 1998). A high homogeneity at particle scale is probably the reason why chalk permeability in this way may be predicted directly from Kozeny's equation without fitting factors. S_{g-eff} can be calculated from rearranging Eq. 3.9 by using core permeability and porosity measured in the laboratory:

$$S_{g-eff} = \sqrt{c(\phi)} \times \phi \frac{\phi}{(1-\phi)} \sqrt{\frac{1}{k}}$$
 Eq. 3.10

 $S_{g\text{-eff}}$ does not depend on the porosity as it is not a property of the bulk rock but a property of the particles that make up the rock. For homogeneous rocks the variation of effective porosity for flow, due to varying porosity is determined by $c(\phi)$, so for a given porosity, permeability variation can be resolved by the difference of specific surface alone.

3.2 Permeability prediction

In order to monitor fluid flow in a CO_2 injected reservoir time lapse permeability measurement is also required. Permeability is preferably measured in the laboratory on core plugs. However, it is unrealistic to collect core material from a CO₂ injected reservoir. Therefore, prediction of permeability is required from other physical properties of rocks, e.g. porosity, seismic velocity and attenuation. Permeability is classically described as a logarithmic function of porosity. Several authors reported variation in the porosity-permeability relationship, which largely depends on sediment composition and diagenesis (Amaefule et al., 1993; Mortensen et al., 1998; Prasad, 2003; Fabricius et al., 2007a). In order to account for differences in sediment composition Kozeny (1927) described permeability as a function of porosity and specific surface as a physical measure of pore radius. Biot (1956a; 1956b) showed theoretically that velocity of elastic waves in rocks depends on both porosity and pore radius as derived from permeability. The findings of Kozeny and Biot indicate that permeability should be related to sonic velocity.

Velocity of elastic waves is the primary data available for acquiring information about subsurface characteristics as lithology and porosity. Cheap and quick (spatial coverage; ease of measurement) information of permeability can be achieved, if sonic velocity is utilized for permeability prediction. Unfortunately velocity-permeability relationships have received less attention compared to velocity-porosity relationships (Wyllie et al., 1956; Raymer et al., 1980; Nur et al., 1998; Prasad and Dvorkin, 2001; Røgen et al., 2005). Prasad (2003) showed that velocity-permeability relationships exist in various rocks according to hydraulic reservoir units as defined by the Flow Zone Indicator (*FZI*), and that *FZI* may be used in Biot's theory. The concept of *FZI* unit is based on modifying Kozeny's (1927) equation so as to improve the porosity-permeability relationships in sandstones (Amaefule et al., 1993). Also based on Kozeny's (1927) equation, Fabricius et al. (2007a) used V_p/V_s ratio and porosity to estimate permeability in carbonate rocks. Therefore an investigation was made on the use of velocity data to predict permeability (Paper II).

Two methods were applied for permeability prediction from sonic velocities. Relationships between permeability and porosity from core data were first examined by using Kozeny's equation. The data were analyzed for any correlations with specific surface of the grains, S_g and with the hydraulic property defined as Flow Zone Indicator (*FZI*). These two methods use two different approaches to enhance permeability prediction from Kozeny's equation. The *FZI* is based on a concept of a tortuous flow path in a granular bed. The specific surface of grains, S_g concept considers the pore space which is exposed to fluid

flow, and models permeability as resulting from effective flow parallel to pressure drop. The porosity-permeability relationships were replaced by relationships between velocity of elastic waves and permeability by using laboratory data, and the relationships were then applied to well log data.

3.2.1 Flow Zone Indicator (FZI)

FZI describes geometrical distributions of pores and grains, Prasad (2003) used this approach to describe the variations in velocity–porosity relations. The geometrical control of pore volume distribution was found to also describe velocity variations with permeability (Prasad, 2003). FZI concept was originated from Carman's (1937) definition of Kozeny's equation;

$$k = \frac{1}{F_s \tau^2 S_g^2} \frac{\phi^3}{(1-\phi)^2}$$
 Eq. 3.11

where F_s is a dimensionless shape factor and τ is tortuosity defined as the ratio between a conceptual actual flow length, l_a and sample length, $l(\tau = l_a/l)$ (Figure 3.2a). It can be seen that, $1/F_s\tau^2$ replaces Kozeny's constant. It varies with the internal structure of the sediments and thus with specific surface, but may be assumed as fairly constant within the same hydraulic unit (Amaefule et al., 1993). Rearranging Eq. 3.11, Amaefule et al. (1993) addressed the variability of Kozeny's constant as follows:

$$\left[\sqrt{\frac{k}{\phi}}\right] = \left[\frac{\phi}{(1-\phi)}\right] \left[\frac{1}{\sqrt{F_s}\tau S_g}\right]$$
Eq. 3.12
$$\left[RQI\right] = \left[\varepsilon\right] \left[FZI\right]$$
Eq. 3.13
$$\log RQI = \log\varepsilon + \log FZI$$
Eq. 3.14

where *RQI* is called Reservoir Quality Index, ε is the void ratio and *FZI* is described as Flow Zone Indicator:

$$FZI = \frac{1}{\sqrt{F_s}\tau S_g} = \frac{1}{\varepsilon}\sqrt{\frac{k}{\phi}}$$
Eq. 3.15

If permeability and FZI are expressed in mD and µm respectively:

$$FZI = \frac{0.0314}{\varepsilon} \sqrt{\frac{k}{\phi}}$$
 Eq. 3.16

3.2.2 Specific Surface of the Grains, S_q

Surface area of minerals is widely estimated by the nitrogen adsorption technique introduced by Brunauer, Emmett and Teller (Brunauer et al., 1938). In this method surface area, S_{BET} per unit weight is estimated by allowing nitrogen gas to adsorb on the surface of the rock. Knowing the grain density, ρ_g of the minerals, specific surface of the grains, S_g is calculated:

$$S_g = S_{BET} \times \rho_g$$
 Eq. 3.17

3.2.3 Use of sonic velocity for permeability monitoring

It was found that, permeability prediction in chalk, and possibly other sediments with large surface areas could be improved significantly by using effective specific surface of the fluid flow concept (Paper II). Separation into *FZI* unit is appropriate for high permeable sedimentary rocks as sandstones and limestones that have small surface areas.

For low permeability (<10 mD) sedimentary rocks as North Sea chalk, permeability variation for the same porosity rock could be described well by separating into units of specific surface, S_g or into Flow Zones Indicator, *FZI*. Grouping samples according to S_g units and *FZI* units improves the permeability prediction from compressional velocity. S_g unit or *FZI* unit splitting according to lithology enables us to predict permeability within less than a single order of magnitude, while the general porosity-permeability relationship varies up to three orders of magnitude in chalk. If specific surface of a particular chalk unit is known, the velocity-permeability relationship for that unit can be applied to predict permeability directly from the compressional wave velocity. S_g unit splitting could be applied effectively to predict permeability of low permeable chalk. Separation into *FZI* unit may give better results for high permeability (>1 mD) sedimentary rocks.

3.3 Surface charge in chalk

Studies on surface chemistry of chalk demonstrated that Ca^{2+} ions on the calcite surface could be exchanged by other ions, e.g. Mg^{2+} (Zhang et al., 2005; Madland et al., 2006; Ahsan and Fabricius, 2010). Several authors described changes in surface charges of chalk particle due to the change in fluid property (as due to supercritical CO₂ injection) as a reason for water weakening (Pierre et al., 1990; Risnes et al., 2005; Strand et al., 2006; Korsnes et al., 2008). An investigation was made on the source of surface charge, its characteristics and influence on petrophysical properties (Paper V; Paper VI).

3.3.1 Surface charge of clay in chalk

The sheet like structure of clay consists of two to three layers of aluminium octahedral or silica tetrahedral lattices. An excess of negative charge may build inside clay due to the replacement of Al^{3+} ion by Mg^{2+} ions. In order to balance this negative charge a positive ion adheres on the surface of clay. In presence of water, silicate layers in clay become negatively charged and positive current-conducting ions adsorbs to the clay surface, which is known as cation exchange capacity (*CEC*) (Wyllie, 1960).

3.3.2 Surface charge of calcite in chalk

The surfaces of calcite in chalk are primarily rhombohedral crystal surfaces. In the calcite atomic structure, calcium atoms are octahedrally coordinated by oxygen from six different CO₃ groups. Net charge on the unreacted crystal surfaces is zero. In presence of water, electrical charges form in the interface between the calcite surface and water. Several authors reported that in a pure aqueous suspension of calcite, the potential determining ions (PDIs) on the surface are Ca^{2+} and HCO_3^{-} (e.g. Yarar and Kitchener, 1970; Thompson et al., 1989).

3.3.3 Cation exchange capacity and excess conductivity

Archie's (1942) equation is widely used to predict brine (and hydrocarbon) saturation by knowing resistivity of the hydrocarbon bearing rock, R_t and pore water resistivity, R_w :

$$S_w^n = F \times \frac{R_w}{R_t}$$
 Eq. 3.18

where n is called saturation exponent. Formation factor, F indicates the degree of difficulty in electrical current flow due to the pore geometry. F could be estimated by (Archie, 1942):

$$F = \frac{R_o}{R_w} = \frac{1}{\phi^m}$$
 Eq. 3.19

where R_o is the 100% brine saturated rock resistivity, *m* is the cementation factor and ϕ is the porosity. If the rock has *CEC*, the apparent pore water resistivity will be smaller than the actual pore water resistivity, R_w . Therefore, excess conductivity must be considered to calculate hydrocarbons in place.



Clay layer

Figure 3.3: Conceptual film of cations on the surface of chalk containing clay and schematic of water and sodium molecule on the outer surface of clay (adapted from Clavier et al., 1984).

As a clay surface becomes negatively charged in a typical aqueous environment, a diffuse layer is formed near the clay surface where Na^+ ion concentration exceeds *Cl* ion concentration. Clavier et al. (1984) showed that at salinity over 0.4 mol/L, a stable layer of thickness x_H is achieved which transmit electric charge. The apparent excess conductivity due to this layer can be calculated by:

$$C_x = \frac{\beta Q_v}{1 - V_Q^H Q_v}$$
 Eq. 3.20

where β is the counterion equivalent conductivity [2.50 (S/m)/(meq/cm³) for the Na⁺ ion (Clavier et al., 1984)], Q_{ν} is counterion concentration in pore space and V_{O}^{H} is the volume of clay water per unit counterion.

3.3.4 Excess conductivity due to surface charge of calcite

A related study on synthetic calcites show that two Ca^{2+} ions from the calcite surface were replaced by one Mg^{2+} ion from the solution (Ahsan and Fabricius,

2010). *CEC* of synthetic calcite was measured to be between 13 μ Eq/m² and 16 μ Eq/m². Calculated *CEC* of Ekofisk Formation chalk varies between 3 μ Eq/m² and 6 μ Eq/m² and *CEC* of Tor Formation is approximately 2.5 μ Eq/m² (Paper V). Therefore, CEC of calcite has a possibility to take part in the excess conductivity in chalk.

Excess conductivity may be calculated from *CEC* of the total particles in chalk (CEC_{rock}) and specific surface for bulk volume, *S*, by rearranging the formula of Clavier et al. (1984):

$$C_{x} = \frac{\beta \times CEC_{rock} \times SSA \times \rho_{g} \times (1-\phi)}{\phi - S \times x_{H}}$$
 Eq. 3.21

where ρ_g is the grain density and ϕ is porosity. *SSA* is the specific surface area measured by BET method. *CEC*_{rock}, for the North Sea chalk may be expressed as:

$$CEC_{rock} = \left\{ CEC_{ir} \times IR \frac{SSA_{ir}}{SSA} + CEC_{calcite} \times \left(1 - IR \times \frac{SSA_{ir}}{SSA} \right) \right\} \times \left(1 - \phi \right) \quad \text{Eq. 3.22}$$

where CEC_{ir} and $CEC_{calcite}$ are the CEC of non-carbonates and the calcite part of the chalk respectively. *IR* is the fraction of irreducible residue by weight (*IR*=1-CaCO₃ fraction).



3.3.5 Influence of calcite surface on excess conductivity

Figure 3.4: Excess conductivity as a function of (a) non-calcite specific surface, (b) calcite specific surface and (c) total specific surface, each with respect to the total porosity. Filled data point indicates less than 5% non-carbonate fraction and unfilled data points indicate more than 15% non-carbonate.

Although it is widely described in literature that excess conductivity is only due to the *CEC* of clay, it was observed that calcite dominates in determining excess conductivity in chalk. Plots of excess conductivity versus non-calcite specific surface and versus total specific surface show no significant relationship (Figure 3.4a, 3.4c). Excess conductivity rather increases with the increase of calcite specific surface in the total pore space (Figure 3.4b). However, if the chalk contains high amount of smectite clay (as in the highly deviated sample) excess conductivity could be significantly higher than the excess conductivity due to calcite (Figure 3.4b).

4 Petrophysical effect of CO₂ EOR in chalk

This section is prepared as the final report for the project "Enhanced Oil Recovery through CO₂ Utilization" (CO₂-EOR project), financed by the Danish National Advanced Technology Foundation (HTF). This report summarizes the results of experimental study performed for Work Package 1.1: "Monitoring Changes in Pore-Structure and Fluid Properties as a Result of CO₂ Injection into Hydrocarbon Reservoirs" under Project 1: "Fluid-Rock Interactions". The project is a collaboration between DONG Energy, DTU Chemical Engineering, DTU Environment, Danish Geotechnical Institute (GEO) and Geological Survey of Denmark and Greenland (GEUS).

4.1 Material

Chalk from the Ekofisk Formation of lower Paleogene age and the Tor Formation of upper Cretaceous age from the South Arne field of Danish North Sea was studied by means of core material of 4 inch (100 mm) diameter collected from the wells SA-1 and Rigs-1 (Figure 4.1). SA-1 is a deviated well and Rigs-1 is a vertical well. Studied intervals are presented in Table 4.1. One an half inch (37.5 mm) vertical plugs as well as centimetre sized chips and side trims were collected for rock-physical and petrophysical laboratory experiments.



Figure 4.1: (a) Location map of South Arne Field, North Sea. (b) Position of the studied wells within the field, plotted on the top of chalk group depth structure map (Modified after Larsen, 1998).

Well	Depth (m)	Formation	Samples for geophysical tests	Samples for rock-mechanics tests
Rigs-1	2803.9	Ekofisk		<u>RE-06A</u> , RE-08B, RE-09B, <u>RE-10A</u> , <u>RE-12B</u>
Rigs-1	2806.9	Ekofisk		RE-14
Rigs-1	2813.0	Ekofisk	RE-22A, <u>RE-23A</u> , <u>RE-24</u>	
Rigs-1	2816.1	Ekofisk	<u>***RE-26B2</u>	<u>RE-26B1</u> , RE-28A1, <u>RE-29</u> , RE-31
Rigs-1	2840.6	Tor	<u>RT-01, RT-02</u>	
Rigs-1	2844.4	Tor	RT-03	
SA-1	3319.8	Ekofisk	SE-05A	
SA-1	3331.8	Ekofisk	SE-02, SE-03	
SA-1	3381.7	Tor	<u>ST-23A</u> , ST-24A, <u>ST-24B</u> , ** <u>ST-26</u>	ST-25B
SA-1	3390.5	Tor		ST-20
SA-1	3399.7	Tor		<u>ST-16B</u> , ST-17B
SA-1	3408.7	Tor		ST-12B, <u>ST-13B</u>
SA-1	3418.8	Tor		ST-01B, <u>ST-03B</u>
SA-1	3427.7	Tor	* <u>ST-08A</u> , * <u>ST-08B</u>	<u>ST-07</u>
SA-1	3437.8	Tor		<u>ST-04B</u>

Table 4.1: Studied geological interval and lab number of the studied samples. The underlined samples were flooded with supercritical CO₂.

* used primarily as filter for the CO₂ flooding test.

** Flooded with rock-mechanics test set of Tor Formation

*** Flooded with rock-mechanics test set of Ekofisk Formation

4.2 Geophysical analysis on 1¹/₂ inch core plugs

Sixteen $1\frac{1}{2}$ inch (37.5 mm) vertical plugs of variable length were prepared by rotary drilling for porosity, permeability, sonic velocity, electrical resistivity and Nuclear Magnetic Resonance (NMR) transverse relaxation time (T_2) measurements. In addition, porosity, permeability and sonic velocity data were collected from twenty $1\frac{1}{2}$ inch (37.5 mm) vertical plugs, which were used primarily by GEO for rock-mechanics testing. An overview of the studied samples is given in Table 4.1.

Based on test plan established at the beginning of the study, the following procedures were applied to collect data from $1\frac{1}{2}$ inch (37.5 mm) samples.

4.2.1 Test plan

Three groups of samples were selected for sonic velocity, electrical resistivity and NMR measurements (Table 4.2). Each group contains four samples representing each of the studied intervals: SA-1 Ekofisk Formation (SE), SA-1 Tor Formation (ST), Rigs-1 Ekofisk Formation (RE) and Rigs-1 Tor Formation (RT). The test plan was designed so that sonic velocity and electrical resistivity (where possible) could be recorded at initial dry conditions (*Dry-I*), initial brine saturated (S_w -*I*), irreducible water saturated (S_{wir}), residual oil saturated (S_{or}), after supercritical CO₂ injected at reservoir condition (S_{CO2}), cleaned-dry after CO₂ injection (*Dry-F*), and brine re-saturated after CO₂ injection (S_w -*F*).

Condition Dry-I		S _w -I			S _{wir}			Sor			S _{CO2}				Dry-F			S _w -F					
Sample	Velocity Resistivity NMR	Thin section Velocity	Resistivity	Thin section	Velocity	Resistivity NMR	Thin section	Velocity	Resistivity	NMK	Thin section	Velocity	Resistivity	NMR	Thin section	Velocity	Resistivity	NMR	Thin section	Velocity	Resistivity	NMR	Thin section
RE-22A																							
RT-03																							
SE-03																							
ST-24A																							
RE-24																							
RT-01																							
SE-05A																							
ST-24B																							
RE-23A																							
RT-02																							
SE-02																							
ST-23A																							
RE-26B2																							
ST-26																							

Table 4.2: Test design for geophysical measurements. Grey boxes indicate intermediate stages of measurement taken on a sample. Black boxes indicate final test of a sample.

In addition, samples ST-26 and RE-26B2 were processed with samples for rockmechanics tests carried out by Danish Geotechnical Institute (GEO) under the CO_2 -EOR project. Geophysical and petrophysical data were collected on these samples and used as a representative of the other samples from the same formation. Details on processing these samples can be found in Paper IV.

Simulated formation brine (HTF brine) and South Arne crude oil were used as water and oil phase respectively for all samples. Due to low permeability (<0.1 mD), South Arne Ekofisk Formation samples were removed from the process after the S_w -I condition. Among the three groups, Group-1 samples were kept at initial brine saturated condition (S_w -I) and used for reference NMR signal in the wettability study. CO₂ was injected into Group-2 samples at S_{or} condition and

into Group-3 samples at S_{wir} condition. NMR T_2 relaxation time was measured in all CO₂ injected samples before they were cleaned for salt and dried. Porosity and permeability were measured at this final condition to quantify the effect of CO₂ injection on these properties. After sonic velocity measurement in dry condition, these samples were re-saturated with brine. Sonic velocity and electrical resistivity were measured at this condition (S_w -F) and compared with data of the S_w -I condition.

4.2.2 Cold flush cleaning

The 1¹/₂ inch vertical plugs were first cleaned for salt and hydrocarbons by cold flush cleaning method with a mixture of methanol and toluene. The plugs were mounted in a Hassler core holder and a confining pressure of 400 psi (2.75 MPa) was applied. The liquids were flushed through the sample with a positive displacement pump. Each step in a cleaning cycle may require a liquid throughput of 5-20 pore volumes or until the effluent is free of salt and colorless. Methanol and toluene were used for the removal of salt and hydrocarbons respectively. Clean samples were dried in an oven at 55°C for two days.

4.2.3 Grain density and porosity

The grain density and porosity was measured on cleaned and dried plugs by a helium porosimeter. The He-porosimeter measures the grain volume V_g of the sample. The empty sample container of the porosimeter has a volume V_s before the sample is inserted. A reference volume V_r is filled by helium and the pressure P_r is recorded. The gas is expanded from the reference volume to the sample container and the resulting pressure P_X is recorded. The grain volume is determined by applying Boyles low: $P_1V_1 = P_2V_2$ or $P_rV_r = P_X(V_r+V_s-V_g)$.

The sample mass *m* was obtained by using an electric balance (± 0.01 gram accuracy) and the grain density ρ_g was calculated. The total volume of the sample V_t of the oven dried (24 hours at 60°C) sample was calculated form the length *l* and diameter *d* as measured by a calliper (accuracy ± 0.05 mm):

$$V_t = \frac{\pi}{4} d^2 l \qquad \text{Eq. 4.1}$$

Dry density was calculated as:

$$\rho_d = \frac{m}{V_t}$$
 Eq. 4.2

Grain density was calculated as:

$$\rho_g = \frac{m}{V_g}$$
 Eq. 4.3

Helium porosity, ϕ was calculated as:

$$\phi = \frac{V_t - V_g}{V_t}$$
 Eq. 4.4

4.2.4 Gas permeability

The permeability is defined by Darcy's law:

$$q = -\frac{k\Delta PA}{\mu l}$$
 Eq. 4.5

where q is the velocity of flow through the sample, k is permeability, ΔP is pressure drop along sample, μ is the absolute viscosity and l is sample length.

Cleaned and dried plug was mounted in a Hassler core holder, and a confining pressure of 400 psi was applied to the sleeve. Nitrogen gas pressures of 3, 5 and 8 atm (0.3, 0.5, 0.8 MPa) (abs) were applied at the upstream end of the plug, and the downstream pressure was regulated until a suitable flow was obtained. The differential pressure was kept approximately constant in order to maintain a similar flow regime during the 3 measurements. When a steady state was reached, the upstream pressure, the differential pressure across the plug and the flow reading were recorded. A linear regression of permeability on inverse mean pressure was performed for the 3 measurements, and the intercept on the permeability axis is the Klinkenberg corrected gas permeability.

A permeability value pertaining to a mean pressure of 1.5 atm. (abs) was calculated from the Klinkenberg regression coefficients. This value was recorded as gas permeability.

4.2.5 Establishing experimental condition

Based on initial porosity, permeability, specific surface and sonic velocity data suitable experimental conditions for sonic velocity, electrical resistivity, irreducible water saturation and fluid flow rate in core plugs was defined before initiating the measurement process.

4.2.5.1 Stress condition for sonic velocity and electrical resistivity measurement

Stress in the horizontal direction in a reservoir is a fraction of the vertical stress. Therefore, a uniaxial confined compression is the most suitable condition in order to mimic the actual reservoir stress on rock. The relationship between radial stress (σ_r) and axial stress (σ_a) for linear elastic media can be expressed by means of Poisson's ratio (ν) (Teeuw, 1971):





Figure 4.2: Poisson's ratio of South Arne field as calculated from sonic velocity measured under uniaxial unconfined condition (Eq. 4.7).

In order to establish a uniaxial condition similar to the South Arne field, Poisson's ratio was calculated from sonic velocity measured under uniaxial unconfined compression:

$$\nu = \frac{V_p^2 - 2V_s^2}{2(V_p^2 - V_s^2)}$$
 Eq. 4.7

where V_p is the compressional wave velocity and V_s is the shear wave velocity. Calculated Poisson's ratio ranges mostly between 0.20 and 0.30 (Figure 4.2). However, for simplicity it was decided to apply a general $v \approx 0.25$. For this v:

$$\sigma_r = 0.33\sigma_a$$
 Eq. 4.8

A generalized radial to axial stress ratio also ease establishing a better control over the radial stress, as the pump for controlling radial stress was semiautomatic. The pump requires adjusting manually with the change in stress level. By using a constant stress ratio for all samples it is possible to control the pump based on experience so that the desired ratio between radial and axial stress can be maintained continuously.

4.2.5.2 Irreducible water saturation to be used during CO₂ flooding

In a water wet system, at irreducible water saturation all the particle surface exposed to pores (S_{ϕ}) will be covered by a film of water. The samples collected for testing vary with respect to porosity and permeability (Figure 4.3), so in order to obtain a common water film thickness in pores during CO₂ injection, a common water saturation for all samples cannot be applied. A suitable water saturations was estimated by using the pseudo water film thickness (PWFT) model of Larsen and Fabricius (2004). From logging data and conventional core analysis data specific surface of the pores was calculated as:

$$S_{\phi} = \sqrt{\frac{c\phi}{k_l}}$$
 Eq. 4.9

where ϕ is porosity and k_l is liquid permeability. When gas permeability (k_g) data is available k_l can be calculated as (Mortensen et al., 1998):

$$k_l = 0.25 (k_g / \text{mD})^{1.083} \text{ mD}$$
 Eq. 4.10

for North Sea chalk and the factor c may be approximated as a function of porosity (Mortensen et al., 1998):

$$c(\phi) = \left[4\cos\left\{\frac{1}{3}\arccos(2\phi - 1) + \frac{4}{3}\pi\right\} + 4 \right]^{-1}$$
 Eq. 4.11



Figure 4.3: Water saturation from log analysis compared to the water saturation recommended for CO_2 flooding, as well as resulting calculated pseudo water film thickness (PWFT); (a) for Rigs-1 well, (b) SA-1 well. Porosity and permeability used for PWFT calculation are given in (i) and (ii). Large black dots are measurements taken in this project. Small circles and dots are core data collected from Geological Survey of Denmark and Greenland (GEUS) core lab database. Permeability indicated by closed data points is measured in the vertical direction whereas open data points represent measurements in the horizontal direction.

Pseudo water film thickness (PWFT) is then calculated from S_{ϕ} and water saturation at irreducible condition, S_{wir} , by (Larsen and Fabricius, 2004):

$$PWFT = \sqrt{\frac{S_{wir}}{S_{\phi}}}$$
 Eq. 4.12

Larsen and Fabricius (2004) found that PWFT is not constant but decreases with increasing capillary pressure. Water saturation and PWFT for Rigs-1 and SA-1 are presented in Figure 4.3. The water saturation of SA-1 and Rigs-1 was

assumed irreducible and that the generally higher PWFT in Rigs-1 was assumed to be the result of lower capillary pressure in that well. So a common PWFT of approximately 20 nm for all samples were selected and S_{wir} was calculated for individual samples corresponding to this PWFT.

4.2.5.3 Injection rate required to avoid worm holes resulting from CO_2 injection.

Previous laboratory test series on carbonates experienced the formation of wormholes, making the interpretation of test results difficult (e.g. Hoefner and Fogler, 1989; Egerman et al., 2005; Lombard et al., 2010). Thus, to avoid wormholes, a suitably low CO_2 injection rate was estimated for this project.



Figure 4.4: Dissolution patterns caused by transport of a reactive fluid in a porous medium. The raise of different dissolution patterns may be described as a function of the Damköhler, *Da*, and Peclet, *Pe*, numbers.

Transport of fluid in a reactive porous medium can result in dissolution of the solid phase. The geometric pattern of dissolution is controlled by flow rate and rate of reaction (Egerman et al., 2005). Where transport of the fluid is the limiting factor, compact dissolution takes place. Where rate of reaction is the limiting factor, uniform dissolution throughout the pore space dominates. Where both factors play a significant role, worm holes may arise (Figure 4.4).

In order to facilitate interpretation of geophysical data after CO_2 injection, uniform dissolution is required. The reactive transport may be described in terms of the Peclet number (*Pe*) and the Damköhler number (*Da*). *Pe*, describes the time for diffusion relative to time for convection and *Da* describes time for convection relative to time for dissolution. Time for diffusion relative to time for dissolution is thus described by the product *PeDa*.

For simplicity and to be on the safe side, injection of a strong acid was assumed. *Pe* and *PeDa* was calculated as functions of injection rate to find a suitable injection rate which will not create wormholes. According to this interpretation, injection rates should be below 6 m/s (10 ml/hr for a $1\frac{1}{2}$ inch plug).

4.2.6 Saturating fluid

Simulated formation brine (HTF brine) was used as the aqueous phase. Depending on the purpose (described later) South Arne crude oil (dead oil) or South Arne live oil (recombined oil) or Isopar-L was used as hydrocarbon phase. Fluid properties are listed in Table 4.3.

Table 4.3: Properties of the used fluid at ambient conditions (15°C/0.1 MPa) and at South Arne reservoir condition (115°C/38 MPa).

Fluid	Densi	ty (g/cm ³)	Viscosity (cP)			
	15°C (atm.)	115°C (38 MPa)	15°C (atm.)	115°C (38 MPa)		
Simulated formation brine (HTF brine)	1.065	1.028 ^b	0.779	0.36 ^b		
South Arne stock tank oil	0.845	-	13.5	-		
South Arne live oil	-	0.63 ^c	-	0.25 ^c		
Isopar-L	0.779 ^c	-	1.29 ^c	-		
Supercritical CO ₂	-	0.71 ^c	-	0.06 ^c		
^a Supercritical CO ₂ in SA-1 live oil	-	0.67 ^c	-	0.21 ^c		

^a 30 (mol%) CO₂ at 115°C and 38 MPa, ^b Calculated by Batzle and Wang (1992) equations and ^c Yan and Stenby (2010).

4.2.6.1 South Arne synthetic brine (HTF brine)

According to the field operators, formation brine composition in the South Arne field is variable and a perfect match with the actual composition of the water in the Rigs-1 and SA-1 wells cannot be expected. For this study brine (HTF brine) was prepared on the basis of a water analysis from well SA-2 from the South Arne field (Table 4.4). The water composition was modified relative to the SA-2 analysis as follows:

- 1) The water analysis is not stoichiometric and to be used as a recipe some Cl⁻ were omitted.
- 2) Sr²⁺ and Ba²⁺ are omitted together with an appropriate amount of Cl⁻ to avoid precipitation of celestine, strontianite, barite and witherite.
- 3) Fe (total) was omitted because; in the experimental work it was not possible to control oxygen fugacity.
- 4) Al^{3+} was omitted because the amount is insignificant.
- 5) B^{3+} was omitted because of lack of experience with this component.
- 6) Si⁴⁺ was omitted because; in order to make it soluble in water it is necessary to add components that are not included in the analysis.
- 7) SO_4^{2-} was omitted to avoid precipitation of sulphate minerals.

An amount of $CaCO_3$ could precipitate from the solution during mixing. The water was filtered and the amount of precipitate was quantified.

Element	SA-2 Water	Simulated formation brine (HTF brine)								
	analysis (mg/l)	Compound	Compound g/l	Concentration mg/l	Concentration mol/l					
Na⁺	31021	NaCl	78.847	31016	1.3491					
		NaHCO ₃	0.018	5	0.0002					
K^{+}	522	KCI	0.995	522	0.0134					
Mg ²⁺	665	MgCl ₂ .6H ₂ O	5.562	665	0.0274					
Ca ²⁺	5667	CaCl ₂ .2H ₂ O	20.788	5667	0.1414					
Sr ²⁺	461	-	-	-	-					
Ba ²⁺	627	-	-	-	-					
Fe(total)	30	-	-	-	-					
Al ³⁺	2	-	-	-	-					
B ³⁺	106	-	-	-	-					
Si ⁴⁺	31	-	-	-	-					
Cl	64040	-	-	60270	1.7000					
HCO3 ⁻	500	-	-	13	0.0002					
SO4 ²⁻	17	-	-	-	-					

Table 4.4: Composition of synthetic brine: salinity 90423 ppm and resistivity 0.077 Ω m at 25°C.

4.2.6.2 Supercritical CO₂

Above the critical point of 31°C and 7.3 MPa, CO₂ behaves as a gas with liquidlike density, which is known as supercritical CO₂. At this condition CO₂ dissolves in the hydrocarbon phase and creates a mixed fluid of lower absolute viscosity and higher density than the original hydrocarbon phase. For South Arne recombined oil (live oil) supercritical CO₂ injection at South Arne reservoir conditions (115°C) increases density from 0.63 g/cm³ to 0.67 g/cm³, while decreasing the viscosity from 0.25 cP to 0.21 cP. 30 (mol %) of CO₂ is dissolved in the oil phase at this condition (Yan and Stenby, 2010). Details of the behavior of supercritical CO₂ dissolved in South Arne live oil are reported by Yan and Stenby (2010).

4.2.7 Saturation processes

Samples were saturated according to the test plan (section 4.2.1). How the desired saturation was achieved is described in the following sections.

4.2.7.1 Initial water saturation

All samples were first saturated with HTF brine aiming at 100% saturation. A vacuum procedure was used for initial brine saturation. Samples were placed in

desiccators and vacuum were created by a water pump while brine was poured into the desiccators gradually until the samples were covered with brine. To increase degree of saturation, while these samples were immersed in brine they were pressurized in a pressure chamber with elevated pressure of 1600 psi (11 MPa) for 3 days. Afterwards the degree of saturation was tested by the Archimedes method. The samples were subsequently subjected to primary drainage, water flooding and CO_2 injection.

4.2.7.2 Irreducible water saturation

To obtain irreducible water saturation (S_{wir}) the brine saturated samples were mounted in a core holder and were heated at 80°C for 2 days to establish uniform reservoir temperature. Holding the sample at 18 barg (1.8 MPa) sleeve pressure, at least 1.9 pore volume of South Arne Crude oil at room temperature (23°C) was then flushed through the samples at a rate of less than 0.5 ml/h to achieve an uniform distribution of the oil phase throughout the sample. Samples were then aged at 80°C for 24 days at 18 barg (1.8 MPa) sleeve pressure. Afterwards, samples were flushed with at least 2.3 pore volume of oil at a rate of less than 0.5 ml/h at a temperature of 23°C and sleeve pressure of 18 barg (1.8 MPa). By this operation any gas evolved during the ageing should be removed from the pores. Archimedes test was then done in oil to calculate oil saturation.

4.2.7.3 Residual oil saturation

To obtain residual oil saturation by waterflooding (S_{or}), the following procedure was followed: Mounted in a core holder the samples at S_{wir} were heated at 80°C for 2 days. The samples were then flushed with degassed HTF brine. The oil produced from each core holder was collected. Differential pressure over samples was aimed not to surpass 5 bar (0.5 MPa). The flushing of each sample was completed with brine flow for 1 day at 2 ml/h, if allowed by the differential pressure. Archimedes test was done in HTF brine to calculate brine saturation.

4.2.7.4 CO₂ injection

The injection experiments were conducted in a reservoir condition rig utilizing a Hassler-type core holder for 1.5" (37.5 mm) plugs with a floating end piece, a number of pressure cylinders for the experimental fluids, two acoustic separators for quantifying the fluid production, a differential pressure transducer for measuring the pressure difference across the sample, a densitometer, and a high pressure pump system for generating confining pressure, flow and pore fluid

pressure. Details of the experimental setup are given in Olsen (2010). A series of samples were placed in a core holder. Plugs were mounted with increasing permeability towards the outlet end of the core holder to form a composite core. A good fit between the individual samples is aimed to assure good capillary contact. The core holder with core plugs was mounted in a vertical position and CO_2 injection was performed vertically from the bottom of the stacked samples towards the top. The injection experiments were conducted at 380 bara (38 MPa) pore pressure, 500 bara (50 MPa) hydrostatic confining pressure and a temperature of 115°C.

For the present study, the objective of CO_2 injection was to identify the changes in chalk when CO_2 is injected into an already waterflooded field and when CO_2 is injected from the beginning of production. Therefore a group of irreducible water saturated and a group of residual water saturated (waterflooded) samples were placed in the rig. In addition filter samples were placed at the inlet and at the outlet in order to minimize possible back-flow and saturation end effects.

Arrangement of samples: (inlet) ST-08B » ST-24B » RE-24 » RT-01 » RE-23A » ST-23A » RT-02 » ST-08A (outlet).

After mounting the samples in the core holder, the core holder was mounted in the reservoir condition rig. Temperature, fluid pressure and hydrostatic confining pressure were increased simultaneously until reservoir pressure conditions were achieved. Samples were held at this condition for one week. The composite core was then injected with 352.5 ml (2.83 PV) supercritical CO_2 at a rate of 2 ml/h.

4.2.7.5 Final water saturation

After necessary data collection CO_2 injected samples were cleaned for salt and oil and re-saturated with HTF brine using the same procedure as described in section 4.2.7.1.

4.2.8 Data collection and analysis

Sonic velocity, electrical resistivity and NMR T_2 data were collected by laboratory measurement at various stages as defined in section 4.2.1.

4.2.8.1 Sonic velocity measurements

Measurements were taken by placing the sample between the two pistons of a loading frame and inside a triaxial cell (Figure 4.5). Maximally 4 MPa axial stress was applied in loading/reloading cycles while pore pressure was kept atmospheric. Each test contains four cycles: (i) loading to 3 MPa axial steress, (ii) unloading to 1 MPa axial steress, (iii) Reloading to 4MPa axial steress, and (iv) unloading to atmospheric condition. In all cycles the radial stress was controlled to satisfy Eq. 4.8. Reservoir rocks are subjected to both vertical and lateral stress as well as high pore pressure (overpressure) in the North Sea Chalk reservoirs. To simulate reservoir stress in a laboratory experiment, only requires the application of the differential stress (total stress minus pore pressure) instead of the actual stresses (Teeuw, 1971). The effective vertical stress in South Arne is between 10 MPa and 20 MPa. However, the velocity variation in North Sea chalk samples was found to be less than 3% between 4 MPa and 11 MPa (Borre and Fabricius, 2001). Therefore, a maximum axial stress of 4 MPa was used in order to avoid damage to the sample as the same sample was used repetitively (Table 4.2).



Figure 4.5: Experimental setup for sonic velocity and resistivity measurements.

Compressional wave velocity V_p and shear wave velocity V_s were measured by recording the travel time of a transmitted ultrasonic wave at 200 KHz through a sample of known length. Travel time was calculated from the first break for P-wave and from the zero crossing for the S-wave (Figure 4.6). Overall accuracy of the measurement is ±50 m/s for P-waves and ±100 m/s for S-waves.



Figure 4.6: Selection of arrival time indicated by a circle, (a) P-wave at first break, (b) S-wave at zero crossing. $S_{average} = (S1+S1)/2$. Shear wave value used for further calculations is $S_{average}$.

4.2.8.2 Modulus and Biot's coefficient from sonic velocity

Biot's coefficient, α was calculated from bulk modulus of the mineral frame, K_{dry} and bulk modulus of the mineral, K_o :

$$\alpha = 1 - \frac{K_{dry}}{K_0}$$
 Eq. 4.13

 K_{dry} is calculated from the compressional velocity, V_p and shear velocity, V_s , as measured on the dry rock, as well as dry density, ρ_{dry} :

$$K_{dry} = \rho_{dry} V_p^2 - \frac{4}{3} \rho_{dry} V_s^2$$
 Eq. 4.14

From V_p and V_s measured on rocks saturated by a fluid, K_{dry} may be calculated by using Gassmann (1951) fluid substitution:

$$\frac{K_{sat}}{K_0 - K_{sat}} \approx \frac{K_{dry}}{K_0 - K_{dry}} + \frac{K_{fl}}{\phi(K_0 - K_{fl})}$$
 Eq. 4.15

where K_{sat} is the bulk modulus for the saturated rock and K_{fl} is the modulus of the saturating fluid.

4.2.8.3 Electrical resistivity measurements

Experimental setup for electrical resistivity measurements is shown in Figure 4.5. The electrical resistance of the samples was measured at 23°C simultaneously with velocity, from a variable resistor connected in series with the sample in a 1 kHz AC circuit of 1 volt power supply. As current flows through the sample and the variable resistor is equal $(i_1=i_2)$:

$$\frac{V_{\text{sample}}}{R_{\text{sample}}} = \frac{V_{\text{supply}} - V_{\text{sample}}}{R_{\text{variable resistor}}}$$
Eq. 4.16

The variable resistor was adjusted by looking at the oscilloscope, so that the voltage drop across the sample becomes half of the supply voltage. At this condition the resistivity set in the variable resistor gives the resistivity of the sample:

$$R_{\text{sample}} = R_{\text{variable resistor}}$$
 Eq. 4.17

Low frequency and supply voltage were selected so that the phase angle shift remains close to zero. Precautions in the sample handling during this procedure setup were taken to avoid evaporation and sample drying.

4.2.8.4 Archie's cementation factor, m from electrical resistivity

Archie's (1942) equation correlates resistivity of brine R_w with the resistivity of a rock saturated with brine R_o by defining a formation factor, F:

$$F = \frac{R_o}{R_w}$$
 Eq. 4.18

The electrical current travels a longer path than the geometrical length of a rock. F indicates the degree of difficulty in electrical current flow due to the pore geometry. F is primarily controlled by porosity and specific surface, but the cementation factor, m determines the degree to which porosity, ϕ should be decreased, so that the pores could be considered as straight continuous channels. F is then (Archie, 1942):

$$F = \frac{1}{\phi^m}$$
 Eq. 4.19

The exponent *m* increases significantly with specific surface (Olsen et al., 2008c) which characterizes the pore geometry. Therefore, if CO_2 changes the pore geometry it would possibly change the cementation factor.

4.2.8.5 NMR T_2 relaxation time measurements

Transverse (spin-spin) relaxation time, T_2 was measured by a standard CPMG (Carr-Purcell-Meiboom-Gill) pulse sequence by using a resonance instruments Maran spectrometer at two steps with different parameter setup due to the use of two different labs.

1.) At initial brine saturated condition taking one representative sample from each of the studied formations of both wells (Table 4.2, group 1).

2.) All CO_2 injected samples after geophysical tests (Table 4.2). Measurement was also repeated in the samples measured at step 1 with the setup of step 2.

Setup for step 1 measurements:

Experiments were made at 35°C with Larmor frequency of 2.12 MHz and low magnetic field, B_0 . Number of echoes collected was 8000 with 300 scans. Echo spacing (τ) which is the time between successive rephasing (P180) pulses of τ =200 microseconds was chosen.

Setup for step 2 measurements:

Experiments were made at 35°C with Larmor frequency of 1.83 MHz and magnetic field, B_0 , as 0.044T. Number of echoes collected was 8192 with 128 scans. Echo spacing (τ) which is the time between successive rephrasing (P180) pulses of τ =200 microseconds was chosen.

The relaxation time (T_2) distribution was obtained with the DXP programmed from Resonance Instruments. With the short echo spacing and low applied magnetic field (B_0) in both steps, the T_2 relaxation is dominated by surface relaxation (Kleinberg et al., 1993) and the contribution from diffusion in T_2 relaxation time can be neglected (Hürlimann, 1998).

4.2.8.6 Surface relaxivity from transverse relaxation time, T_2

Transverse relaxation time, T_2 is the characteristic time that proton aligned by a magnetic field take to flip 90° after the magnetic field disappears. Relaxation of protons close to the solid surface is faster than of protons in the free flowing fluid (Kenyon, 1997). Transverse relaxation rate, $1/T_2$ in an *NMR* experiment is proportional to the surface to volume ratio (*S/V*) (Coates et al., 1999):

$$\frac{1}{T_2} = \rho \frac{S}{V} = \rho S_{\phi}, \qquad \text{Eq.4.20}$$

where ρ is relaxivity and S_{ϕ} is the specific surface of pore space.

Protons in water relax faster in water-wet system than in an oil-wet system (Brown and Fatt, 1956; Williams, 1982, Hsu, 1992; Chen et al., 2006). Therefore, a change in wettability may result in a change in transverse relaxation time, T_2 .

4.3 Characterization by chips and side trims

An overview of the studied samples is given in Table 4.1. Side trims of all $1\frac{1}{2}$ inch samples were collected to prepare polished thin sections for backscattered electron (BSE) microscopy. Centimetre size chips were also collected from the core material from the wells SA-1 and Rigs-1 for measurement of carbonate content, specific surface, cation exchange capacity (CEC) and mineralogical composition.

After finishing the designed geophysical tests the samples were cleaned for brine and dried. These samples were then characterized by measuring carbonate content, specific surface of both crushed sample and insoluble residue and by Backscatter Electron microscopy of thin sections.

4.3.1 Soxhlet extraction cleaning

Trims were cleaned for salt and hydrocarbons by Soxhlet extraction. The samples were first refluxed by methanol to remove salts. Methanol was boiled at 110°C and the vapour was condensed by flowing water at 12°C. The absence of measurable chloride was checked by 0.03M AgNO₃ after stopping the process for three days, while the samples in the flask were immersed in methanol. After removing chloride, the samples went through toluene refluxing for hydrocarbon removal. Toluene was boiled at 64.5°C and the vapour was condensed by flowing water at 12°C. This process continued until clear toluene solution was found after interrupting the process for three days, with the samples were dried in an oven at 55°C for two days.

4.3.2 Carbonate content

Approximately 0.30 gram of the powdered sample was weighed with accuracy ± 0.01 . The sample was suspended in 250 ml distilled water and 25.00 ml (± 0.01) of 0.500 N (± 0.001) HCl was added. After 24 hours the solution was boiled on a hot plate for 20 minutes to remove CO₂. The solution was then cooled to room temperature. After adding 5 drops of Phenolphthalein indicator, the solution was titrated with NaOH of 0.50N (± 0.01). Carbonate content was calculated by using the following equation:

%CaCO₃ =
$$\frac{[(ml_{HCl} \times N_{HCl}) - (ml_{NaOH} \times N_{NaOH})]M_{CaCO_3}}{2 \times 1000 \times m} \times 100$$
 Eq. 4.21

where ml_{HCl} is the volume of HCl added in ml, N_{HCl} is the normality of HCl, ml_{NaOH} is the volume of NaOH used to get endpoint of titration in ml (accuracy ±0.025), N_{NaOH} is the normality of NaOH, M_{CaCO_3} is the molecular weight of CaCO₃ (100.09 g/mol) and m is the sample weight.

Quality control: Because of the hygroscopic nature of the NaOH solution, its normality can be changed by absorbing moisture. Therefore, normality of the NaOH solution was checked immediately before the test. It was done by titrating 25.00 ml (± 0.01) of 0.500N (± 0.001) HCl and noting the amount (accuracy ± 0.025 ml) of NaOH required:

$$N_{\text{NaOH}} = \frac{ml_{\text{HCI}} \times N_{\text{HCI}}}{ml_{\text{NaOH}}}$$
Eq. 4.22

4.3.3 Collection of Irreducible Residue (IR)

Carbonate was totally dissolved in 2 N CH₃COOH solution at pH = 2.23:

$$CaCO_3 + 2CH_3COOH \rightarrow 2CH_3(COO)_2^- + Ca^{2+} + H_2O + CO_2\uparrow Eq. 4.23$$

The products of the reaction and excess acetic acid were removed by washing with distilled water. The insoluble residue was dried at 60°C for 48 hours to make it ready for specific surface measurement (of IR) and qualitative determination of insoluble minerals by XRD.

4.3.4 Specific surface

The nitrogen adsorption technique by Brunauer, Emmet and Teller (BET) (Brunauer et al., 1938) was applied to determine the specific surface by using a Micrometritics Gemini III 2375 analyzer. The accuracy of the instrument is $\pm 0.5\%$. 1.500 to 2.250 g of coarsely ground sample or 0.600 to 1.500 grams of IR was placed in a tube. The sample was degasified inside the tube with nitrogen gas at 70°C for 4 hours before putting it in the instrument for adsorption. Both multipoint and single point data were recorded. In order for quality control two tests were done for each sampling interval (Table 4.1).





Figure 4.7: A set of XRD diffractograms from which minerals in the studied sample were determined

Both powdered original sample and IR were analyzed by X-ray diffraction (XRD) by using Cu K- α radiation with a Philips PW 1830 diffractometer. For the

identification of clay minerals, a film of IR was produced on a 15mm×30mm test slide. Approximately 0.03g (±0.0001) of ground residue was mixed with 1.5 ml water and then the mixture was spread over the entire slide. The slide was then kept at laboratory temperature (22°C) for 24 hours for air drying. Four X-ray diffractograms was produced, following the sequence: Air-dried > Ethylene Glycol-Solvated at 60°C for two days > Oven-dried at 350°C for 1 hour (cooled to room temperature before putting into the machine) > Oven-dried at 550°C for 1 hour (cooled to room temperature before putting into the machine). The heating steps transform some of the clay minerals. Diffraction data were recorded in the Bragg's angle 20 interval of 2° to 65° for the powdered original material and 2° to 40° for the residue (Figure 4.7). All diffractrograms are given in Appendix VII.

4.3.6 Cation Exchange Capacity (CEC)

CEC of the irreducible residue was estimated by replacing the exchangeable bases by Barium using BaCl₂. CEC of calcite was estimated by adsorbing Mg^{2+} ions onto the calcite surface and replacing Ca^{2+} ions.

4.3.6.1 BaCl₂ method

The exchangeable bases are removed with an excess of Ba^{2+} . Thereafter, the sample is brought to an ionic strength of about 0.01M. Then the Ba^{2+} is removed with an excess of MgSO₄. The *Mg* lost for the exchange with Ba^{2+} is measured to determine the CEC. The exchangeable bases and the Mg^{2+} are measured with inductively coupled plasma optical emission spectrometry (ICP-OES). A Varian Vista MPX Axial View Inductively Coupled Plasma OES was used for all measurements.

A 0.5g (with 4 decimals) sample was weighted into a clean, dry, numbered centrifuge tube with screw cap. Weight of the tube with sample (FW) was recorded. 30 ml of 0.1M BaCl₂ was added into the tube from a diluter and shaken (200 /min.) for 1 hour. The solution was then centrifuged for 10 min. at 2500 rpm. The supernatant was decanted into a 100 ml volumetric flask. Shaking/centrifugation steps were repeated two times. Every time, the supernatant was decanted into a 100 ml volumetric flask was filled with 0.1M BaCl₂ and homogenized. In this solution (I) the exchangeable bases are measured:

Cation mEq/100g =
$$\frac{(C-B) \times D \times 100 \times 100}{D \times E \times 1000}$$
 Eq. 4.24

where *B* is the concentration of cation in blank (mg/L), *C* is the concentration of cation in sample (mg/L), *D* is dilution factor, *W* is the sample weight (g) and *E* is the equivalent mass of respective cation.

Thirty ml of -25M BaCl₂ was added to solution *I*. The sample was shaken overnight in a centrifuge tube. The solution was then centrifuged for 10 min. at 2500 rpm. The supernatant was decanted and weight of the tube with the sample (*SW*) was measured. After adding 30 grams of 0.02 M MgSO₄ solution to the sample, the tube with the sample was weighted and it was shaken for 2 hours. It was then centrifuged for 10 min. at 2500 rpm and the supernatant was decanted over an OOR-filter into a bottle. In this filtrated solution (*II*) the CEC is measured:

CEC mEq/100g =
$$\frac{(B-C) \times D \times (30+SW-FW) \times 100}{W \times E \times 1000}$$
 Eq. 4.25

where *B* is the concentration of Mg^{2+} in blank (mg/L), *C* is the concentration of Mg^{2+} in sample (mg/L), *D* is the dilution factor, *W* is the sample weight (g), *E* is the equivalent mass of Mg^{2+} and 30 is the added weight of 0.02M MgSO₄.

4.3.6.2 Mg²⁺ adsorption method

Two synthetic calcites, *CCL* (low specific surface area, $0.24 \pm 0.05 \text{ m}^2/\text{g}$) and *CCH* (high specific surface area, $11.0 \pm 0.2 \text{ m}^2/\text{g}$) were used by Ahsan and Fabricius (2010) to study the effect of grain size on the ion exchange capacity of calcite. Results of Ahsan and Fabricius (2010) were used to calculate the CEC of bulk sample (section 3.3.4).

Synthetic calcites were washed for more than 50 hours with a Mg^{2+} containing (50 ppm) solution to displace Ca^{2+} from the calcite surface until Ca^{2+} ions concentration in the solution became stable. The initial concentration of Mg^{2+} ions is less than 5% of the concentration in sea water. The concentration is so low that it has insignificant effect on calcite solubility (Berner 1975). The Mg^{2+} containing solution was prepared from an equilibrated calcite solution, so that, it cannot cause net dissolution of calcite.

Concentrations of Ca^{2+} and Mg^{2+} were measured at time intervals by Atomic Adsorption Spectroscopy. The longer the Mg^{2+} containing solution is allowed to come in contact with calcite surface, the more Ca^{2+} goes into the solution and the more Mg^{2+} ions adsorbs on the surface, until it approaches equilibrium

4.4 Uncertainty analysis

In order to simplify the experimental work and due to instrumental limitations, the experimental conditions used may differ from ideal conditions. In the following section the error involved in the experimental data is described.

4.4.1 Dependencies of strain rate

In order to avoid evaporation of pore fluid and to complete one combined sonic velocity and electrical resistivity test a day, a strain rate of 1% per hour was used. Experimental studies were made by taking one sample from each interval to examine the effect of strain on the measured values. Three strain rates were used in order $2\%/h \rightarrow 1\%/h \rightarrow 0.5\%/h$, while following the procedure described in section 4.2.8.1 and 4.2.8.3 for recording sonic velocity and electrical resistivity.





Figure 4.8: Dependencies of strain rate on velocity measurement

The average value of sonic velocity is plotted in Figure 4.8 which has an uncertainty of 0.05 km/s for the compressional wave velocity and 0.1 km/s for the shear wave velocity. Within the applied strain rates all data points remain within the uncertainty range. An effect of strain rate is difficult to recognize. However, data recorded at the later stage of the experimental procedure (lower strain rate) shows a minor increasing trend. This may be due to the closing of micro-fractures due to the repetitive loadings so that the variation becomes

smaller at higher stresses. Within the studied formation the influence of strain rate on different formation chalk is fairly similar.



4.4.1.2 Dependencies of strain rate on resistivity measurement

Figure 4.9: Dependency of strain rate on resistivity measurement

The average value of electrical resistivity is plotted in Figure 4.8 which has an uncertainty of 3%-5% (Table 4.5). Within the applied strain rates the variation of resistivity data at a particular stress is slightly larger than the uncertainty of the value. The variation is larger at lower stresses and tends to diminish at higher stresses. This observation is accordance with the sonic velocity measurement. However the variation is larger compared to sonic velocity as the influence of micro-cracks on electrical current flow is larger than the propagation of elastic waves. However, a variation might have occurred also due to evaporation of pore fluid as tests using three strain rates take approximately 10 hours. Therefore higher resistivity values were obtained at the later stage of the measurement $(2\%/h \rightarrow 1\%/h \rightarrow 0.5\%/h)$. Within the studied formation the influence of strain rate on different formation chalk is fairly similar.



4.4.2 Dependency of frequency on resistivity measurement

Figure 4.10: Dependency of frequency on resistivity measurement

In porous rocks, the electrical field in the low frequency range causes the ions to polarize around the grains (Maxwell-Wagner polarization) and may give rise to large dipoles and to large apparent dielectric constants (Mendelson and Cohen, 1982; Chelidze and Guéguen, 1999). Therefore, rocks appear less conductive (high resistance) at low frequency. On the other hand, at higher frequency phase shift occurs. An optimal frequency of 1 kHz was used when phase shift is close to zero and lower capacitance effect is expected (Figure 4.10).

4.4.3 Precision of instrument

For uncertainty calculation by the error propagation method, the following general instrumental errors were assumed for the measurements. Errors associated with each individual procedure are mentioned in section 4.2 and 4.3.

- 1. Diameter and length measurement by calliper: 0.1 mm
- 2. Weight <0.1g =0.0001g and 0.1g-100g =0.01g
- 3. Axial stress: 0.01 MPa Confining stress: 0.05 MPa
- 4. Resistance by variable resistor: 1Ω

4.4.4 Uncertainty

Uncertainties calculated by the error propagation method for the most used data are presented in Table 4.5.

Measurement	Range	Uncertainty
Bulk volume	37.5 mm×30mm to 50 mm	1%
Grain density	-	0.5%
Helium porosity	> 20%	1%
	10-20%	2%
Liquid permeability	0.01-0.1 mD	15%
(Klinkenberg correction)	0.1-1 mD	10%
	> 1 mD	4%
Brine saturation	-	1%
(Archimedes method)		
Carbonate content	>90%	0.5%
(by titration)	75%-90%	1%
Specific surface	Chalk (<4 m²/g)	0.2%
(BET method)	IR (>10 m²/g)	2.5%
P-wave velocity	-	50 m/s
S-wave velocity	-	100 m/s
Electrical resistivity	< 1 Ωm	5 %
-	1-10 Ωm	3 %

Table 4.5: Uncertainty associated with the measurement of petrophysical properties.

4.4 Results and discussion

This section contains the experimental results and a discussion of the achieved values. Discussion on the CO_2 effect on chalk along with rock-mechanics test results is given in Paper IV.

4.4.1 Sample characterization

Rigs-1 and SA-1 Ekofisk Formation samples contain up to 25% and 20% noncarbonate fraction respectively. By contrast Tor Formation samples from Rigs-1 and SA-1 contains less than 5% and 2% non-carbonate respectively (Table 4.6). Quartz is the dominant non-carbonate mineral in both wells. Clay minerals in the Rigs-1 samples are predominantly kaolinite whereas in SA-1 smectite dominates. Distribution of non-carbonates is recognizable in BSE images at large magnification and pores are found to be partially filled with clay in samples from Ekofisk Formation of both wells (Figure 4.11a). The Ekofisk Formation also contains considerable amounts of preserved large hollow microfossils and has carbonate wackstone or mudstone texture. The Tor Formation samples by contrast typically contain a homogeneous matrix of calcareous nannofossil debris and have carbonate wackstone or mudstone texture.

	2	1 1										
Well	Depth	Formation	Carbo cont (%	onate ent o)	Sp. surface of chalk (m²/g)		Sp. su of res (m²/	rface idue ⁄g)	Minerals	Cation Capac (µE	nange CEC) ²)	
			Before	After	Before	After	Before	After		Calcite	IR	Bulk
Rigs-1	2803.9	Ekofisk	75.9		3.88		9.6		C, Q, K	1.9	10	5.1
Rigs-1	2806.9	Ekofisk	77.9		3.74		7.9		C, Q, K	1.6	8	3.9
Rigs-1	2813.0	Ekofisk	86.4	89.0	3.77	3.4	11.9	15.0	C, Q, K	1.6	8	3.7
Rigs-1	2816.1	Ekofisk	89.7		2.93		11.2		C, Q, K	2.0	7	3.1
Rigs-1	2840.6	Tor	95.2	97.3	2.05	1.5	8.9	12.3	C, Q, K	2.4	8	2.4
Rigs-1	2844.4	Tor	96.7		1.91		9.9		C, Q, K	2.4	9	2.3
SA-1	3319.8	Ekofisk	80.8		5.50		23.4		C, Q, S	3.3	9	6.0
SA-1	3331.8	Ekofisk	80.3		6.40		34.5		C, Q, S	2.5	9	6.3
SA-1	3381.7	Tor	98.5	97.2	1.61	1.4	20.1	25.4	C, Q, S, K*	3.0	10	2.7
SA-1	3390.5	Tor	98.0		2.19		30.5		C, Q, S, K*	2.5	9	3.1
SA-1	3399.7	Tor	99.3		1.82		12.5		C, Q, S, K*	2.3	16	2.3
SA-1	3408.7	Tor	99.0		1.86		14.4		C, Q, S, K*	2.3	17	2.6
SA-1	3418.8	Tor	99.1		1.71		14.6		C, Q, S	2.5	14	2.4
SA-1	3427.7	Tor	99.7	94.5	1.70	1.4	16.6	9.5	C, Q, S	2.4	14	1.9
SA-1	3437.8	Tor	99.4		1.63		14.8		C. Q. S	2.6	17	2.4

Table 4.6: Physical properties of the studied interval.



Figure 4.11: Backscatter electron (BSE) micrographs of epoxy-impregnated and polished samples from the two studied formations of the wells SA-1 and Rigs-1: (a) before CO_2 injection and (b) after CO_2 injection. Dark is porosity and bright is calcite. Clay and quartz appear as grey as indicated with arrows. Ekofisk Formation: porosity: 32%, CaCO₃: 88%, gas permeability: 0.6 mD, sp. surface: 3.5 m²/g and Tor Formation: porosity: 26%, CaCO₃: 98.6%, gas permeability: 0.8 mD, sp. surface: 1.7 m²/g. All BSE images (before and after CO_2 injection) is given in Appendix VII.

4.4.1 Saturation

Brine saturation achieved at different stages of the tests is shown in Table 4.7. It is apparent from the brine saturation at S_{CO2} conditions that supercritical CO₂ injection allows extraction of more oil than waterflooding alone.
Sample	S _w -I	S _{wir}	Sor	S _{CO2}	S _w -F
RE-22A	0.98	-	-	-	-
RT-03	0.96	-	-	-	-
SE-03	0.98	-	-	-	-
ST-24A	0.98	-	-	-	-
RE-24	0.99	0.32	0.68	0.94	0.97
RT-01	0.99	0.20	0.80	0.86	0.95
SE-05A	0.97	-	-	-	-
ST-24B	0.98	0.30	0.70	0.82	0.93
RE-23A	0.98	0.28	_	0.69	0.90
RT-02	0.98	0.17	-	0.83	0.96
SE-02	0.93	-	-	-	-
ST-23A	0.94	0.18	-	0.51	0.89
RE-26B2	0.99	0.28	_	0.93	
ST-26	0.99			0.84	0.93
ST-08A	0.99			0.98	0.98
ST-08B	0.99	-	-	0.98	0.98

Table 4.7: Brine saturation achieved at different stages of the geophysical tests.

4.4.3 Petrophysical properties

The average porosity of Rigs-1 Ekofisk, Rigs-1 Tor, SA-1 Ekofisk and SA-1 Tor is 30%, 35%, 20% and 30% respectively (Table 4.8). The relationship between porosity and permeability is influenced by the non carbonate content as specific surface of the bulk is mostly determined by it. Due to high specific surface of Ekofisk Formation chalk, permeability is lower than Tor Formation chalk (Figure 4.12a). Kozeny permeability (k_k) calculated from the specific surface ($k_k=c\phi^3/S^2$) is less than the measured permeability. This is expected, as some fractures may open during the core retrieval process which may increase the permeability measured in core plugs. In addition, during crushing of chalk in preparation for the specific surface measurement (BET method) some grain contacts are exposed, which will be included in the measured specific surface and reduce Kozeny permeability. However, the consistent increasing trend indicates homogeneity of the tested samples (Fig. 4.12b).

Due to supercritical CO_2 injection an increase in porosity of 1% to 2% was observed in Ekofisk Formation samples, while the increase in Tor Formation samples is 2% to 3% (Figure 4.13a). In most cases an increase in permeability was also observed (Figure 4.13b, c).

Sample	Diameter (mm)	Length (mm)	Grain density (g/m ³)	Poro (V/	sity V)	Ga Perme (ml	is ability D)	Carbo conte %)	nate ent)	Sp. su Cha (m²/	rface alk ′g)	Sp. su IR (m²/	rface ((g)
				Before	After	Before	After	Before	After	Before	After	Before	After
RE-22A	37.3	30.9	2.71	0.33	-	1.1	-	88	-	3.8	-	12	-
RT-03	36.8	31.3	2.71	0.42	-	4.8	-	97	-	1.9	-	10	-
SE-03	37.4	45.4	2.71	0.18	-	0.04	-	78	-	6.4	-	35	-
ST-24A	37.4	43.7	2.72	0.26	-	0.8	-	98	-	1.7	-	20	
RE-24	37.3	38.9	2.72	0.36	0.37	0.9	0.8	88	90	3.6	3.6	12	16
RT-01	37.0	29.7	2.71	0.39	0.41	4.4	8.2	95	97	2.1	1.6	9	13
SE-05A	37.5	30.7	2.72	0.26	-	0.1	-	81	-	5.2	-	23	-
ST-24B	37.4	34.0	2.72	0.25	0.26	0.8	0.9	98	97	1.7	1.0	20	26
RE-23A	37.2	26.5	2.72	0.32	0.33	0.6	1.3	88	88	3.5	3.2	12	14
RT-02	37.1	24.8	2.72	0.35	0.36	2.3	8.2	95	97	2.1	1.3	9	11
SE-02	37.5	20.8	2.71	0.16	-	0.02	-	78	-	6.4	-	35	-
ST-23A	37.5	27.0	2.72	0.26	0.28	0.8	1.9	99	97	1.7	1.7	20	25
RE-26B2	37.5	44.3	2.71	0.29	-	0.5	-	90	-	2.9	-	11	-
ST-26	37.5	72.7	2.71	0.28	0.29	1.1	0.4	99	97	1.6	1.5	20	26
ST-08A	36.8	30.0	2.71	0.32	0.35	3.2	4.7	100	94	1.7	1.2	19	9
ST-08B	37.2	40.5	2.71	0.31	0.32	2.6	2.2	100	95	1.6	1.5	19	10
RE-14	37.4	74.8	2.701	0.31	-	0.5	-	78	-	4.7	-	8	-
RE-08B	37.4	74.9	2.698	0.32	-	0.5	-	76	-	3.9	-	10	-
RE-09B	37.4	74.7	2.694	0.30	-	0.5	-	79	-	3.6	-	10	-
RE-28A1	36.9	74.7	2.704	0.29	-	0.8	-	90	-	2.9	-	11	-
RE-31	37.3	69.4	2.707	0.29	-	0.6	-	89	-	3.2	-	11	-
RE-26B1	37.5	72.8	2.71	0.31	0.32	0.5	-	90	-	2.9	-	11	-
RE-06A	37.5	75.3	2.70	0.32	0.33	0.5	-	76	-	3.9	-	10	-
RE-12B	37.6	75.2	2.69	0.30	0.34	0.5	-	79	-	3.6	-	10	-
RE-29	37.4	75.1	2.71	0.28	0.29	0.4	-	89	-	3.2	-	11	-
RE-10A	37.5	75.2	2.70	0.31	0.31	0.5	-	79	-	3.6	-	10	-
ST-01B	38.2	74.7	2.71	0.30	-	1.8	-	99	-	1.7	-	15	-
ST-12B	37.0	75.0	2.714	0.31	-	1.6	-	99	-	1.9	-	14	-
ST-20	37.4	75.2	2.712	0.28	-	1.6	-	98	-	2.1	-	31	-
ST-17B	37.3	75.2	2.713	0.29	-	1.1	-	99	-	1.8	-	13	-
ST-25B	37.4	75.1	2.713	0.28	-	1.0	-	99	-	1.6	-	20	-
ST-03B	37.5	75.5	2.71	0.29	0.32	1.7	-	99	-	1.7	-	15	-
ST-07	37.1	74.9	2.72	0.31	0.29	2.7	-	100	-	1.6	-	19	-
ST-16B	37.5	75.2	2.72	0.28	0.29	1.2	-	99	-	1.8	-	13	-
ST-13B	37.2	75.2	2.71	0.31	0.28	2.2	-	100	-	1.9	-	14	-
ST-04B	37.5	74.9	2.71	0.28	0.31	1.3	-	99	-	1.6	-	15	-

Table 4.8: Physical properties of the studied samples before and after CO₂ injection.



Figure 4.12: (a) Variation of porosity-permeability relationship according to the specific surface (BET method). Liquid (equivalent to Klinkenberg corrected) permeability was calculated from air permeability by using (Eq. 4.10). (b) Relationship between liquid permeability and permeability calculated from porosity and specific surface (by BET method) by using Kozeny's equation. Unfilled markers represent Ekofisk Formation and filled markers represent Tor Formation. Black markers indicate before CO_2 injection and grey markers indicate after CO_2 injection.



Figure 4.13: Change in physical properties due to CO_2 injection, (a) porosity, (b) liquid (klinkenberg corrected) permeability, (c) equivalent liquid permeability calculated from porosity and specific surface by Kozeny's equation. Filled data points represent Tor Formation and unfilled data points represent Ekofisk Formation.

4.4.4 Geophysical properties

Compressional wave velocity, shear wave velocity and electrical resistivity measured at different stages of the experimental procedure are presented in Table 4.9. Shear wave velocity is significantly lower in saturated samples as compared to the dry samples. There is a minor increase in compressional wave velocity in the saturated Tor Formation samples and notable increase in SA-1 Ekofisk Formation samples. Unexpectedly a decrease is observed in compressional wave velocity of the Rigs-1 Ekofisk samples. There is a possibility of water weakening in these samples due to high content of kaolinite. The effect of brine saturation is

better understood from the V_p / V_s plots (Figure 4.14b). In contrast, no marked effect of replacing brine with hydrocarbon was observed. Only SA-1 Tor Formation indicates an increase in V_p / V_s after CO₂ injection.

Table 4.9: Compressional and shear wave velocity as well as electrical resistivity at different experimental conditions. Data presented here were taken at 3 MPa axial stress and 1 MPa confining stress because it is the maximum stress level in a reloading cycle (minimum bedding effect under the experimental condition). Pore pressure was atmospheric for all tests.

	Compressional wave velocity (km/s)						Shear wave velocity (km/s)							Resistivity (ohm-m)					
Sample	Dry-I	S _w -I	S _{wir}	Sor	S _{CO2}	Dry-F	S _w -F	Dry-I	S _w -I	S _{wir}	Sor	S _{CO2}	Dry-F	S _w -F	S _w -I	S _{wir}	Sor	S _{CO2}	S _w -F
RE-22A	3.20	3.17	-	-	-	-	-	1.95	1.60	-	-	-	-	-	0.9	-	-	-	-
RT-03	1.98	2.43	-	-	-	-	-	1.26	1.48	-	-	-	-	-	0.4	-	-	-	-
SE-03	2.80	3.32	-	-	-	-	-	1.89	1.77	-	-	-	-	-	4.6	-	-	-	-
ST-24A	3.68	3.67	-	-	-	-	-	2.23	1.97	-	-	-	-	-	1.7	-	-	-	-
RE-24	2.80	2.86	2.75	2.82	2.74	2.59	2.78	1.84	1.43	1.40	1.47	1.48	1.77	1.35	0.7	7.7	3.2	0.8	1.0
RT-01	2.70	2.81	2.60	2.79	2.70	2.41	2.73	1.68	1.65	1.58	1.54	1.59	1.57	1.65	0.6	17.6	1.4	0.7	0.7
SE-05A	3.10	3.01	-	-	-	-	-	2.07	1.63	-	-	-	-	-	1.5	-	-	-	-
ST-24B	4.11	4.12	3.91	3.99	3.83	3.75	3.87	2.42	2.20	2.21	2.22	2.02	2.39	2.26	1.0	14.9	1.3	1.5	1.6
RE-23A	3.29	3.28	3.07	-	3.05	2.97	3.09	1.97	1.64	1.68	-	1.54	1.81	1.68	0.5	10.5	-	1.3	1.0
RT-02	3.37	3.40	3.19	-	3.18	3.09	3.29	2.02	1.70	1.66	-	1.64	1.75	1.66	0.7	16.2	-	0.9	0.9
SE-02	2.99	3.39	-	-	-	-	-	1.99	1.54	-	-	-	-	-	3.9	-	-	-	-
ST-23A	3.59	3.82	3.61	-	3.47	3.22	3.58	2.31	1.90	1.85	-	1.70	1.90	1.86	1.1	22.2	-	2.1	1.8
RE-26B2	-	3.30	3.26	-	3.24	-	-		1.77	1.75	-	1.76	-		2.2	12.5		1.1	
ST-26	3.55	3.54	-	-	3.41	3.30	3.46	2.14	1.84	-	-	1.76	2.02	1.79	-	-		-	1.3
ST-08A	3.04	3.13	-	-	2.99	2.51	2.97	1.91	1.66	-	-	1.52	1.97	1.70	0.8	-	-	0.9	0.9
ST-08B	2.84	3.02	-	-	2.86	2.55	2.90	1.80	1.48	-	-	1.43	1.71	1.45	-	-	-	-	-
RE-14A	:	3.28		_			-		1.72		-	_		-	1.6	-	-	-	-
RE-08B	3.52	3.28	-	-	-	-	-	2.06	1.59	-	-	-	-	-	1.6	-	-	-	-
RE-09B	3.49	3.39	-	-	-	-	-	2.05	1.85	-	-	-	-	-	1.7	-	-	-	-
RE-28A1	-	3.30	-	-	-	-	-	-	1.77	-	-	-	-	-	2.4	-	-	-	-
RE-31	- 1	3.29	-	-	-	-	-	-	1.65	-	-	-	-	-	2.4	-	-	-	-
RE-26B1		3.21	3.11	-	_		-		1.66	1.64	-	-	-	-	2.1	11.4	-	_	-
RE-06A	3.63	3.10	3.16	-	-	-	-	2.16	1.57	1.67	-	-	-	-	1.6	6.8	-	-	-
RE-12B	3.85	3.43	3.35	-	-	-	-	2.29	1.85	1.73	-	-	-	-	1.7	5.5	-	-	-
RE-29	3.63	3.33	3.23	-	-	-	-	2.20	1.74	1.79	-	-	-	-	2.6	13.1	-	-	-
RE-10A	3.77	3.34	3.30	-	-	-	-	2.34	1.80	1.82	-	-	-	-	1.6	5.3	-	-	-
ST-03B	3.35	-	-	-	-	-	-	2.02	-	-	-	-	-	-	-	-	-	-	-
ST-07	3.13	-	-	-	-	-	-	1.93	-	-	-	-	-	-	-	-	-	-	-
ST-16B	3.46	-	-	-	-	-	-	2.11	-	-	-	-	-	-	-	-	-	-	-
ST-13B	3.12	-	-	-	-	-	-	1.94	-	-	-	-	-	-	-	-	-	-	-
ST-04B	3.76	-	-	-	-	-	-	2.20	-	-	-	-	-	-	-	-	-	-	-



Figure 4.14: (a) Measured velocities at different stages of the experimental procedure as defined in Table 4.2. Filled markers represent compressional wave velocity and open markers indicate shear wave velocity. (b) Ratio between compressional and shear wave velocity. Experimental stages are indicated by colors in the legend.



Figure 4.15: Biot's coefficient calculated from sonic velocity and bulk density at different stages of the experimental procedure as defined in Table 4.2. Experimental stages are indicated by colors in the legend.



Figure 4.16: Effect of CO_2 injection on stiffness (a) compressional modulus calculated from sonic velocity and bulk density and (b) Biot's coefficient. Black data points are immediately after CO_2 injection and grey data points are after re-saturation with formation brine. Circle, diamond, triangle and rectangle indicate Rigs-1 Ekofisk, Rigs-1 Tor, SA-1 Ekofisk and SA-1 Tor Formation respectively.

In order to estimate the effect of CO_2 injection on the stiffness of the chalk frame, Biot's coefficient was calculated from V_p and V_s and density (Eq. 4.13; Eq. 4.14) measured at different stages of the experimental procedure and applying Gasmann's (1951) fluid substitution (Eq. 4.15) (Figure 4.15). Flooding with supercritical CO_2 leads to a decrease in frame stiffness of Tor Formation chalk as indicated from the decrease in compressional modulus (Figure 4.16a) and increase in Biot's coefficient (Figure 4.16b) Biot's coefficient increases most for samples with low Biot's coefficient (from below 0.8 to above 0.8) (Figure 4.16b). For samples with high Biot's coefficient of both Ekofisk Formation and Tor Formation this effect is relatively small.

In general, Archie's cementation factor shows a decrease after CO_2 injection (Figure 4.17a). The factor indicates the ease of electrical current flow through the sample. After CO_2 injection, the Tor Formation samples fall below the cementation factor trend of North Sea chalk as defined by Olsen et al., (2008c) and follows the trend of some of the Ekofisk Formation chalk which is more likely to be fractured (Figure 17b). This may be due to the opening of micro-fracture as the samples had gone through several procedures as, saturation where a vacuum was applied, CO_2 injection where pore pressure and confining stress

were applied, as well as velocity and resistivity measurement where axial stress and confining stress were applied.



Figure 4.17: (a) Effect of CO₂ injection on the cementation factor as calculated from electrical resistivity Eq. 4.18 and Eq. 4.19. (b) Relationship between cementation factor and effective specific surface of the bulk ($S=\phi \times S_{\phi}$). Circle, diamond, triangle and rectangle indicate Rigs-1 Ekofisk, Rigs-1 Tor, SA-1 Ekofisk and SA-1 Tor Formation respectively. Black data points represent initial brine saturated condition and grey data points are after re-saturation with formation brine. Note: Which brine was used during re-saturation after CO₂ injection and cleaning was not noted. However, the brine was one of the brines for which resistivity was 0.22 Ω m, 0.13 Ω m or 0.077 Ω m. 0.13 Ω m was used in this calculation as 0.22 Ω m and 0.077 Ω m gives value of cementation factor below 1.5 and above 2.2 respectively, which is unrealistic for chalk (Olsen et al., 2008c).

CEC of synthetic calcite was measured to be between 13 μ Eq/m² and 16 μ Eq/m² by Ahsan and Fabricius (2010). Using their data for calcite surface and measuring CEC of IR of this project samples *CEC* of Ekofisk Formation chalk was calculated between 3 μ Eq/m² and 6 μ Eq/m² and *CEC* of Tor Formation was calculated approximately 2.5 μ Eq/m². Relative proportion of clay surface and calcite surface was calculated by Nuclear Magnetic Resonance (*NMR*). It was observed that the North Chalk has excess conductivity and that a part of this is contributed by the calcite surface in addition to excess conductivity due to clay.

Normalized T_2 peaks do not move on the time scale after CO₂ injection irrespective of the state at which CO₂ was injected (Figure 4.18b). It indicates that there is no significant effect of CO₂ injection on the wettability of the calcite surface.



Figure 4.18: NMR transverse relaxation time (T_2) distribution normalized to helium porosity at (a) initial brine saturated condition with larger scanning interval, (b) initial brine saturated condition along with after CO₂ injection at irreducible water saturated condition and residual water saturated condition with smaller scanning interval. Left peaks in the figures (a) represent clay bound and right peak is for calcite bound water. In figures (b) clay bound peaks were not recorded due the use of different scanning parameters in two different laboratories. For reference, same initial brine saturated (S_w -I) samples were used in both sets of experiments. The peaks in (b) does not show any significant movement along the time scale which indicates that the calcite surface does not change wettability due to CO₂ injection.

5 Conclusions

Diagenesis of chalk involves recrystallization, grain contact cementation and pore filling cementation. During the diagenetic process large pores (intraparticle) remain preserved while matrix porosity (inter-particle) decreases slowly due the increase in overburden stress as new sediments deposits. At first few hundred meters compaction dominates in reducing porosity. However, most of the porosity reduction is caused by the time (in geological scale) dependent creep stress. At deeper burial depth pore filling cementation also causes a large porosity reduction. From the rate of decrease in Biot's coefficient it is possible to predict the diagenesis process involved in the natural porosity reduction. Biot's coefficient decreases with the decrease of porosity. The rate of decrease is low for recrystallization and compaction and high when contact cementation is involved. Porosity reduction due to the depletion of pore fluid pressure in hydrocarbon reservoir is a fast process. Porosity reduces mainly due to the increase of effective stress in this case. Therefore, results from compaction tests rather than creep tests should be used to predict compaction in a hydrocarbon reservoir.

Permeability in chalk is highly influenced by its specific surface which is mostly controlled by content of non-carbonates as clay and silica. Permeability prediction from sonic velocity can be improved by establishing and applying velocity-permeability relationship in stratigraphic units as defined by specific surface. As Tor Formation chalk is less affected by mineralogical variation, its permeability was predicted very closely to the core permeability by considering its S_g between 2 and 7 μ m⁻¹ and *FZI* value between 0.08 and 0.2 μ m. However in the low permeable Ekofisk Formation, permeability could only be predicted within one order of magnitude of the core measured permeability.

Due to the high specific surface area of the calcite particles in chalk, CEC resulting from the surface charge of calcite may influence the flow of electric current. This may lead to wrong fluid saturation calculation by using Archie's equation.

For predicting effective stress in producing hydrocarbon reservoirs, the static effective stress coefficient estimated from rock-mechanics tests is highly relevant, as it is directly related to mechanical strain in the elastic stress regime.

The dynamic effective stress coefficient is easy to estimate from density and velocity of acoustic (elastic) waves and cheap, however, its relationship with static value must be established based on rock-mechanics testing.

It was observed that Ekofisk Formation chalk is generally less affected by the CO_2 injection process compared to Tor Formation chalk. It may be due to the high content of silicates and clay which inhibit calcite dissolution. Another reason may be less exposure to CO_2 during the experiment. Distribution of non-calcite particles inside the pore space of calcite matrix contribute to the high specific surface and small pore size of Ekofisk Formation. NMR transverse relaxation time, T_2 is smaller in Ekofisk Formation, which indicates smaller pore size. Smaller pore size is being the primary cause for low permeability, which restricts the flow of CO_2 inside pore space. Therefore less CO_2 per unit surface area is available in Ekofisk Formation and the chalk may for this reason experience less calcite dissolution.

Injection of supercritical CO₂ leads to an increase in porosity. A decrease in specific surface area of the particles indicates that a reaction between CO₂ enriched water and particles takes place which smoothens the particle surface. Accordingly, a partial effect on permeability was also seen. A decrease in stiffness, as indicated by Biot's coefficient was observed. No significant effect on wettability as indicated by NMR T_2 relaxation time was observed. Rockmechanics testing indicates that in 30% porosity chalk from the South Arne field injection of supercritical CO₂ has no significant effect on shear strength and compaction properties, while there is probably a slight decrease in stiffness properties. The time dependent properties for both Tor and Ekofisk formation does not seem to be affected by CO₂ flooding in the relevant stress regime.

Decrease in stiffness due to the increase of Biot's coefficient could raise a concern on the stability of the reservoir. However effective stress on a reservoir would decrease if there is no change in pore pressure. It means that, although the rock becomes less stiff after CO_2 injection it also becomes subjected to a smaller effective stress. This phenomenon might have been involved in rock-mechanics testing, as only a minor change in failure strength was observed. It suggests that a combined rock-physical and rock-mechanical model is required for failure prediction and reservoir monitoring when CO_2 is involved in enhanced oil recovery and geological sequestration.

6 Recommendation for future work

Following recommendation are made for future work

- Upscaling lab data to reservoir scale
- Modelling long term effects based on short term laboratory data achieved in this project.
- Experimental study for long term effect of CO₂ injection.
- Experimental study of changes due to WAG process as brine will get more time to react with CO₂ during the alternation process.
- Experimental study on the dependency of injection rate.
- Attenuation of sonic waves and its relation to fluid and electrical conductivity.
- Both geophysical and rock-mechanics tests using higher pore pressure and temperature (up to reservoir level).

7 List of references

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8 Papers

- I Alam, M.M., Borre, M.K., Fabricius I.L, Hedegaard, K., Røgen, B, Hossain, Z and Krogsbøll, A.S., 2010, Biot's coefficient as an indicator of strength and porosity reduction: Calcareous sediments from Kerguelen Plateau. Journal of Petroleum Science and Engineering 70 (2010) 282-297.
- **II** *Alam, M.M.*, Prasad, M and Fabricius, I.L., Permeability prediction in Chalks. Accepted manuscript in AAPG Bulletin.
- **III** *Alam, M.M.*, Fabricius, I.L. and Christensen H.F., Static and dynamic effective stress coefficient of chalk. Submitted to Geophysics.
- **IV** *Alam, M.M.*, Hjuler, M.L., Christensen H.F. and Fabricius, I.L., Petrophysical and rock-mechanics effects of CO₂ injection for enhanced oil recovery: chalk from South Arne field, North Sea. Submitted to Geophysical Prospecting.
- V Alam, M.M., Ahsan, R., Shaik, A. K. and Fabricius, I. L., 2010, Surface charge of calcite and its influence on the electrical conductivity in chalk. Presented in the SEG International Exposition and 80th Annual Meeting, 17–22 October 2010, Denver, Colorado, USA.
- **VI** *Alam, M.M.* and Fabricius, I.L., 2010, NMR as a Tool for Estimation of Excess Conductivity in Chalk. Poster presented in 72nd EAGE Conference and Exhibition, Barcelona, Spain 14-17 June 2010.

Ι

Biot's coefficient as an indicator of strength and porosity reduction: Calcareous sediments from Kerguelen Plateau

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ABSTRACT

Chalk develops as a result of diagenesis of pelagic calcareous ooze. In a newly deposited ooze sediment, porosity ranges from 60% to 80% but porosity reduces with burial. We studied how different porosity reduction mechanisms change the strength of these deep sea carbonate-rich sediments and effect Biot's coefficient, β . In calcareous ooze, β is one. Mechanical compaction reduces porosity, but only leads to a minor decrease in β . Recrystallization renders particles smoother, but does not lead to reduction in β unless it gives rise to pore stiffening cementation. Pore stiffening cementation causes β to fall, even when porosity remains constant. Biot's coefficient correlates with strength-indicating properties: compressional and shear modulus, oedometer modulus, yield strength, strain from direct loading and creep strain. Our data indicate that β may be used for predicting the diagenetic process involved in porosity reduction and strengthening of chalk during burial diagenesis.

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1. Introduction

Hydrocarbon reservoir rocks face change in physical properties during the production of oil and gas. Decrease in pore pressure as a consequence of oil and gas production increases the effective stress on the reservoir rock and causes elastic deformation or even compaction of reservoirs. Compaction may play a major role in hydrocarbon production. For example, compaction drive resulting from pressure depletion in the Valhall field in the North Sea helps getting extra 800 million STB oil more than the predicted 250 million STB (Barkved and Kristiansen, 2005). On the other hand platforms in the Ekofisk field in the North Sea faced severe subsidence due to subsurface compaction. This resulted in abandonment of the whole facility and a cost of \$2.5 billion for redevelopment (Hermansen et al., 2000). Compaction is most likely to occur in high-porosity rock. Therefore, better understanding on the behavior of high-porosity rock under altering effective stress state is required to calculate recoverable reserves, well placing, platform design etc.

Biot (1941) defined the effective stress, σ' , as the difference between the total stress, σ (stress from the weight of sediments and water) and a fraction called Biot's coefficient, β of the pore pressure, P_f :

$$\sigma' = \sigma - \beta P_{\rm f}.\tag{1}$$

This theory of Biot (1941) is based on the effective stress concept introduced by Terzaghi (1925). Terzaghi's concept is suitable for loose grainy sediments (e.g. sand), where β is unity and the differential stress (total stress – pore pressure) is equal to the effective stress. In cemented rocks, resistance to the overburden load is partly obtained from the rock skeleton and β is less then unity. Biot's coefficient thus describes to which extent this pressure counteracts elastic deformation of porous rock. High-porosity North Sea chalk is characterized by high β (Fabricius, 2007) and in some cases β can be used to predict the inelastic (permanent deformation) behavior of chalk under stress (Teufel and Warpinski, 1990).

We studied the natural porosity reduction mechanisms of chalk facies sediments from Kerguelen Plateau in the Indian Ocean (Fig. 1). In Kerguelen Plateau, a 700 m thick sedimentary sequence overlies a Turonian (89–93 Ma) basaltic basement (Coffin et al., 2000). The upper 660 m of these sediments are carbonate-rich (Fig. 2) and the porosity ranges from 75% at the top to 25% at the bottom. Water depth is 1141.4 m. Due to the deep water, pore pressure is high. Therefore, high influence of Biot's coefficient in defining effective stress is

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Fig. 1. Map of eastern Indian Ocean showing the location of Kerguelen Plateau (modified after Coffin et al., 2000). The studied bore hole (site 1138) is located in Central Kerguelen Plateau (CKP) and is marked with a rectangle.

expected (Fabricius et al., 2008). We studied the change in β during natural porosity reduction. We also studied how β influences the rapid porosity reduction during mechanical testing, which mimics the rapid compaction of high-porosity hydrocarbon-producing reservoirs.

Chalk is largely composed of coccolith skeletons with minor contribution from planktonic microfossils (Scholle, 1977). Many chalk reservoirs are characterized by high porosity and low permeability (Andersen, 1995) and mechanical compaction of high-porosity reservoir has been studied by many authors (Ruddy et al., 1989; Teufel and Warpinski, 1990). Several studies were also done on the porosity reduction mechanisms in deep sea carbonate-rich sediment: ooze, chalk and limestone (Schlanger and Douglas, 1974; Hamilton, 1976; Scholle, 1977; Wetzel, 1989; Lind, 1993; Bassinot et al., 1993; Borre and Fabricius, 1998; Grützner and Mienert, 1999; Fabricius, 2003). Mazzullo et al. (1988) defined ooze as an unconsolidated calcareous and/or siliceous pelagic sediment while chalk is a firm pelagic sediment composed predominantly of calcareous pelagic particles. Limestone is a hard calcareous sedimentary rock. Based on material from Magellan Rise, Schlanger and Douglas (1974) proposed that during the burial diagenesis of carbonate ooze, mechanical compaction reduces the porosity from 80% near the seafloor to 60% at 200 mbsf (meters below the sea floor) transforming the ooze into chalk. Hamilton (1976) indeed found that calcareous ooze of porosity close to 80% compact by mechanical loading, reducing the porosity to 60%. Lind (1993) found that deep sea chalk with matrix porosity down to around 40% may compact by mechanical loading. Schlanger and Douglas (1974) incurred recrystallization as a porosity reducing mechanism, whereas Borre and Fabricius (1998) found that recrystallization only changes the shape of the particles. By recrystallization, irregular and small calcite crystals dissolve and re-precipitate on larger and smoother crystals. Fabricius (2003) found that recrystallization may lead to the formation of contact cement, which counteracts mechanical compaction and thus tends to preserve porosity. Porosity reduction due to chemical action probably takes place by pressure dissolution. Pressure dissolution between calcite crystals in chalk was proposed, but not documented by Scholle (1977), whereas signs of pressure dissolution are observed at stylolites, indicating that pressure dissolution more likely takes place at silicate–calcite contacts as discussed by Fabricius and Borre (2007).

Porosity is defined as the total void space in the rock relative to the bulk volume. However, the volumetric composition of a chalk sample can be divided into solid phase, *G* and porosity, ϕ . The solid phase is composed of large grains, *G*₁, smaller matrix grains, *G*_s, and fine grained insoluble residue, *G*_{ir} (Fig. 3). The large grains include calcareous microfossils where as clay minerals, pyrite and silica constitute the insoluble residue. The porosity can be subdivided into large porosity, ϕ_1 and small porosity, ϕ_s . Matrix porosity, ϕ_m is the pore space between the small grains, expressed as:

$$\phi_{\rm m} = \frac{\phi_{\rm s}}{\phi_{\rm s} + G_{\rm s} + G_{\rm ir}}. \tag{2}$$

Porosity reduction is governed by the effective stress as defined by Eq. (1). Diagenetic porosity reduction may be associated with sediment stiffness as described by Biot's coefficient. In a linear-elastic isotropic sediment β may ideally be calculated from sonic velocity (compressional velocity, V_p and shear velocity, V_s) and bulk density ρ_b (Biot and Willis, 1957):

$$M = \rho_b V_p^2 \tag{3}$$

$$\mu = \rho_b V_s^2 \tag{4}$$

$$K = M - \frac{4}{3}G \tag{5}$$

$$\beta = 1 - \frac{K_{\rm dry}}{K_0} \tag{6}$$

where, M, μ and K are the compressional, shear and bulk modulus of the rock respectively. K_{dry} is the bulk modulus of the dry rock and K_0 is the mineral bulk modulus. During mechanical compaction porosity decreases, but β remains close to one, as compaction requires movement of particles relative to each other. Recrystallization in itself should not influence β , unless it leads to contact cementation, where the sediment stiffens, so that β declines although porosity remains constant. Porosity reduction via pressure dissolution and pore-filling cementation is associated with declining β .

Biot's coefficient is a measure of sediment stiffness. In the present paper we addressed how this is related to the stress of pore collapse and creep for the calcareous sediments of Kerguelen Plateau. This may point to a route for prediction pore collapse in porous North Sea chalk from data on porosity and seismic velocity.

2. Kerguelen Plateau

Kerguelen Plateau is a topographic high surrounded by deep ocean basins. We studied Site 1138 of ODP Leg 183 in the Central Kerguelen Plateau, which is located at 53°33.105′S and 75°58.493′E (Fig. 1). Site 1138 was rotary cored to a depth of 842.7 mbsf. The sediments in the studied borehole include chalk and calcareous ooze (Fig. 2). No presence of limestone was reported at any depth of the well. At the studied site, the first 112 mbsf are dominated by foraminifer-bearing diatom clay



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of amorphous silica.

3. Sampling and ODP data



Fig. 3. Schematic figure of the phases of a chalk sample. Intra-particle or large pores, ϕ_l and inter-particle or matrix pores, ϕ_s constitute the pores. The solid is composed of large calcitic grains, G_h small calcitic grains, G_s and other solid minerals, G_{ir} as clay, silica etc. Modified after Rogen et al. (2001).

(smectitic) with inter-bedded foraminifer-bearing diatom ooze: diatoms are composed of amorphous silica. Carbonate content of this section is low (average 23%). Between 112.0 and 265.9 mbsf, sediments contain foraminifer-bearing nannofossil clay and foraminifer-bearing nannofossil ooze. Carbonate content keeps increasing with depth in this interval, with 55% average at the top to 90% at the bottom. Amorphous silica (Opal-A) is the second major component. XRD analysis also shows the presence of alkali feldspar whereas clay mineral content is minor. Coffin et al. (2000) reported the presence of sand-sized grains of basalt

Table 1

General description of the samples used in this project from ODP Leg 183, Site 1138, Kerguelen Plateau. (Coffin et al., 2000).

Sample ID	Top (cm)	Bot. (cm)	Depth (mbsf)	Epoch	Age (Ma)	Description
008R4	140	150	70.2	Late Pliocene	2.6	Foraminifer-bearing diatom clay and foraminifer-bearing diatom ooze
013R4	135	150	117.8	Late Miocene	4.85	Nannofossil clay
019R2	135	150	172.5	Middle Miocene	11.7	Foraminifer-bearing nannofossil ooze
024R1	135	150	219.1	Middle Miocene	17.4	Foraminifer-bearing nannofossil ooze
029R2	135	150	268.7	Late Oligocene	25.5	Foraminifer-bearing nannofossil chalk and foraminifer-bearing nannofossil ooze
036R4	135	150	338.8	Late Eocene to Early Oligocene	35	Foraminifer-bearing nannofossil chalk
042R2	135	150	393.6	Middle Eocene	42	Foraminifer-bearing nannofossil chalk
048R1	135	150	449.9	Late Paleocene	53.7	Foraminifer-bearing nannofossil chalk
051R1	135	150	478.4	Early Paleocene	62.5	Foraminifer-bearing nannofossil chalk
059R1	123	138	554.8	Late Campanian	78	Foraminifer-bearing chalk
061R2	124	139	575.6	Late Campanian	79.9	Foraminifer-bearing chalk
066R3	135	150	625.4	Santonian to Turonian	85	Chalk

Table 2

Physical properties from core analysis and minerals from XRD. Specific surface of solid mass was measured by BET method on both original powdered sample and on irreducible residue (IR) after removing carbonate fraction form the sample. C = calcite, Q = quartz, O-A = opal-A, HA = high albite, S = smectite, I = illite, $F_k = potassium feldspar$, Ct = clinoptilolite, Ba = Barite.

Sample	Grain	Wet bulk	Initial	CaCO ₃	Specific sur	face (grain)	Specific sur	face (IR)	Mineral composition	
ID	(g/cm ³)	(g/cm ³)	porosity (%)	(%)	(m^2/g)	(μ^{-1})	(m^2/g)	(μ^{-1})	from XRD analysis	
008R4	2.63	1.52	69	30.8	32	84	84	220	C, Q, O-A, A _h , B	
013R4	2.57	1.43	73	38.6	13.1	34	34	86.3	C, Q, O-A, A _h	
019R2	2.70	1.68	60	92.4	2.8	7.7	48	130.5	C, Q, O-A, A _h , B, I	
024R1	2.71	1.73	58	94.9	2.3	6.2	90	243	C, Q, O-A, A _h , F _k , Ct, S, I	
029R2	2.70	1.78	55	93.3	3.2	8.7	119	321	C, Q, O-A, A _h , B, S, I	
036R4	2.70	1.87	49	82.5	16.1	43	142	382	C, O-A, A _h , F _k , Ct, S	
042R2	2.70	1.89	47	94.0	4.3	11.6	137	369	C, Q, O-A, B, Ct, S	
048R1	2.69	1.86	50	93.9	2.5	6.7	73	197.3	C, O-A, A _h , B, Ct, S	
051R1	2.72	2.01	42	91.0	4.7	12.9	30	82.2	C, B, Ct, S	
059R1	2.72	2.01	41	94.3	3.1	8.5	90	245	C, B, S	
061R2	2.71	2.11	35	95.5	1.68	4.7	99	268	C, Q, O-A, A _h , B, F _k , S	
066R3	2.73	2.29	26	85.8	11	30	112	306	C, O-A, A _h , B, Ct, S, I	

and black silt in some intervals. Lithology changes from foraminifer-

bearing nannofossil clay to white foraminifer-bearing nannofossil ooze reflected in a considerable increase in grain density (~2.3 to 2.8 g/cm³),

decrease in porosity (~80% to 50%) and increase in bulk density (1.2 to

1.8 g/cm³). Between 265.9 and 601.8 mbsf, the sediment consists of light gray and light greenish gray foraminifer-bearing nannofossil chalk.

However, nannofossils cannot be identified in smear slides after

496.4 mbsf (Coffin et al., 2000). Average carbonate content increases from 90% to 94% in this depth interval. Between 601.8 and 655.6 mbsf,

the characteristic sediment is light gray foraminifer-bearing chalk with occurrence of gray, greenish gray and black intervals of nannofossil clay.

Average carbonate content ranges from 93% to 96%. However, the

amount of carbonate is remarkably low in some intervals rich in opal-A

and quartz. Distinct opal-CT peaks in XRD analysis of samples from this interval was reported by Coffin et al. (2000) indicating recrystallization

We analyzed 12 whole round samples from Site 1138 (Fig. 1). The

samples (Table 1) were preserved in sealed containers and stored in refrigerator in order to avoid drying. Vertical 1 in. plugs were cut from

these samples for sonic velocity measurement and compaction

testing. Useful samples for compaction tests could not be cut from

samples 24R1 and 29R2. Chips and side trims were also collected to

measure physical properties (Table 2) and for preparing polished thin

sections. In the soft ooze section, plugs were cut by hand with a steel

pipe, while plugs from the chalk section were drilled with diamond

bit. Laboratory tests were run as soon as possible after the collection of

plugs in order to maintain natural water saturation. Later, one dry

plug was also collected from each of the sections 036R4, 042R2 and

4. Theory and method

059R1 as velocity data achieved from saturated sample were not reliable due to the weak signal achieved during sonic measurement. A total of 46 saturated plugs and 3 dry plugs were collected.

4.1. Mineralogy

Physical properties from ODP core database were compared with laboratory measured data from this project. Shipboard bulk density, grain density and porosity were measured by gravimetric methods on discrete samples. Compressional wave velocity was measured on split core sections or on cut samples. We used the data measured in the vertical direction of the core (*x* direction). Shipboard velocity was also measured in radial directions, which indicated that velocity anisotropy at this site is less than 15% (Coffin et al., 2000).

Carbonate content of each sample was measured by treating the finely powdered sample with surplus of 0.5 M hydrochloric acid and subsequent titration with 0.5 M sodium hydroxide. XRD tests were conducted on orientated samples using Cu K- α radiation, with Philips PW 1830 diffractometer to determine the mineral compositions of each sample. We analyzed both the powdered bulk sample and the residue after removing carbonates. We run the tests from 5° to 65°



Fig. 4. Backscattered Electron (BSE) images used for the analysis of porosity, specific perimeter and grain size distribution. Images marked with (a1) to (11) are small magnification images (1280×960 µm) and (a2) to (12) are large magnification images (42.1×31.6 µm). The black part is the pore space and white is solid calcite. Light gray is silicate. The bar between two images shows the distribution of different components of the rock.

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 (2θ) for the powdered original material and 5° to 40° (2θ) for the residue (Table 2).

Specific surface of each sample was measured by nitrogen adsorption technique (BET) (Brunauer et al., 1938). Grain density, $\rho_{\rm g}$ and porosity, ϕ were obtained from helium porosimetry. Bulk density, $\rho_{\rm b}$ was calculated from the volume and weight of the core plugs (Table 2).

4.2. Image analysis

Polished sections were prepared from epoxy-impregnated samples. Porosity, specific perimeter, grain size distribution and texture were determined from image analysis of Backscatter Electron (BSE) micrographs (Fig. 4). BSE images were recorded by a JEOL JSM 5900 LV electronic microscope at 1280×960 pixels resolution and at two different magnifications. The high magnification image is the centre part of the small magnification image. Two sets of images from each core were taken at each stated magnification. Chalk matrix, insoluble residue and matrix porosity were determined from the large magnification image (Fig. 4, Table 3). Microfossils, chalk clasts and shell debris as well as intra-particle porosity were identified from the small magnification images (Fig. 4). The image analysis procedure is sensitive to choice of porosity threshold. Values were estimated by setting the porosity threshold at visually estimated maximum,



Fig. 4 (continued).

minimum and best possible position. Texture was determined from $1280 \times 960 \,\mu\text{m}$ (small magnification) BSE images. We used Dunham (1962) classification to define texture (Table 3).

We examined the porosity reduction process using the diagenesis model based on image analysis introduced by Borre and Fabricius (1998). They defined three different processes during the diagenesis: compaction, recrystallization and cementation. Compaction reduces porosity by reallocating the particles closer to each other; specific perimeter with respect to particles, *S*_{par} remains constant, while specific perimeter with respect to pores, S_{ϕ} increases. Recrystallization is a time dependent process, where particles become smoother without making any change in the pore volume; both S_{par} and S_{ϕ} reduce. However, recrystallization allows the particles to come closer if mechanical compaction is active; thus reducing porosity. Porefilling cementation, pore volume decreases at a greater rate than the particle-pore interface; S_{par} will decrease, while S_{ϕ} will increase. Where mechanical compaction is not active for some time, recrystallization

Table 3

Results from image analysis. Specific perimeter with respect to pores and grains is calculated from specific perimeter with respect to bulk area (Eqs. (7) and (8)). Texture is classified according to Dunham (1962).

Sample ID	Grain Pore (%) (%)			Matrix porosity (%)				Specific perimeter (μ^{-1})				Texture			
	Large	Std. dev.	Large	Std. dev.	Small	Std. dev.	100 μ image	Std. dev.	5 µm image	Std. dev.	Bulk (S)	Std. dev.	Pore (S_{ϕ})	Grain (S _{par})	
008R4	12.9	1.7	11.0	1.6	58.0	1.6	76.3	1.2	74.5	4.1	12.4	0.05	16.2	52	Mudstone
013R4	7.8	1.2	11.0	1.1	62.0	1.1	76.3	1.0	74.0	1.8	10.3	0.25	13.5	44	Mudstone
019R2	11.9	2.2	6.0	2.3	54.0	2.3	65.5	0.8	61.9	2.9	10.2	0.22	15.6	30	Mudstone
024R1	11.7	2.2	7.0	1.7	53.0	1.7	65.4	1.2	61.3	3.6	10.3	0.26	15.8	30	Mudstone
029R2	12.3	2.7	7.0	2.5	53.0	2.5	65.2	1.2	60.8	3.9	9.9	0.14	15.2	29	Wackestone
036R4	15.1	1.9	2.5	1.2	46.5	1.2	56.2	0.9	52.6	4.3	9.3	0.25	16.5	21	Mudstone
042R2	14.7	1.2	4.0	1.0	43.0	1.0	52.4	0.6	51.0	4.4	8.5	0.18	16.1	17.8	Mudstone
048R1	11.2	1.1	8.0	0.8	42.0	0.8	52.4	0.4	51.6	4.2	8.5	0.27	16.3	17.9	Wackestone
051R1	10.8	1.3	4.9	1.0	37.1	1.0	44.0	0.4	46.0	3.8	8.3	0.18	19.0	14.9	Mudstone
059R1	13.2	2.5	6.5	1.6	34.5	1.6	43.2	0.4	43.6	3.1	7.6	0.19	17.7	13.5	Wackestone
061R2	13.3	2.1	4.2	0.6	30.8	0.6	37.5	0.6	39.0	5.8	6.6	0.34	17.5	10.5	Wackestone
066R3	11.5	3.2	3.3	1.1	23.7	1.1	26.9	0.3	30.4	3.6	5.3	0.25	19.9	7.3	Mudstone

may lead to contact cementation, thus preventing compaction (Fabricius, 2003).

Specific perimeter was determined from the large magnification BSE images (Borre et al., 1997). Specific perimeter with respect to bulk area, *S* is calculated from the ratio between the total perimeter and total area of the image. S_{ϕ} and S_{par} is calculated by dividing *S* by porous fraction, ϕ and grain fraction, $(1 - \phi)$, respectively:

$$S_{\phi} = \frac{S}{\phi} \tag{7}$$

$$S_{\text{par}} = \frac{S}{(1-\phi)} \tag{8}$$

4.3. Biot's coefficient from sonic velocity

We calculated β from the bulk modulus of the sediment as determined from sonic tests on core plugs (Eqs. (3)–(6)). Compressional wave velocity, V_p and shear wave velocity, V_s were measured at 700 kHz. We calculated K_{dry} (to use in Eq. (6)) in three different ways: (1) direct measurement on dry sample. (2) Iso-frame modeling under assumption of a critical porosity of 100% (Fabricius, 2003) when there was no shear wave velocity data. For this modeling we assumed calcite mineralogy, hence considered a bulk modulus for pure calcite, K_0 (75 MPa, citation in Mavko et al., 1998). (3) By using Gassmann's (1951) equation (Eq. (9)) when velocity was measured on saturated plugs:

$$\frac{K_{\text{sat}}}{K_0 - K_{\text{sat}}} \approx \frac{K_{\text{dry}}}{K_0 - K_{\text{dry}}} + \frac{K_{\text{fl}}}{\phi(K_0 - K_{\text{fl}})}; \mu_{\text{dry}} = \mu_{\text{sat}}$$
(9)

where, K_{sat} is the bulk modulus for the saturated rock and K_{fl} is the modulus for saturating fluid. μ_{dry} and μ_{sat} are shear modulus of dry and saturated sample respectively (Table 4).

4.4. Mechanical compaction test

We performed compaction tests in a 1-inch (25 mm) stainless steel, uniaxial confined compaction cell (Lind, 1993) to determine elastic modulus and the porosity reduction under incremental loading (consolidation), as well as under constant loading for a longer period (creep). All the tests were conducted in drained (through upper filter) condition and at room temperature. Sample length varies from 31 mm to 48 mm. Two pre-determined strain rates were applied for the tests: $1.1 \times 10^{-6} \, \rm s^{-1}$ and $2.2 \times 10^{-6} \, \rm s^{-1}$ (0.4%/h and 0.8%/h); but in order to examine the effect of strain rate we run tests at four different strain rates $(1.7 \times 10^{-6} \, \rm s^{-1}, 0.78 \times 10^{-6} \, \rm s^{-1}, 0.33 \times 10^{-6} \, \rm s^{-1}$ and $0.22 \times 10^{-6} \, \rm s^{-1}$ or 0.62%/h, 0.28%/h, 0.12%/h and 0.08%/h respectively) using four different plugs. We also run tests with different sample length to observe the effect of friction with the steel cell. To check the repeatability of the test, we applied the same strain rate on equally

Table 4

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Compressional (P) wave velocity, V_p and shear (S) wave velocity, V_s of the samples at water saturated condition. Bulk density and velocities were used to calculate Biot's coefficient to estimate the effective stress at the studied depth.

Sample ID	Depth (mbsf)	P-wave velocity (km/s)	S-wave velocity (km/s)	Bulk density (g/cm ³)	Bulk modulus (GPa)	Total vertical stress (MPa)	Hydrostatic pressure (MPa)	Biot's coefficient Error \pm		Diff. stress (MPa)	Eff. stress (MPa)
008R4	70.20	1.720	0.47	1.35	3.6	12.47	12.25	1.00	0.01	0.25	0.25
013R4	117.8	1.700	0.68	1.48	3.4	13.17	12.74	1.00	0.01	0.46	0.46
019R2	172.5	1.721	0.82	1.63	3.4	14.04	13.29	1.00	0.01	0.71	0.71
024R1	219.1			1.69		14.81	13.76	-		1.04	-
029R2	268.7			1.73		15.65	14.26	-		1.44	-
036R4	338.8	1.871	1.26	1.68	2.3	16.81	14.97	0.99	0.01	1.83	2.0
042R2	393.6	2.02	1.16	1.84	4.2	17.80	15.53	0.96	0.01	2.2	2.9
048R1	449.9			1.89		18.85	16.09	-		2.7	-
051R1	478.4	2.58	1.30	2.00	8.8	19.41	16.38	0.93	0.01	3.0	4.2
059R1	554.8	2.64	1.25	2.02	9.9	20.9	17.16	0.92	0.001	3.7	5.1
061R2	575.6	2.87	0.94	2.04	14.4	21.4	17.36	0.91	0.002	3.9	5.5
066R3	625.4	2.94	1.31	2.15	13.7	22.4	17.87	0.89	0.003	4.5	6.5

sized samples. We run each test in a sequence: (1) loading to 80 MPa at pre-determined strain rate, (2) keeping the sample under 80 MPa load for approximately 100 h in order to obtain creep strain (3) unloading to atmospheric pressure.

Several authors (e.g. Mese and Tutuncu, 2000; Alam et al., 2009) have found that pore pressure associated with the Biot's coefficient (Eq. (1)) plays a significant role in deformation. Mese and Tutuncu (2000) obtained experimental data on bulk compressibility that vary by an order of magnitude depending on the way the load was applied e.g. by increasing the confining stress or by decreasing the pore pressure. Alam et al. (2009) found that static Biot's coefficient is a stress path controlled parameter. However, in order to avoid too many variables, we performed the tests at constant pore pressure condition. Effective stress was varied only by changing the axial stress.

We calculated oedometer modulus from the slopes of the axial stress, σ_a and axial strain, ε_a curve (Feeser and Brückmann, 1995):

$$E_{\text{oed}} = \frac{\Delta \sigma_a}{\Delta \varepsilon_a}.$$
 (10)

Yield stress was determined by choosing the point in the strainstress curve where it moves from the elastic to the elastoplastic region. Yield stress indicates the elastic to plastic transformation during a loading test. For loose sediment yield stress is the same as the maximum stress the sediment has experienced after its deposition (preconsolidation stress). Cementation may increase the yield stress significantly above preconsolidation stress.

We used a constitutive model (De Waal and Smits, 1985) to simulate the creep obtained in the laboratory. It was done by changing the parameters in Eq. (11) and Eq. (12) until the simulated curve fairly fits the laboratory curve:

$$\varepsilon_{\rm creep} = bc_{\rm m0}\sigma \ln \left(1 + \frac{\varepsilon_{\rm a}'t}{bc_{\rm m0}\sigma}\right) \tag{11}$$

$$\frac{d\varepsilon_{\rm creep}}{dt} = \left(\frac{t}{bc_{\rm m0}\sigma} + \frac{1}{\varepsilon_{\rm a}'}\right)^{-1} \tag{12}$$

where, *b* is the time-delay factor (to be fitted), $\varepsilon_{\text{creep}}$ is the creep strain, ε'_a is the strain rate before creep (to be fitted), c_{m0} is the compressibility at specific stress ($c_{m0} = 1/E_{\text{oed}}$ at 80 MPa), σ is the creep stress (80 MPa for our case) and *t* is the time the sample was subjected to stress σ .

5. Results

5.1. Porosity and bulk density

Reduction of porosity with depth was observed from the shipboard data and laboratory data of this project (Table 2). However,



Fig. 5. Summary of rock physical properties for brine saturated samples: (a) helium porosity, (b) carbonate content, (c) bulk density, (d) sonic velocity and (e) Biot's coefficient. Lithologic units are defined according to Coffin et al. (2000) (Fig. 2). Dark dotted lines indicate shipboard measurement on discrete samples and fade dash-dotted line indicates calculated values by using shipboard data. Symbols are data measured in the present study. In panel (d) Vp-Gassman is the compressional velocity calculated for 100% water saturated samples by using Gassmann's (1951) equations on velocity data of dry samples. Vs-IF modeled is the shear wave velocity calculated by using iso-frame model (Fabricus, 2003) from shipboard compressional wave velocity and Vg-Gassmann's (1951) equations. Vp-best and Vg-best and Vg-best are vere used for calculation of Biot's coefficient. The low shear wave velocity at 478 mbsf is most probably related to the interpretation of a weak compressional wave signal. Vs-best at this depth was calculated from the best compressional velocity data by using is on-frame model as indicated by a dark square.

depending on the type of sediment, age and burial depth, the rate of porosity reduction varies. We tried to correlate the porosity reduction and density change with the lithologic units described by Coffin et al. (2000) (Fig. 5). It shows that faster porosity reduction occurs in the ooze (Sections I and IIA). Porosity reduces at a slower rate in the deeper ooze in Section IIB and chalk in the Section IIIA until 500 mbsf. The reason for the high porosity shown in the shipboard measurement between depth 280 mbsf and 325 mbsf was not explained, as we did not have samples from that interval. However, it may be a high content of opaline fossils. Below the depth 500 mbsf until 625 mbsf in the deeper chalk Sections IIIB and IV, the rate of porosity reduction is slightly lower than in the previous section. The low porosity of a sample from 625 mbsf is probably due to the poor sorting of particles (Fig. 4i). A high non-carbonate fraction (clay) occupies some of the pore space in this sample. Image analysis shows that intrafossil (large) porosity does not change significantly with depth and time (Fig. 6a). Change in total porosity with depth is mainly due to the change in small porosity.

5.2. Mineralogy and texture

The sediments are mostly carbonate mudstone, but wackestones (samples 029R4, 048R1, 059R1 and 061R2) were also found (Fig. 4). Mineralogy in the investigated interval is not homogeneous. Some intervals are rich in amorphous silica (Opal-A), indeed the amount of non-carbonates exceeds 60% in the top 120 m (Late Pliocene and Late Miocene). More than 15% non-carbonate fraction (mainly amorphous silica) was also found in samples near 340 mbsf (Late Eocene to Early Oligocene) and below 625 mbsf (Santonian to Turonian). High specific surface was found in intervals where the non-carbonate



Matrix porosity • Helium porosity • Sp. surface from BET (bulk)

Carbonate content

Fig. 6. Comparison of laboratory data and image analysis data. (a) He-porosity compared to image analysis porosity. Carbonate content is plotted in order to illustrate the effect of mineralogy. Large porosity does not vary much with depth. Change in total porosity is mainly due to the reduction of small porosity. (b) Specific perimeter estimated from image analysis tends to be significantly smaller than the specific surface determined from BET method in intervals where carbonate content is low.

fraction is high (Table 2). This may be due to the high specific surface of amorphous silica and clay. Transformation of Opal-A to Opal-CT was not observed in the studied samples.

Specific perimeter estimated from image analysis differs from specific surface calculated from BET analysis (Fig. 6b). This is to be expected because BET method is a 3D method where image analysis only looks at 2D images. The difference tends to be high where carbonate content is low (Fig. 6b). In clay rich samples the image analysis procedure would give a relatively low specific perimeter value, because clay particles may be smaller than the pixel size (980 nm²) of the image, while the nitrogen atom (0.16 nm²) is smaller than clay particles.

5.3. Sonic velocity

Compressional wave velocity, V_p measured in core plugs compares fairly with shipboard data (Fig. 5). Error in V_p measurement is \pm 50 m/s. Shear wave velocity was measured with high uncertainty on brine saturated samples due to the very weak signal and the error in measurement may exceed \pm 100 m/s. We checked the acceptability of shear wave velocity data by using iso-frame model (Fabricius, 2003); in which we predicted shear wave velocity from the compressional wave velocity (Fig. 5). The reliability of the data was also checked by comparing to data by using Gassmann (1951) equation (Eq. (9)) (Fig. 5). One value which differs more than \pm 100 m/s from the modeled value was discarded.

Shear wave velocity and compressional wave velocity do not follow the same depth trend as porosity and bulk density (Fig. 5). Changes in sonic velocity with depth cannot be correlated according to the lithologic units described by Coffin et al. (2000). From sea floor to a depth of 300 mbsf shear wave velocity increases faster than compressional wave velocity. Due to the recrystallization process, grains become smoother at this interval and probably attain more grain to grain contact and the sliding ability among grains reduces. This process increases the shear strength (and shear velocity) of the rock. After 300 mbsf contact cementation is indicated by the rapid increase of compressional wave velocity. On the other hand porosity reduction rate reduces due to the stiffening of sediments.

5.4. Biot's coefficient

Biot's coefficient was found to decrease from 1 to 0.89 with depth in the studied interval (Fig. 5). Biot's coefficient is 1.00 for loose sediment and β below 1.00 indicates the development of contact cement between particles and stiffening of the sediment. The studied samples do not show β values less than unity above the depth 339 mbsf. This indicates the development of contact cement below this depth. BSE images show contact cement from 339 mbsf and below (Fig. 4), reducing the Biot's coefficient to 0.89. Low porosity between depth 575 mbsf and 625 mbsf may be due to the high content of fine grained non-carbonate fraction rather than pore-filling cementation (Figs. 6 and 4).

5.5. Strength properties from mechanical test

The general observation from the strain-stress curves (Fig. 7) is that strain increases with stress. The sediment will deform permanently (porosity reduction) with the applied load. However, the actual amount of strain due to the in-situ effective stress in the field case may only be obtained with approximation. This is because the laboratory tests may be influenced by the selection of sample, sample size, strain rate and test procedure.

For the same amount of stress, a very short sample got more strain than the longer ones (Fig. 7g). This could be due to the friction between the cell and the sample, so that actual strain could be restricted in the long samples. On the other hand results of shorter


Fig. 7. Strain–stress curves produced during mechanical loading tests. In the legend, sample names include the core section followed by plug no., plug length in mm and strain rate in 10^{-6} s^{-1} (strain rate $1.1 \times 10^{-6} \text{ s}^{-1}$ and $2.2 \times 10^{-6} \text{ s}^{-1}$ is equal to 0.4%/h and 0.8%/h respectively). Strength of the sediments increases with deeper burial and strain gets smaller. Steel cell restricts the radial deformation and axial strain gives the volume change due to applied stress. Therefore, elastic strain was calculated from the compressional modulus (Eq. (3)).

samples could have higher influence from the instrument. We found that the strain obtained for sample length between 35 mm and 50 mm is comparable (Fig. 7d, g, h and i).

Strain rate in the laboratory is too high compared to natural strain rate. We applied 6.5 MPa (which is the effective stress at 625 mbsf) stress to the samples taken from 70 mbsf and their porosity reduced to 49% from 70% initial porosity, whereas the porosity at 625 is as low as 26%. By assuming that all the porosity reduction in nature is due to the direct mechanical load and creep due to the effective stress, the

strain rate in the Kerguelen Plateau was calculated as $1.1 \times 10^{-16} \text{ s}^{-1}$ (0.4×10^{-10} %/h), while the applied strain rate in the laboratory was $1.1 \times 10^{-6} \text{ s}^{-1}$ (0.4%/h). At the same applied stress, less strain tends to occur while the applied rate of strain is higher (Fig. 7a, b, c, and j). However, for the same sample length and the same strain rate, different amounts of strain can be achieved (Fig. 7d). On the other hand samples of same size may have same amount of strain should thus be considered with an error margin of $\pm 5\%$.

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Table 5

Consolidation test data. Creep obtained at 80 MPa.

Sample	Depth (mbsf)	Before loading		After loading		Loading			Yield stress	Creep		
ID		Length (mm)	Porosity (%)	Length (mm)	Porosity (%)	Strain rate (%/h)	E _{oed} at in-situ stress (GPa)	Strain (%)	(MPa)	Time (h)	Strain ɛ _{creep} (%)	Fitting parameter $b \ (\times 10^{-2})$
008R4a	70.20	42.45	69	19.35	40.2	0.4	0.003	55.9	0.4	62.0	0.56	2.9
008R4d	70.20	43.32	69	19.79	39.3	0.8	0.005	51.9	0.5	66.7	0.51	2.8
013R4a	117.8	41.05	73	19.32	38.5	0.4	0.006	50.8	1.1	97.3	0.51	5.5
013R4d	117.8	47.74	73	22.05	41.1	0.8	0.003	49.3	1.2	173.8	0.49	4.8
019R2a	172.5	36.79	60	24.77	40.8	0.8	0.067	28.2	3.0	103.1	0.28	6.7
019R2d	172.5	48.20	60	31.37	44.4	0.4	0.061	30.9	2.8	99.5	0.31	7.3
024R1	219.1	None	58	-	-	-	-	-	-	-	-	-
029R2	268.7	None	55	-	-	-	-	-	-	-	-	-
036R4a	338.8	44.25	49	34.70	41.0	0.4	0.415	20.9	11	104.6	0.21	8.0
036R4c	338.8	44.70	49	36.70	39.1	0.4	0.676	16.41	13	68.1	0.16	9.5
042R2b	393.6	43.81	47	36.70	39.1	0.8	0.704	13.63	13	120.2	0.14	11
042R2c	393.6	42.78	47	36.05	39.5	0.4	0.509	13.42	11	96.8	0.13	13
048R1b	449.9	34.15	50	26.47	33.5	0.4	0.287	21.9	8.0	77.5	0.22	10
051R1a	478.4	35.25	42	32.12	34.2	0.4	1.112	10.14	20	83.9	0.10	12
051R1b	478.4	39.05	42	35.77	35.3	0.6	1.182	7.27	20	74.4	0.07	11
051R1c	478.4	47.92	42	44.33	37.2	0.4	1.469	7.96	20	52.8	0.08	12
051R1d	478.4	22.20	42	18.78	30.1	0.8	0.441	16.85	18	69.0	0.17	12
059R1b	554.8	38.19	41	33.49	32.5	0.2	0.871	11.58	19	29.0	0.12	8.0
059R1d	554.8	38.90	41	33.49	32.4	0.4	0.619	13.24	18	91.7	0.13	8.0
061R2d	575.6	39.15	35	37.50	32.3	0.4	1.662	4.12		96.3	0.04	10
066R3e	625.4	41.30	26	36.44	25.2	0.2	1.450	3.10	21	100.2	0.03	9.0
066R3f	625.4	31.12	26	30.34	27.8	0.8	0.510	7.51	17	96.5	0.08	8.0

Strength related properties achieved from the mechanical loading tests include oedometer modulus, yield stress, strain from direct loading, creep strain and the fitting parameter b (Eqs. (11) and (12)) (Table 5, Fig. 8). Ooze and chalk samples showed distinct behavior during compaction test. The ooze samples have very small oedometer modulus and yield strength as they were not subjected to high effective stress in nature and they have no particle contact cementation, as indicated by high β . Ooze samples obtained high

loading strain as well as creep strain. Oedometer modulus and yield stress gradually increase in the chalk samples with deeper burial. These samples obtained lower loading strain and creep strain. The higher yield strength in the chalk samples compared to the in-situ effective stress is probably due to the development of contact cement as indicated by β ranging between 0.99 and 0.89.

Creep strain develops as a function of logarithmic time (Fig. 9a). The rate of creep strain decreases logarithmically with time (Fig. 9b).



Fig. 8. Results obtained from the interpretation of the curves produced from the steel cell loading tests. Circles indicate tests run at 1.1×10^{-6} s⁻¹ (0.4%/h) and triangles indicate tests run at 2.2×10^{-6} s⁻¹ (0.8%/h). Samples shorter than 37 mm are indicated by a solid marker.



Fig. 9. Creep strain (a) and creep strain rate (b) modeled by De Waal and Smits' (1985) Eqs. (11) and (12) (sample 59R-1B). The solid-dark line shows the experimental curve and the fade-dotted line is the fitted curve.



Fig. 10. Relationship between strain and porosity at the beginning of the application of load. Circles indicate tests run at $1.1 \times 10^{-6} \text{ s}^{-1}$ (0.4%/h) and triangles indicate tests run at $2.2 \times 10^{-6} \text{ s}^{-1}$ (0.8%/h). Samples shorter than 37 mm are indicated by solid marker. Both loading strain (a) and creep strain (b) increase logarithmically, with the increase of initial porosity.

Loading strain and creep strain per logarithmic period correlate with porosity (Fig. 10b).

6. Discussion

6.1. Porosity reduction mechanism

Using the diagenetic model of Borre and Fabricius (1998) and Fabricius (2003) and based on specific perimeter from image analysis, we found that a combination of mechanical compaction and recrystallization and a contact cementation process is involved in the porosity reduction of the studied sediment (Fig. 11). Until 150 m from the sea floor, recrystallization dominates. Although recrystallization dominates the change in specific perimeter, porosity reduction is high (Fig. 5) due to mechanical compaction which causes specific perimeter with respect to pores to increase slightly with depth (Figs. 5 and 11). Between depth 150 mbsf and 450 mbsf the overall trend in specific perimeter corresponds to combined recrystallization and compaction. However, the effect of compaction dominates over recrystallization (Figs. 5 and 11). The rate of porosity reduction decreases below the depth of 500 mbsf (Fig. 5). This may be a result of resistance from the contact cement between the calcite grains. The cement may be partly pore-filling (Fig. 4) which is also indicated by the diagenesis model of Borre and Fabricius (1998) (Fig. 11).

6.2. Compaction studies

Our compaction tests show that loading strain decreases logarithmically with initial porosity (Fig. 10a). After applying 80 MPa stress,



Fig. 11. (a) and (b) Specific perimeter plotted against the sample depth and age respectively. Solid circles represent specific perimeter with respect to particle and open circles indicate specific perimeter with respect to pores. (c) The diagenetic model of Borre and Fabricius (1998).

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porosity reduces about 30 points in the ooze having 73% porosity (Table 5). Chalk having 26% porosity at 625 m depth (mbsf) looses only about 1.5 porosity points. This indicates the stiffening of sediment with deeper burial.

A higher non-carbonate fraction in the chalk may have influence on the mechanical strength. Clay particles residing between the calcite grains restrict the development of contact cement. Contact cement between silica grains and calcite grains is also unlikely. This phenomenon is reflected in the compaction pattern. After the yield stress, the slope of compaction curves for samples with high noncarbonate fraction is steeper than for the clean samples (Fig. 12).

The total porosity-applied stress plot does not show any obvious common trend between porosity and stress (Fig. 12a, c). However, if matrix porosity is plotted against the applied stress a fairly common trend is found in the pure samples (Fig. 12b, d). The large pores (intraparticle porosity) inside the foraminifera most probably remained unaffected during the compaction tests. Our study indicates that porosity reduction in chalk subjected to mechanical load is more likely due to the volume change of the small pores (inter-particle porosity). This is in accordance with other geotechnical studies (Valent et al., 1982; Lind, 1993) and demonstrates the usefulness of discussing compaction in terms of matrix porosity.

From the loading tests, we calculated the porosity reduction that could have occurred by the present in-situ effective stress in each sample (Fig. 13). This indicates that only a very small amount of porosity was reduced by direct loading. As only minor pore-filling cementation was observed in the BSE images (Fig. 4), we conclude that, most of the porosity was reduced by creep. Laboratory tests show that strain rate during creep keeps decreasing with time. In geological timescale recrystallization may also influence the creep strain. Grain smoothing or grain-contact cementation may also alter the creep strain rate. Therefore, creep strain rate stated in Section 5.5 may differ from the natural creep strain rate.



Fig. 13. Porosity reduction by other sources (creep, recrystallization and cementation) than direct loading. Solid (large) circles indicate (a) the total porosity measured in core plugs by helium porosimetry and (b) matrix porosity measured from image analysis. Other data points are calculated from strain when stress equivalent to different sample depths was applied on the core plug during oedometer testing.



Fig. 12. Porosity change calculated from the strain achieved in the mechanical loading. Panels (a) and (b) represent samples which have a silica content of more than 5%, panels (c) and (d) represent relatively pure calcitic samples. When the change is plotted in terms of matrix porosity (b and d) the pure calcitic set shows more similar compaction trends.

6.3. Biot's coefficient

From the rate of decrease in Biot's coefficient it is possible to predict the diagenetic process involved in the natural porosity reduction. Biot's coefficient decreases with the decrease of porosity (Fig. 14a). The rate of decrease is low for recrystallization and compaction and high when contact cementation is involved (Fig. 14).

Samples down to 300 mbsf have Biot's coefficients close to unity, hence strength-indicating properties show very low values. Samples with low moduli (Fig. 14b, c, d) get huge plastic deformation (Fig. 7). Time dependent strain is also high in these samples (Fig. 14f). These results indicate that the contacts between the grains are not strong enough to support mechanical load, although recrystallization and compaction are active. All the physical properties in Fig. 14 do not show significant variation as long as β is close to 1. Compressional modulus, shear modulus, oedometer modulus and yield stress increase with the decrease of Biot's coefficient (Fig. 14b, c, d, e)

indicating the increase of strength due to the development of graincontact cement. Cemented sediments (deeper) with lower value of β get lower creep strain than loose sediment (Fig. 14f).

7. Conclusion

Our study indicates that in the deep sea pelagic carbonates in the Kerguelen Plateau, porosity reduction by compaction and creep takes place by the reduction of the matrix porosity, whereas the large (intra-particle) porosity does not change significantly. Our data show that the majority of the burial-related porosity loss at Kerguelen Plateau is due to the time dependent creep which is a very slow process. By contrast, porosity reduction due to the depletion of pore fluid pressure in a hydrocarbon reservoir is a fast process. Porosity reduces mainly due to the increase of effective stress in this case. Therefore, results from compaction tests should be used to predict compaction in a hydrocarbon reservoir.



Fig. 14. Relationship of Biot's coefficient with different properties of water saturated samples, (a) porosity, small dots indicate shipboard measurement, (b) compressional modulus calculated from compressional velocity and bulk density, (c) shear modulus calculated from shear velocity and bulk density, (d) oedometer modulus, (e) yield strength and (f) creep strain obtained after applying 80 MPa load for longer period (Table 5). Sample depth is indicated next to the data point.

Biot's coefficient is used to calculate the effective stress on subsurface sediments. It reduces with burial depth. The rate of change of Biot's coefficient with porosity reflects the diagenetic process causing porosity reduction. Biot's coefficient has fair correlation with mechanical strength of the rock. Mechanical strength does not increase with porosity reduction as long as $\beta = 1$. Mineralogy does not affect the strength of chalk if $\beta = 1$. Biot's coefficient has negative relationship with compressional modulus, shear modulus, oedometer modulus and yield strength. It has positive relationship with creep strain. Biot's coefficient has the potential to be used as a tool for predicting mechanical strength of reservoir rock due to the changed stress state during hydrocarbon production.

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Permeability prediction in Chalks

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Permeability Prediction in Chalks

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ABSTRACT

Velocity of elastic waves is the primary data available for acquiring information about subsurface characteristics as lithology and porosity. Cheap and quick (spatial coverage; ease of measurement) information of permeability can be achieved, if sonic velocity is utilized for permeability prediction, so we have investigated the use of velocity data to predict permeability. Compressional velocity from wireline logs and core plugs of the chalk reservoir in South Arne (SA) field, North Sea has been used for this study. We compared various methods of permeability prediction from velocities. Relationships between permeability and porosity from core data were first examined by using Kozeny's equation. The data were analyzed for any correlations with specific surface of the grains, S_g and with the hydraulic property defined as Flow Zone Indicator (FZI). These two methods use two different approaches to enhance permeability prediction from Kozeny's equation. The FZI is based on a concept of a tortuous flow path in a granular bed. The specific surface of grains, S_g concept considers the pore space which is exposed to fluid flow, and models permeability as resulting from effective flow parallel to pressure drop. The porosity-permeability relationships were replaced by relationships between velocity of elastic waves and permeability by using laboratory data, and the relationships were then applied to well log data. We found that, permeability prediction in chalk, and possibly other sediments with large surface areas could be improved significantly by using effective specific surface as the fluid flow concept. FZI unit is appropriate for high permeable sedimentary rocks as sandstones and limestones that have small surface areas.

INTRODUCTION

Permeability describes the movement of fluid in a reservoir. Degree of ease associated with fluid movement in rocks determines the fluid and fluid pressure distribution in a reservoir, and it helps to estimate how much oil can be produced economically. Permeability is an important parameter in 3D reservoir modeling and in assessing production strategy. Direct in situ permeability measurements are largely unavailable, so permeability prediction remains an art rather than a science in petrophysical studies. Models come in numerous flavors from empirical, simple capillary tubes, to neural networks. However, they fail because; whereas porosity only depends on the volume of pores, permeability depends on the volumetric and geometric distribution of pores.

Permeability is preferably measured in the laboratory on core plugs. Recovering useable core material by drilling is often costly. Therefore, permeability is frequently predicted from other physical properties of rocks, e.g. porosity, seismic velocity and attenuation. Permeability is classically described as a logarithmic function of porosity. Several authors reported variation in the porosity-permeability relationship, which largely depends on sediment composition and diagenesis (Amaefule et al., 1993; Mortensen et al., 1998; Prasad, 2003; Fabricius et al., 2007a). In order to account for differences in sediment composition Kozeny (1927) described permeability as a function of porosity and specific surface as a physical measure of pore radius. Biot (1956a; 1956b) showed theoretically that velocity of elastic waves in rocks depends on both porosity and pore radius as derived from permeability. The findings of Kozeny and Biot indicate that permeability should be related to sonic velocity. However, using Biot's theory is often stymied by lacking information on pore space parameters.

Velocity-porosity relationships have been extensively studied (Wyllie et al., 1956; Raymer et al., 1980; Nur et al., 1998; Prasad and Dvorkin, 2001; Røgen et al., 2005), whereas velocity-permeability relationships have received less attention. Prasad (2003) showed that velocity-permeability relationships exist in various rocks according to hydraulic reservoir units as defined by the Flow Zone Indicator (*FZI*), and that *FZI* may be used in Biot's theory. The concept of *FZI* unit is based on modifying Kozeny's (1927) equation so as to improve the porosity-permeability relationships in sandstones (Amaefule et al., 1993). Also

based on Kozeny's (1927) equation, Fabricius et al. (2007a) used V_p/V_s ratio and porosity to estimate permeability in carbonate rocks.

Although porosity can be correlated to velocity and to permeability, the relationships are not straightforward. Grain size and shape, sorting, distributions of secondary minerals (e.g. dolomite) determine the surface area to pore volume ratio (specific surface of pores) and thus the difficulty to fluid flow. A presence of fractures can dramatically influence the porosity permeability relationship on a reservoir scale, indeed the magnitude of fracture-permeability in chalk reservoirs (e.g. Valhall field, North Sea) may be in the range of 1000 md to 10000 md, while fracture porosity has insignificant contribution to total porosity (Rogers et al., 2007). However, in the present paper we limit our scope to matrix properties. Size and distribution of grains in a carbonate rock can cause a distinction between pore-body size and pore throat size to be relevant (Pourmohammadi et al., 2007). In this case permeability is defined by the pore throat size, not the pore size and permeability could be significantly low even if the porosity is high. However, North Sea chalks are primarily mudstones and wackestones according to the Dunham (1962) classification, where pore connectivity is high and pore size is fairly uniform (Røgen et al., 2005). From Nuclear Magnetic Resonance (NMR) transverse relaxation time (T_2) relaxation, Alam et al. (2010a) found that there is no free flowing fluid in chalk. Therefore, we did not consider the effects of pores in these sediment types.

Sedimentary rocks undergo diagenetic processes after burial. Mechanical compaction causes porosity reduction: velocity may increase due to increased grain contact and permeability decreases as porosity decreases. Recrystallization by contrast makes the grains smoother, in principle without change in porosity: permeability increases due to smaller specific surface but the effect on velocity is only minor, unless recrystallization causes cementation at the grain contacts. Contact cementation thus increases velocity, whereas porosity is unaffected. Pore filling cementation (lithification) causes porosity to decrease and velocity to increase significantly (Dvorkin and Nur, 1996; DuBernard et al., 2003), while specific surface with respect to pore space becomes larger (Borre and Fabricius, 1998) and permeability decreases. Therefore, a relationship between velocity and permeability should take these geological and geometric factors into consideration.

The diagenetic processes that any given chalk went through can be identified by changes in specific surface (Borre and Fabricius, 1998). Specific surface may be expressed relative to total volume, or relative to pore space, or relative to grain volume. Earlier studies of chalk indicate that specific surface of grain volume tends to be closer to constant for a given stratigraphic unit than specific surface of pores or of total volume (Fabricius et al., 2007a). As changes in specific surface affect both permeability and sonic velocity, we examined the variation of permeability with compressional velocity of sound waves in chalk while referring to specific surface of the grain volume, S_g . We also examined the applicability of the Flow Zone Indicator (FZI) method in chalk that Prasad (2003) had successfully applied in sandstones and limestones. Velocitypermeability and velocity-porosity relationships from the core plug data were checked in terms of S_g units and FZI units. The established relationships between velocity and permeability as derived from core data according to S_g units and FZI units were then used to predict permeability directly from velocity. For comparison permeability was also predicted from porosity, calculated from velocity-porosity relationship for each S_g unit and FZI unit. Each method was tested for permeability prediction by using well-log compressional wave velocity data. We were specifically interested in understanding the controls on permeability in the high-specific surface area chalks as opposed to the lowspecific surface area sandstones and limestones.

North Sea Chalk

Calcareous sediments cover about 48% of the world's seafloor (Sverdrup et al., 1942) and 60% of the world's oil lies in carbonate reservoirs (Akbar et al., 2000). A significant amount of hydrocarbons in the North Sea is placed in chalk reservoirs. Low permeability of this chalk is a great challenge for hydrocarbon production. More efficient production strategies could be designed by having better means of mapping its permeability.

Chalk is a sedimentary rock, developed from the diagenesis of pelagic calcareous ooze. Particles in calcareous ooze are primarily the skeletons of algae called coccospheres. The spherical shaped coccospheres are between 10 and 30 μ m in diameter and composed of 7-20 wheel shaped coccolith platelets of 2 to 20 μ m diameter and 0.5 to 2.5 μ m across (Scholle, 1977; D'Heur, 1984). However, North Sea chalk is predominantly composed of coccolith fragments or aggregates of coccolith platelets: entire coccospheres are relatively rare (Scholle, 1977). This

makes chalk a very fine grained homogeneous rock with high specific surface area. A high specific surface of grains means that also the fluid is exposed to a large surface. Therefore, more force is required to move this fluid to overcome friction leading to very low permeabilities (fraction of milli-Darcy to a few milli-Darcy) in chalk.



Figure 1. (a) Location map of South Arne Field, North Sea. (b) Position of the studied wells within the field, plotted on top of the chalk group depth structure map (Modified after Larsen, 1998). Depth indicates true vertical depth sub sea (TVDSS) in feet.

Despite low permeability, North Sea chalks may have high porosity (up to 50%). Newly deposited oceanic calcareous ooze has porosity between 70% and 80%. Porosity reduces to 60% during the first hundreds meters of burial, mostly due to the mechanical compaction (Schlanger and Douglas, 1974; Hamilton, 1976; Scholle, 1977). Shortly after deposition, recrystallization process starts and smoothens the calcite crystals and allows further compaction and porosity reduction, until grain contact cement starts to form (Borre and Fabricius, 1998; Fabricius, 2003). Fabricius (2003) proposed that grain contact cement is most likely to form at low compaction rate, whereas high compaction rate allow further mechanical compaction. Below a burial depth of around 1 km, in fully drained oceanic settings, pore filling cementation reduces porosity to 10% to 20%. North Sea hydrocarbon reservoirs may be situated at more than two kilometers depth. Porosity of chalk at this depth should be around 15% under normal circumstances (Scholle, 1977). Overpressure causing low normalized or "effective" burial depth (Japsen, 1998) and also incursion of hydrocarbons prior to significant pore filling cementation are possible porosity preserving mechanisms in North Sea chalk (Scholle, 1977; D'Heur, 1984; Andersen, 1995).

The Ekofisk Formation of Paleocene age and the Tor Formation of Upper Cretaceous age from the South Arne field, Danish North Sea were investigated (Figure 1), as these are hydrocarbon reservoirs. These two formations are largely calcitic but have different silica and clay content. In general, the Ekofisk Formation rocks have high specific surface area due to their high content (>12%) of silica and clay (Røgen and Fabricius, 2002). The smaller specific surface area in the Tor Formation rocks is due to low (<5%) content of silica and clay (Fabricius et al., 2008). Typical specific surface areas for the various constituents of a typical North Sea chalk are given in Table 1. Specific surface of chalk containing clay and silica largely depend on the contribution from these phases. Therefore, by accounting for the specific surface area we can indirectly evaluate lithology variations.

Mineral	Specific	Reference					
	surface						
	(m^2/g)						
Calaita	2*	Madsen and Lind, 1998					
Calcile	0.5 - 3.5*	Røgen and Fabricius, 2002					
Quartz	App. 5 [*]	Røgen and Fabricius, 2002					
Qualiz	0.7^{*}	Madsen and Lind, 1998					
	10^{*}	Madsen and Lind, 1998					
Kaolinite	15^{*}	Røgen and Fabricius, 2002					
	5-40	Britannica online, 2010					
Smaatita	60^*	Røgen and Fabricius, 2002					
Smeethe	40 - 800	Britannica online, 2010					

Table 1. Typical specific surface of the minerals in North Sea chalk.

* indicate North Sea data

Due to the variation in specific surface with chalk composition, porositypermeability relationships vary significantly stratigraphically. As a rule for a given porosity, permeability of the Ekofisk Formation is lower than the permeability of the Tor Formation (Andersen, 1995). The variation in permeability of chalk can be addressed by dividing the formations into units according to specific surface area of grains. An equivalent strategy is to assign a series of different flow zone indicator.



Figure 2. (a) Porosity-permeability trends for chalk published in literature. Dark closed and dark open data points are chalk from Tor Formation and Ekofisk Formation of North Sea respectively. Grey closed points represent North Sea chalk, from unknown formations. Limestone and sandstone (samples of Prasad, 2003) are indicated respectively by grey and black dashes with a circle in the middle. Trends for North Sea chalk can be primarily divided into two segments. Sandstone and limestone as studied by Prasad (2003) have significantly higher permeability for a given porosity than North Sea Chalk. (b) Relationship between porosity and compressional wave velocity (V_{p-sat}) as measured in brine saturated North Sea chalk and a few other sedimentary rocks.

Porosity-Permeability Relationship

Despite high porosity, chalk can have low matrix permeability. Several authors (Scholle, 1977; Munns, 1985; Klimentos and McCann, 1990; Mortensen et al., 1998; Bramwell et al., 1999; Frykman, 2001; Røgen et al., 2005; Fabricius et al., 2007b) have published porosity-permeability data for North-Sea chalk (Figure 2). For porosity over 20%, permeability of chalk may be several orders of magnitude lower than that in sandstones (Figure 2a). Chalk with high carbonate content (pure chalk) and a porosity above 20% has around 1md permeability. Permeability of impure chalk (>10% non carbonate fraction) is sometimes below the detection limit (typically 0.01 md) of a conventional gas permeameter.

Published data presented in Figure 2a shows that despite having similar porosity, North Sea chalk permeability varies up to three orders of magnitude. This variation can be explained by a difference in content of clay and silica as expressed in specific surface (Røgen and Fabricius, 2002). Therefore, the variation in the porosity-permeability relationship in North Sea chalk is highly influenced by the non-carbonate fraction that determines the specific surface area of grains.

Mortensen et al. (1998) found that air permeability in chalk is independent of the type of porosity (e.g. intra-particle, inter-particle) and they suggested a porosity-permeability relationship avoiding the tortuosity concept by introducing a porosity dependent 'c' factor, $c(\phi)$ in the Kozeny's equation. The physical meaning of $c(\phi)$ is described in the theory section.

Porosity-Velocity Relationship



Figure 3. Porosity and compressional wave velocity (V_{p-sat}) versus true vertical depth sub sea (TVDSS) shows change in porosity and sonic velocity during burial diagenesis: example from ODP Leg 130, site 807 – core data from ODP database (Kroenke et al., 1991). Both porosity and velocity trends depends on type of sediment or sedimentary rock.

Porosity is considered to be the major controlling factor of the velocity of elastic wave in rocks (Figure 2b). In clay-free, homogeneous chalk at a given stage of diagenesis, velocity may be inversely correlated with porosity. In analogy to the work on sandstones (Han et al., 1986), it is plausible that only a few volume fractions of clay could change such a trend significantly (Han et al., 1986). Røgen et al. (2005) found that the porosity-velocity relationship in chalk also depends on the type of clay minerals. For the same porosity, samples with kaolinite have higher velocity than samples with smectite. Based on data from ODP Leg 130, site 807, Fabricius (2003) showed that the porosity-velocity trend

changes during the diagenetic process (Figure 3). Compressional wave velocity remains almost constant until the ooze starts to transform into chalk. Velocity increases with depth in the chalk interval indicating the growth of grain contact cement. Limestone develops as a result of pore filling cementation. Decrease in porosity and increase of velocity over a short depth interval occurs at the transition between chalk and limestone (Figure 3). Thus we see that the velocity – porosity relationship is made complicated by the geometric distribution of pores and cements (Prasad, 2003).

In this paper, we will compare permeability predicted from velocity with the more conventional indirect process involving porosity predictions from velocity and then the use of sonic porosity to estimate permeability. Since both velocity and permeability are governed by volumetric and geometric considerations, whereas porosity is only a volumetric description, the factors controlling the porosity-velocity relationship could also govern the porosity-permeability relationship. Therefore, by statistical analysis of the data we will assign a Flow Zone Indicator and for comparison a specific surface of the grains to intervals of the reservoir.

THEORY

Tortuosity and Flow in Porous Media



Figure 4. Conceptual flow through a porous rock. All porosity shown in grey shade. (a) Flow in a tortuous path. Actual equivalent flow length (l_e) is longer than the net travelled distance, due to the curved flow path. (b) Concept of flow path in pore space with high connectivity (adapted form the concept of Mortensen et al., 1998). Branches with dark grey shade are aligned in the direction of flow.

It is widely defined in literature that fluid flow in porous media occurs in a tortuous path (Kozeny, 1927; Carman, 1937; Amaefule et al., 1993), where the length of actual equivalent channel for fluid flow is longer than the physical length of a porous medium (Figure 4a). On the more simple assumption that a

granular bed is analogous to a group of capillaries parallel to the direction of flow, Darcy (1856) developed a fluid flow equation through porous media:

$$Q = k \frac{A}{\mu} \frac{\Delta P}{l},\tag{1}$$

where, k is permeability, ΔP is the pressure difference over length, l, with cross sectional area A. μ is the dynamic viscosity of the flowing fluid. Darcy's equation is based on Poiseuille's law for the flow of a viscous fluid through a capillary tube:

$$Q = \frac{\pi d_e^4}{128\mu} \frac{\Delta P}{l},\tag{2}$$

where, d_e is the equivalent diameter of the capillary tube.

Flow Zone Indicator (FZI)

Based on laminar flow of fluid in porous media, Kozeny (1927) derived:

$$k = c \frac{\phi^3}{S^2},\tag{3}$$

$$k = c \frac{1}{S_g^2} \frac{\phi^3}{(1 - \phi)^2},$$
(4)

where, k is liquid permeability (Klinkenberg, 1941), ϕ is porosity and c is Kozeny's constant. Kozeny (1927) found that the value of c is around 0.25. S and S_g are grain surface per unit bulk volume and grain surface per volume of grains, respectively. Carman (1937) presented Kozeny's equation as:

$$k = \frac{1}{F_s \tau^2 S_g^2} \frac{\phi^3}{(1-\phi)^2},$$
(5)

where, F_s is a dimensionless shape factor and τ is tortuosity defined as the ratio between a conceptual actual flow length, l_a and sample length, $l(\tau = l_a/l)$ (Figure 4a). It can be seen that, $1/F_s\tau^2$ replaces Kozeny's constant. It varies with the internal structure of the sediments and thus with specific surface, but may be assumed as fairly constant within the same hydraulic unit (Amaefule et al., 1993). Rearranging Eq. 5, Amaefule et al. (1993) addressed the variability of Kozeny's constant as follows:

$$\left[\sqrt{\frac{k}{\phi}}\right] = \left[\frac{\phi}{(1-\phi)}\right] \left[\frac{1}{\sqrt{F_s}\tau S_g}\right],\tag{6}$$

$$[RQI] = [\varepsilon][FZI], \tag{7}$$

$$\log RQI = \log \varepsilon + \log FZI , \qquad (8)$$

where, RQI is called Reservoir Quality Index, ε is the void ratio and FZI is described as Flow Zone Indicator:

$$FZI = \frac{1}{\sqrt{F_s} \tau S_g} = \frac{1}{\varepsilon} \sqrt{\frac{k}{\phi}}.$$
(9)

If permeability and *FZI* are expressed in md and μ m respectively.

$$FZI = \frac{0.0314}{\varepsilon} \sqrt{\frac{k}{\phi}}.$$
 (10)

Since the *FZI* describes geometrical distributions of pores and grains, Prasad (2003) used this approach to describe the variations in velocity–porosity relations. The geometrical control of pore volume distribution was found to also describe velocity variations with permeability (Prasad, 2003).

Specific Surface of the Grains, S_q

Surface area of minerals is widely estimated by the BET nitrogen adsorption technique introduced by Brunauer, Emmett and Teller (Brunauer et al., 1938). In this method surface area, S_{BET} per unit weight is estimated by allowing nitrogen gas to adsorb on the surface of the rock. Knowing the grain density, ρ_g of the minerals, specific surface of the grains, S_g is calculated:

$$S_g = S_{BET} \times \rho_g. \tag{11}$$

Specific surface with respect to the bulk, S and specific surface with respect to pore, S_{ϕ} is calculated as (Borre and Fabricius, 1998):

$$S = (1 - \phi)S_g, \tag{12}$$

$$S_{\phi} = \frac{S}{\phi}.$$
 (13)

Effective Specific Surface, S_{g-eff}

For homogeneous, fine-grained sediments like chalk, pores are likely to have high connectivity, so the concept of a torturous flow path is difficult to perceive. In such rocks, in addition to the capillaries parallel to the direction of flow (as defined by Darcy, 1856), there should be capillaries in the directions perpendicular to the flow (Figure 4b). Even though the resultant flow occurs only in one direction, fluid flows in all capillaries. Major loss of pressure (according to Poiseuille's law) occurs in the direction of resultant flow. In the direction normal to the direction of pressure drop, fluid flow may be seen as practically instantaneous pressure transfer (Røgen and Fabricius, 2002). This perception could be compared with the process of climbing a hill, where work required for the movement parallel to the horizon is negligible compared to the work required for vertical movement.

Mortensen et al. (1998) used this concept by projecting the pore space into the form of orthogonal interpenetrating tubes. Rocks with high connectivity in pore space could be imagined as a system of such tubes (Figure 4b). A part of the porosity in such a system is thus insignificant in the resultant flow due to shielding by solid. Mortensen et al. (1998) quantified the porosity that is active to the flow in a given direction where Poiseuille's law is valid by introducing a porosity dependent $c(\phi)$: (to distinguish from Kozeny's constant c in eq.3

$$c(\phi) = \left[4\cos\left\{\frac{1}{3}\arccos(2\phi - 1) + \frac{4}{3}\pi\right\} + 4 \right]^{-1}.$$
 (14)

Theoretically value of c is 1 when all the pores are aligned as parallel tubes in the direction of flow and is 0 when aligned as perpendicular tubes to the flow. This porosity dependent $c(\phi)$ replaces the term c of Kozeny's equation (Eq. 5). $c(\phi)$ increases with increasing porosity as visualized by the volume of perpendicular interpenetrating tubes in Figure 4b. The point is that this volume increases as porosity increases. Decreasing $c(\phi)$ results in higher shielding effect and will have the same effect in the equation as a conceptual tortuous path with higher actual equivalent travel length (l_e) . The advantage of using the concept of $c(\phi)$ is that it can be predicted directly from ϕ , and does not affect the specific surface term. With porosity dependent c, Kozeny's equation becomes:

$$k = c(\phi) \frac{\phi^3}{S^2}.$$
 (15)

Using the relation stated in Eq. 12:

$$k = c(\phi) \frac{1}{S_{g-eff}^2} \frac{\phi^3}{(1-\phi)^2},$$
(16)

where, $S_{g\text{-eff}}$ is the effective specific surface, which in chalk is similar to or only slightly lower than S_g measured by BET (Brunauer, Emmett and Teller) nitrogen adsorption technique (Mortensen et al., 1998). A high homogeneity at particle scale is probably the reason why chalk permeability in this way may be predicted directly from Kozeny's equation without fitting factors. We calculated $S_{g\text{-eff}}$ from Eq. 16 using core permeability and porosity measured in the laboratory:

$$S_{g-eff} = \sqrt{c(\phi)} \times \phi \frac{\phi}{(1-\phi)} \sqrt{\frac{1}{k}}.$$
 (17)

Effective specific surface, S_{g-eff} does not depend on the porosity as it is not a property of the bulk rock but a property of the particles that make up the rock. For homogeneous rocks the variation of effective porosity for flow, due to varying porosity is determined by $c(\phi)$, so for a given porosity, permeability variation can be resolved by the difference of specific surface alone.

Sample ID	Formation	TVDSS (m)	φ (%)	Grain density (g/cm ³)	Carbonate content (%)	<i>k_g</i> (md)	Sp. Surface (m²/g)	V _{p-dry} (km/s)	V _{s-dry} (km/s)	V _{p-sat} (km/s)	V _{s-sat} (km/s)
RE-06A	Ekofisk	2762.2	32.1	2.70	75.9	0.5	3.9	3.63	2.16	3.06	1.83
RE-08B	Ekofisk	2762.2	31.9	2.70	75.9	0.5	3.9	3.51	2.07	3.62	2.17
RE-09B	Ekofisk	2762.3	30.0	2.69	79.0	0.5	3.6	3.55	2.09	3.63	2.18
RE-10A	Ekofisk	2762.3	30.7	2.70	79.0	0.5	3.6	3.76	2.26	3.34	1.80
RE-12B	Ekofisk	2762.3	29.9	2.69	79.0	0.5	3.6	3.85	2.29	3.42	1.84
RE-14A	Ekofisk	2765.1	31.1	2.70	77.9	0.5	3.7			3.63	2.18
RE-22A	Ekofisk	2771.3	32.9	2.71	88.2	1.1	3.8	3.20	1.95	3.17	1.60
RE-23A	Ekofisk	2771.4	32.0	2.72	88.3	0.6	3.5	3.29	1.97	3.28	1.62
RE-24	Ekofisk	2771.5	35.9	2.72	88.3	0.9	3.6	2.81	2.16	2.86	2.19
RE-26B1	Ekofisk	2774.3	30.9	2.71	89.7	0.5	2.9	-	-	3.20	1.67
RE-26B2	Ekofisk	2774.3	29.5	2.71	89.7	0.5	2.9	-	-	3.30	2.10
RE-28A1	Ekofisk	2774.3	28.9	2.70	89.7	0.8	2.9	-	-	3.63	2.18
RE-29	Ekofisk	2774.5	28.0	2.71	89.0	0.4	3.2	3.62	2.29	3.33	1.74
RE-31	Ekofisk	2774.5	29.1	2.71	89.0	0.6	3.2	-	-	3.29	2.02
RE-C2E-A	Ekofisk	2765.3	18.3	2.72	84.8	0.1	3.6	-	-	-	-
RE-C2E-B	Ekofisk	2765.3	17.7	2.71	84.8	0.1	3.6	-	-	-	-
RT-01	Tor	2798.7	38.9	2.71	95.2	4.4	2.1	2.70	1.68	2.81	1.65
RT-02	Tor	2798.8	35.0	2.72	95.2	2.3	2.1	3.37	2.02	3.40	1.70
RT-03	Tor	2802.5	42.3	2.71	96.7	4.8	1.9	1.98	1.26	2.43	1.48
RT-C3G-A	Tor	2802.7	42.5	2.74	96.7	5.6	2.0				
SE-02	Ekofisk	2791.6	16.3	2.71	77.5	0.02	6.4	2.99	1.99	3.39	1.54
SE-03	Ekofisk	2791.6	17.6	2.71	77.5	0.04	6.4	2.71	1.89	3.32	1.77
SE-05A	Ekofisk	2783.6	26.2	2.72	81.2	0.1	5.2	2.81	2.07	3.01	1.79
SE-C1B7-A	Ekofisk	2783.7	26.1	2.71	77.5	0.1	5.2	-	-	-	-
ST-03B	Tor	2849.6	29.2	2.71	99.1	1.7	1.7	3.18	2.08	-	-
ST-04B	Tor	2862.2	27.8	2.71	99.0	1.3	1.6	3.76	2.20	-	-
ST-07	Tor	2855.6	31.3	2.72	99.9	2.7	1.6	3.13	1.92	-	-
ST-08A	Tor	2855.6	32.3	2.71	99.9	3.2	1.7	3.03	2.05	-	-
ST-08B	Tor	2855.5	31.0	2.71	99.9	2.6	1.6	2.81	1.86	-	-
ST-13B	Tor	2843.0	30.8	2.71	99.5	2.2	1.9	3.11	1.94	-	-
ST-16B	Tor	2837.0	28.5	2.72	99.0	1.2	1.8	3.46	2.11	-	-
ST-23A	Tor	2825.1	26.2	2.72	98.6	0.8	1.7	3.90	2.14	3.82	1.90
ST-24A	Tor	2825.1	26.3	2.72	98.2	0.8	1.7	3.68	2.23	3.67	1.97
ST-24B	Tor	2825.1	24.8	2.72	98.2	0.8	1.7	4.11	2.42	4.12	2.20
ST-26	Tor	2825.0	28.2	2.71	98.5	1.1	1.6	3.57	2.13		
ST-C5B11-C	; Tor	2830.9	28.4	2.72	97.8	0.6	2.1	-	-	-	-
ST-C5B20-D) Tor	2837.0	27.6	2.73	99.3	1.1	1.8	-	-	-	-
ST-C5B2-C	Tor	2825.1	29.1	2.72	98.6	0.8	2.3	-	-	-	-
ST-C6B12-F	Tor	2849.6	31.2	2.73	99.1	2.0	1.7	-	-	-	-
ST-C6B2-C	Tor	2843.1	29.9	2.73	99.5	1.6	1.8	-	-	-	-
ST-C7B14-C	; Tor	2862.2	29.6	2.73	99.0	1.9	1.6	-	-	-	-
ST-C7B4-A	Tor	2855.6	26.1	2.74	98.9	3.7	1.4	-	-	-	-
ST-C7B4-I	Tor	2855.6	32.7	2.74	98.9	3.6	1.4	-	-	-	-

Table 2. Physical properties of the tested samples from Rigs-1 (RE and RT) and SA -1 (SE and ST).

DATA Data Set

We used 31, 1½ inch and 12, one inch core samples from SA-1 and Rigs-1 wells of South Arne field in central North Sea (Table 2). Carbonate content of each sample was measured by treating the finely powdered sample with an excess of 0.5M hydrochloric acid and subsequent titration with 0.5M sodium hydroxide. Specific surface of each sample was estimated by nitrogen adsorption technique (BET) (Brunauer et al., 1938). Grain density, ρ_g and porosity, ϕ were obtained from helium porosimetry. Qualitative information of mineralogy was obtained by the X-ray diffraction (XRD) method.

Gas permeability, k_g was measured by nitrogen injection. Equivalent liquid (Klinkenberg corrected) permeability, k was calculated by using the relationship for North Sea chalk presented by Mortensen et al., (1998):

$$k = 0.52 \times k_g^{1.083},$$
 (18)

where, k and k_g are given in md.

Compressional wave velocity V_p and shear wave velocity V_s were measured by recording the travel time of transmitted ultrasonic waves at 132 kHz through a sample of known length. Measurements were taken while the sample was placed between the two pistons of a loading frame and applying 4 MPa axial stress and 1.33 MPa radial stress, which simulates the effective stress geometry at reservoir conditions. Reservoir rocks are subjected to both vertical and lateral stress as well as high pore pressure (overpressure) in the North Sea Chalk reservoirs. To simulate reservoir stress in a laboratory experiment, only requires the application of the differential stress (total stress minus pore pressure) instead of the actual stresses (Teeuw, 1971). The effective vertical stress in South Arne is between 10 MPa and 20 MPa, but because velocity variation in North Sea chalk samples was found to be less than 3% between 4 and 11 MPa (Borre and Fabricius, 2001) we used 4 MPa for our sample to avoid damage in the sample

As a reference, 44 core data from Fabricius et al. (2008) were also used; they include data from wells Rigs-1, Rigs-2 and SA-1. Compressional wave velocity data from wireline logs of SA-1 and Rigs-1 were used for permeability

prediction. Predicted permeability was compared with core permeability from Geological Survey of Denmark and Greenland (GEUS) core lab database. All core datasets include porosity, permeability as well as V_p and V_s under both water saturated and dry conditions.

RESULTS

Mineralogy of the Studied Interval

The samples from Ekofisk Formation contain up to 25% non-carbonate fraction (Table 2). Distribution of non-carbonates is recognizable in BSE images at large magnification and some of the pores are thus partially filled with clay (Figure 5, Figure 6, indicated by arrow). Fabricius et al. (2008) showed that varying amounts of quartz could reside as submicrometer-size crystal aggregates loosely arranged with clay in interparticle porosity. Such allocation of carbonate and non carbonate phase will increase the surface to pore volume ratio and make fluid flow difficult in the kaolinite-rich Rigs-1 well. The Ekofisk Formation in SA-1 is rich in smectite and almost impermeable (Table 2). The Ekofisk Formation also contains considerable amounts of preserved large hollow microfossils, which would tend to reduce the surface to pore volume ratio, but the effect of this does not make up for the effect of clay. The Tor Formation on the other hand contains a homogeneous matrix of calcareous nannofossil debris (Figure 6).



Figure 5. Backscatter Electron (BSE) micrographs of epoxy-impregnated and polished samples from well SA-1 at two magnifications, plotted according to true vertical depth sub sea (TVDSS) in meters. Dark is porosity and bright is calcite. Clay and quartz appear as grey (indicated by arrows). Top two are Ekofisk Formation samples and bottom four are Tor Formation samples. Q, S and K represent quartz, smectite and kaolinite respectively. Specific surface of the grains (*S*_g) is calculated from bulk specific surface measured by BET (Brunauer, Emmett and Teller) nitrogen adsorption technique (Brunauer et al., 1938) and grain density (Eq. 11). Flow Zone Indicator (*FZI*) is calculated from porosity and measured liquid permeability (Eq. 10).



Figure 6. Backscatter Electron (BSE) micrographs of epoxy-impregnated and polished samples from well Rigs-1 at two magnifications, plotted according to true vertical depth sub sea (TVDSS) in meters. Dark is porosity and bright is calcite. Clay and quartz appear as grey (indicated by arrows). Top four are Ekofisk Formation samples and bottom two are Tor Formation samples. Q, and K represent quartz and kaolinite respectively. Specific surface of the grains (S_g) is calculated from bulk specific surface measured by BET (Brunauer, Emmett and Teller) nitrogen adsorption technique (Brunauer et al., 1938) and grain density (Eq. 11). Flow Zone Indicator (*FZI*) is calculated from porosity and measured liquid permeability (Eq. 10).

Selection of Method



Figure 7. Relationship of Flow Zone Indicator (*FZI*) with (a) effective specific surface of the grains (S_{g-eff}) calculated from Eq. 17 using measured liquid permeability and (b) specific surface of the grains (S_g) calculated from bulk specific surface measured by BET (Brunauer, Emmett and Teller) nitrogen adsorption technique (Brunauer et al., 1938) and grain density (Eq. 11). (c) Calculated (S_{g-eff}) versus measured (S_g) specific surface. Open symbols indicate Ekofisk Formation and closed symbols indicate Tor Formation.

In practice, effective S_g and FZI work the same way and only use a different approach in describing the difficulty of flow in porous media. The difference in the approach by using S_g and FZI may be expressed as follows: in the S_g unit approach; the Kozeny *c-factor* is seen as a function of porosity only, whereas in the FZI unit approach, the Kozeny *c-factor* is expressed in terms of specific surface. Therefore, effective S_g and FZI differ roughly by a multiplier in a loglog scale plot (Figure 7a). On the other hand, the relationship between S_g calculated from the BET (Brunauer, Emmett and Teller) nitrogen adsorption technique (Brunauer et al., 1938) and S_{g-eff} is scattered around a linear trend on a log-log plot (Figure 7c). A minor part of the difference may arise from the crushing of samples before BET measurement, but the difference between S_g and S_{g-eff} in the studied samples are larger than in Gorm (Mortensen et al., 1998), so the difference may well be due to a still small but not insignificant heterogeneity on the pore scale of the South Arne samples. S_{g-eff} calculated from porosity and permeability may tend to be low because gas permeability is measured at ambient conditions or at pressures lower than reservoir pressures. Thus, some fractures that would normally be closed at reservoir conditions may remain open in the laboratory (Hamilton, 1976). In this case, permeability measured form gas injection should be higher than the matrix permeability and thus cause relatively low S_{g-eff} . On the other hand, permeability calculated from specific surface could give lower than actual permeability (Figure 8), as the BET method estimate all the surface area exposed to nitrogen gas and Kozeny's equation assumes sample

homogeneity. However, some of this surface may not active in flow according to Poiseuille's law, but be the relevant interface for description of sonic wave transmission.



Figure 8. Relationship between Klinkenberg permeability calculated from air permeability (Mortensen et al., 1998) and permeability calculated from specific surface measured by BET (Brunauer, Emmett and Teller) nitrogen adsorption technique (Brunauer et al., 1938) by using modified Kozeny's equation (Eq. 15). Open symbols represent Ekofisk Formation and closed symbols represent Tor Formation. Data points with a circle inside indicate present dataset.

In our velocity-permeability study, we used S_g calculated from BET. As the modeling by effective S_g and *FZI* are so similar in practice, we chose for comparison to use the *FZI* concept in the velocity-permeability study in order to be able to compare with literature data (Prasad, 2003).

FZI Unit and S_g Unit Separation

The porosity-permeability relationship shows a notable separation of samples from Ekofisk and Tor formations (Figure 9). From the distribution of permeability, we could define three S_g units in Ekofisk Formation and one S_g unit in Tor formation (Figure 10). Similarly, two *FZI* units in Ekofisk Formation and two *FZI* units in Tor Formation were also assigned.

Our data show that from the variation of S_g and FZI with depth, we could separate distinct units that coincided with stratigraphic units (Figure 11). Not all S_g units and FZI units are present in every well. The studied wells are situated several kilometers apart (Figure 1b). This indicates stratigraphic variation in distribution of minerals and spatial variation in deposition or preservation of units. With respect to S_g both Tor and Ekoisk formations vary among the wells (Figure 5, 6). The Rigs-1 well contains mostly kaolinite clay; whereas SA-1 contains smectite clay, which has much higher specific surface than kaolinite (Madsen and Lind, 1998). Although, the studied formations in the SA-1 well are deeper than in Rigs-1 they are located in the same stratigraphic unit. Therefore, we expect that the variation in non-carbonate content is due to the spatial position of the wells rather than stratigraphy.



Figure 9. Theoretical and experimental relationships between porosity and permeability according to (a) specific surface of the grains, S_g units and (b) Flow Zone Indicator, *FZI* units. Curves of (a) was calculated from Eq. 15 using $c (\phi)$ values from Eq. 14. Curves of (b) were calculated from Eq. 10. Data points with a circle inside indicate present dataset.

 S_g units do not show significant variation in the Tor Formation (Figure 10). According to *FZI* units one additional stratigraphic unit (*TFZI2*) could be defined at the bottom of Tor Formation (Figure 11f). In Rigs-1 and Rigs-2 there are two S_g units in Ekofisk Formation (*ESG2* and *ESG3*), whereas SA-1 is only represented by *ESG*1.



Figure 10. Distribution of samples according to (a) specific surface of the grains, S_g units and (b) Flow Zone Indicator, *FZI* units. S_g units and *FZI* units are assigned when there is a peak in distribution, as indicated on the plots. In order to get a reasonable trend, S_g units and *FZI* units were only assigned, where numbers of samples are three or more. Distribution of *FZI* for sandstone (thin continuous line), calculated by using Prasad's (2003) porosity and permeability data, indicates significant difference from *FZI* distribution of chalk.



Figure 11. Specific surface of the grains, S_g units and Flow Zone Indicator, *FZI* units in the wells Rigs-1, Rigs-2 and SA-1. In a plot of true vertical depth sub sea (TVDSS), S_g units and *FZI* units indicate a distinct stratigraphic unit.

Velocity-Permeability Relationship in Assigned S_g Unit and FZI Units We examined the relationship between compressional wave velocity and permeability (both measured in core plugs in the laboratory) according to the assigned S_g units and FZI units for samples in both dry and saturated condition (Figure 12). Within the assigned S_g units and FZI units, significant correlations were found where there are a large number of samples (ESG3, TSG1, EFZI2 and TFZI1); the correlation coefficients for velocity – permeability correlations were 0.7 or better. In ESG1, ESG2, EFZI1 and TFZI2, no significant correlation could be achieved, due to low number of samples. These samples may represent local variation of mineralogy.



Figure 12. Compressional wave velocity (V_p) -Klinkenberg permeability (*k*) relationships according to the designated specific surface of the grains, S_g units (a), (c) and Flow Zone Indicator, *FZI* units (b), (d). (a), (b) for dry data (V_{p-dry}) and (c), (d) for saturated data (V_{p-sat}) . Solid data points are Tor Formation and open data points are Ekofisk Formation. Ekofisk Formation trends are indicated by broken lines and Tor Formation trends are indicated by continuous lines.

The velocity-permeability relationships established here were then applied to the same set of velocity data to calculate permeability for the respective S_g units and *FZI* units. Predicted permeability was then compared with the Klinkenberg permeability. Furthermore, these relationships were applied to log measured compressional wave velocity data and compared with the GEUS database permeability.



Figure 13. Compressional wave velocity (V_p) -porosity (ϕ) relationships according to the designated specific surface of the grains, S_g units and Flow Zone Indicator, *FZI* units. (a), (b) for dry data (V_{p-dry}) and (c), (d) for saturated data (V_{p-sat}) . Solid data points are Tor Formation and open data points are Ekofisk Formation. Ekofisk Formation trends are indicated by broken lines and Tor Formation trends are indicated by continuous lines.

Velocity-Porosity Relationship in Assigned S_g Unit FZI Units

In a more traditional procedure, V_p -porosity relationships were established according to the designated S_g units and *FZI* units (Figure 13). Porosity calculated from these relationships was used for permeability calculation. Predicted permeability was then compared with the Klinkenberg permeability. The same relationships were applied to log measured compressional wave velocity data to compare predicted permeability with GEUS database permeability.



Figure 14. Predicted permeability directly form velocity versus measured Klinkenberg permeability (*k*) according to: (a) and (c) the designated specific surface of the grains, S_g units; (b) and (d) Flow Zone Indicator, *FZI* units. (a) and (b) are using compressional wave velocity (V_{p-dry}) measured in dry samples and (c) and (d) are using compressional wave velocity (V_{p-sal}) measured in saturated samples. Shaded area indicates 5% standard deviation and area between two dotted lines indicate 35% standard deviation. Deviation (in percentage) from the measured permeability in the lab for different stratigraphic units is given below each figure in a plot of deviation versus true vertical depth sub sea (TVDSS).



Figure 15. Predicted permeability from porosity (ϕ), where, porosity was calculated form velocity data plotted against measured Klinkenberg permeability according to the designated specific surface of the grains, S_g units, (a) and (c); Flow Zone Indicator, *FZI* units (b) and (d). (a) and (b) are using compressional wave velocity (V_{p-dry}) measured in dry sample and (c) and (d) are using compressional wave velocity (V_{p-sal}) measured in saturated samples. Shaded area indicates 5% standard deviation and area between two dotted lines indicate 35% standard deviation. Deviation (in percentage) from the measured permeability in the lab for different stratigraphic units is given below each figure in a plot of deviation versus true vertical depth sub sea (TVDSS).

Predicted permeability according to S_g units and *FZI* units is close to the measured permeability when permeability is predicted directly from V_p according to S_g units and *FZI* units (Figure 14). Variation between measured and predicted permeability is higher when predicted indirectly via porosity from velocity and then permeability from porosity (Figure 15). In the indirect method the predicted permeability could be underestimated by more than 35% in Tor Formation, when S_g method is applied as specific surface measured by BET method is higher. *FZI* method works satisfactorily in this case. However, for the low permeable and impure Ekofisk formation permeability is overestimated when the indirect method is used in the *FZI* method. By knowing the specific surface of Ekofisk formation permeability prediction could be improved marginally, although scatters more than $\pm 35\%$ of the measured permeability.

DISCUSSION

Permeability prediction from velocity

In general, permeability and velocity have negative correlation (Figure 12). However, the slope of the relationship defines a specific S_g unit or *FZI* unit. Permeability decreases faster as velocity increases in chalk with higher specific surface and lower *FZI* (*ESG3*, *EFZI2*) compared to the chalk with lower S_g because of low clay and silicates (*TSG1*, *TFZI1*).

At very high porosity, the assigned S_g units become close to each other and *FZI* units show a similar trend. This indicates that at high porosity, velocity is less influenced by the impurities in chalks or by permeability itself. With the decrease in porosity, a general trend is that, velocity increase faster in cleaner chalk (lower S_g and higher *FZI*) than chalks containing clay and quartz (higher specific surface and higher *FZI*) (Figure 13).

Sound wave propagation in chalk primarily depends on the contact between chalk grains; whereas, permeability in chalk largely depends on dispersed clay and silicate grains (Figure 5, Figure 6) inside the pore space, as they provide most of the flow hindering surfaces (Table 1). These suspended particles has comparatively less influence on the stiffness (and velocity) of chalk (Fabricius, 2003). At lower porosity, some of these silicates can act as a frame and increase stiffness and thus velocity of elastic waves. For the same porosity a cemented pure calcite frame is stiffer than a frame made of several minerals due to poor or

no contact cement. Therefore, velocity is higher in a pure calcite frame compared to a combined mineral frame.

During the diagenetic process of chalk major porosity reduction occurs due to compaction (Fabricius, 2001; Alam et al., 2010b). During compaction, calcite grains come close to each other pushing the suspended non-carbonates into the pore space. Thus the ratio of non-carbonate volume to pore volume increases. This process decreases the permeability substantially. Therefore, permeability reduction is much faster in impure chalk compared to velocity increase from the same amount of porosity reduction.

In a V_{psat} -porosity plot the assigned S_g units and *FZI* units may be easily detected, whereas it is difficult to distinguish the assigned S_g units and *FZI* units in a V_{pdry} -porosity plot (Figure 13). This could be caused by specific surface-dependent influence of water (water softening) (Fabricius et al., 2010).

Prediction of permeability from porosity alone is only possible with a high degree of uncertainty. Permeability in chalk is highly influenced by its content of non-carbonates. By using S_g unit separation we may take into account the non carbonate fraction in chalk because it constitutes a significant part of the specific surface. On the other hand *FZI* units separate rocks with different degrees of difficulty to fluid flow into different hydraulic flow units. It is possible to define a relevant S_g unit or *FZI* unit for a particular formation from the porosity-core permeability plot. By comparing Figure 12 and Figure 13, it can be seen that in the velocity-permeability plot, separation is marginally better by using S_g units as compared to in the velocity-porosity plot. Permeability relationship for that particular specific surface (Figure 14, Figure 15). Use of dry velocity data or saturated velocity data does not make significant difference in permeability prediction for cores.

Predicted Permeability by S_q Unit and *FZI* Unit Separation

A plot of porosity versus effective specific surface for grains measured by the BET method (Brunauer et al., 1938) and calculated from permeability (Eq. 17) does not show significant variation with porosity (Figure 16). By using porosity dependent $c(\phi)$ in Eq. 17, S_{g-eff} becomes independent of porosity for a particular S_g unit. Thus in the velocity-permeability relationship, S_{g-eff} remains the only
dependent factor. It enables us to predict permeability from velocity, if S_{g-eff} is known.



Figure 16. (a) Relationship of porosity with effective specific surface of the grains (S_{g-eff}) calculated from Eq. 17 using measured liquid permeability and specific surface of the grains (S_g) calculated from bulk specific surface measured by BET (Brunauer, Emmett and Teller) nitrogen adsorption technique (Brunauer et al., 1938) and grain density (Eq. 11). Grey data points indicate S_{g-eff} and black data pints indicate S_g (b) Relationship between porosity and Flow Zone Indicator, *FZI* units.

We observed that samples with high non-carbonate content show low FZI value (low connectivity) (Figure 5 and Figure 6). By assigning a FZI value for a particular lithology the permeability-velocity and porosity-velocity relationships could be narrowed. Thus, a better prediction of permeability was achieved (Figure 14, Figure 15). However, below 1 md permeability, predicted permeability varies significantly from the calculated permeability. It indicates the difficulty of defining a hydraulic unit by means of FZI unit separation in low permeable chalk. Variation between the predicted permeability from the calculated permeability from the calculated permeability in low permeable chalk. However, it requires more core data and makes it difficult to apply in well logs.

Calculated Mean Standard Error (MSE), Mean Absolute Error (MAE) and correlation coefficient (R) between predicted and measured permeability is presented in Table 3. Although the error in prediction in the SA-1 Tor Formation by S_g method is higher *FZI* method, both methods show high correlation coefficient (0.8 or more) which validates the applicability of the methods for permeability prediction. However, S_g method has one advantage that, it is

applicable without knowing the permeability: it requires specific surface which is measured from the side trims and end trims or cuttings and therefore no core plug is required.

	MSE		MAE		R	
Method	Ekofisk	Tor	Ekofisk	Tor	Ekofisk	Tor
V _{p-sat} →k, SG	0.07	0.3	0.12	0.43	0.87	0.89
V _{p-sat} →k, FZI	0.08	0.3	0.13	0.43	0.87	0.89
V _{p-dry} →k, SG	0.07	0.7	0.11	0.59	0.86	0.82
V _{p-dry} →k, FZI	0.09	0.7	0.15	0.59	0.85	0.82
V _{p-sat} → <i>φ</i> →k, SG	0.12	2.0	0.18	1.1	0.87	0.89
V _{<i>p-sat</i>} → <i>φ→k</i> , FZI	0.23	0.4	0.39	0.5	0.86	0.89
V _{p-dry} → <i>φ→k</i> , SG	0.10	2.3	0.15	1.2	0.86	0.83
$V_{p-dry} \rightarrow \phi \rightarrow k$, FZI	0.22	0.8	0.39	0.6	0.85	0.81

Table 3. Statistical analysis of permeability prediction. Calculated Mean Standard Error (MSE), Mean Absolute Error (MAE) and correlation coefficient (R).

Implication to Well Log Velocity



Figure 17. Predicted permeability for Rigs-1 logging data. (a) compressional wave velocity at saturated condition (V_{p-sat}). (b) and (c) Permeability estimated directly from V_{p-sat} , for the assigned specific surface of the grains, S_g units and Flow Zone Indicator, *FZI* units respectively. (d) and (e) permeability predicted from porosity (calculated from V_{p-sat}), for the assigned S_g units and *FZI* units respectively.

We applied relationships established between velocity and permeability and velocity and porosity to predict permeability for wells Rigs-1 (Figure 17) and SA-1 (Figure 18). We used V_p -sat data achieved from wireline logging. Predicted permeability was compared to the lab permeability database. As Tor Formation chalk is less affected by mineralogical variation, its permeability can be predicted very closely to the core permeability by considering its S_g between 2 and 7 μ m⁻¹

(*TSG*1) and *FZI* value between 0.08 and 0.2 μ m (*TFZI1*). However in the low permeable Ekofisk Formation, permeability could only be predicted within one order of magnitude of the core measured permeability. Core data of Rigs-1 and SA-1 indicate that S_{g-eff} of Ekofisk Formation is between 7 and 10 μ m⁻¹ (*ESG*2) and *FZI* value between 0.04 and 0.2 μ m (*EFZI*2).



Figure 18. Predicted permeability for SA-1 logging data. (a) compressional wave velocity (V_{p-sat}) at saturated condition. (b) and (c) Permeability estimated directly from V_{p-sat} , for the assigned specific surface of the grains, S_g units and Flow Zone Indicator, *FZI* units respectively. (d) and (e) permeability predicted from porosity (calculated from V_{p-sat}), for the assigned S_g units and *FZI* units respectively.

CONCLUSION

For low permeability (<10 md) sedimentary rocks as North Sea chalk, permeability variation for the same porosity rock could be described well by separating into units of specific surface, S_g or into Flow Zones Indicator, *FZI*. Grouping samples according to S_g units and *FZI* units improves the permeability prediction from compressional velocity. S_g unit or *FZI* unit splitting according to lithology enables us to predict permeability within less than a single order of magnitude, while the general porosity-permeability relationship varies three orders of magnitude in chalk. If specific surface of a particular chalk unit is known, the velocity-permeability relationship for that unit can be applied to predict permeability directly from the compressional wave velocity. S_g unit splitting could be applied effectively to predict permeability of low permeable chalk. *FZI* unit separation may give better results for high permeability (>1 md) sedimentary rocks.

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III

Static and dynamic effective stress coefficient of chalk

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Static and dynamic effective stress coefficient of chalk

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ABSTRACT

Deformation of a hydrocarbon reservoir can ideally be used to estimate the effective stress acting on it. The effective stress at the subsurface is the difference between the stress due to the weight of the sediment and a fraction (effective stress coefficient) of pore pressure. The effective stress coefficient is thus relevant for studying reservoir deformation and for evaluating 4-D seismic for the correct pore pressure prediction. The static effective stress coefficient, n, is estimated from mechanical tests and is highly relevant for effective stress prediction, as it is directly related to mechanical strain in the elastic stress regime. The corresponding dynamic effective stress coefficient β is easy to estimate from density and velocity of acoustic (elastic) waves. We studied n and β of chalk from the reservoir zone of the Valhall field, North Sea and found that both *n* and β vary with differential stress (overburden stress – pore pressure). For Valhall reservoir chalk with 40% porosity, β ranges between 0.98 and 0.85 and decreases by 10% if the differential stress is increased by 25 MPa. In contrast, chalk with 15% porosity from the same reservoir β ranges between 0.85 and 0.70 and decreases by 5% due to a similar increase in differential stress. Our data indicate that β measured from sonic velocity data falls in the same range as for n, but that n is always below unity. Stress dependent behavior of n is similar (decrease with increasing differential stress) to that of β during elastic deformation caused by pore pressure buildup, for example, during waterflooding. By contrast, during the increase in differential stress, as in the case of pore pressure depletion due to production, *n* increases with stress while β decreases.

INTRODUCTION

The effective stress of a hydrocarbon reservoir typically increases during primary production of oil and gas or may decrease due to water-flooding. In both cases the stress changes as a result of altering the pore fluid pressure. A high porosity and low induration makes the hydrocarbon reservoirs in chalk relatively susceptible to deformation when subjected to increasing effective stress. Compaction in the reservoir and subsidence at the surface may occur due to this deformation. This is a major challenge during production, as exemplified in the North Sea chalk fields (Hermansson and Gudmundsson, 1990; Kristiansen, 1998; Barkved and Kristiansen, 2005).



Figure 1: Location of Valhall field in the Norwegian sector of the North Sea (adapted from Barkved and Kristiansen, 2005).

The Valhall field is a mid sized (167 million Sm³) North Sea oil field (Figure 1) at a depth of approximately 2400 meters. The chalk is characterized by high overpressure, undersaturated oil and high porosity. Typical porosity in this reservoir is 35% to 50% and typical matrix permeability is 1mD to 10 mD, but presence of fractures increases overall permeability (Kristiansen et al., 2005). The exceptionally high porosity was probably preserved in the chalk by early oil emplacement and an overpressure of approximately 20 MPa (Andersen 1995). Due to production for more than 20 years, the overpressure has declined to 17 MPa (Tjetland et al., 2007). Consequently, part of the reservoir has compacted and subsidence of the sea floor has reached more than 5 m and increases by 0.25m/year (Kristiansen et al., 2005). Geomechanics modeling related to stress and strain associated with this compaction is required for estimating the stability of wells and platform as well as for the selection of future well locations.

Compaction due to reduction of pore pressure is inevitable in chalk reservoir. Prediction of compaction in advance could help designing production strategy. If 4D seismic data can be used for the prediction of pore pressure, it is possible to establish a realistic geomechanics model. However, pore pressure should be utilized in a proper way for more accurate compaction prediction.

We studied the effect of pore pressure in terms of the effective stress. The effective stress concept was originally introduced by Terzaghi (1923) as the difference between the overburden stress (from the weight of the sediments) σ_{ov} and pore pressure P_p . From a rock mechanics view, pore pressure can be seen as working on the internal surface of the rock grains (Engstrøm, 1992). The more the horizontal projection of surface of grains are in contact with pore fluid the more resistance pore fluid can offer against the overburden stress. Reduction of the pore pressure effect on the effective stress is caused by an increase in surface contact between the rock grains. Biot (1941) characterized this reduction by a coefficient, α . The effective stress is then ideally the difference between the total stress σ_{ov} and a fraction α of the pore pressure P_p ;

$$\sigma_{eff} = \sigma_{ov} - \alpha P_p \tag{1}$$

Terzaghi (1923) studied loose granular sediments, where the contact area among the grain surfaces negligible and consequently α is close to unity. Therefore the differential overburden stress ($\sigma_{ov} - P_p$) is equal to the effective stress for these sediments. However, most rocks are cemented to some extent and therefore have more stable grain to grain contacts. It makes α less than unity. Due to deformation in a rock mechanics process, there is a possibility of increased or decreased grain contact (softening or hardening behavior). If this happens, the value of α will also change. For this reason, mechanical behavior of a rock should be affected by the changing coefficient α .

Biot's (1941) theory was developed on the basis of linear elasticity and reversible strain. Therefore, the effective stress coefficient is typically calculated from the density and velocity of ultrasonic sound wave propagation in dry rocks (Banthia et al., 1965, Todd and Simmons, 1972; Christensen and Wang, 1984; Mavko and Jizba, 1991; Prasad and Manghnani, 1997; Frempong et al., 2007; Mavko and Vanorio, 2010); which produces very small linear elastic strain. We denote it as

dynamic effective stress coefficient, β . β is calculated from dry bulk modulus K_{dry} and bulk modulus of the mineral frame, K_o ;

$$\beta = 1 - \frac{K_{dry}}{K_0} \tag{2}$$

 K_{dry} is calculated from the compressional velocity, v_p and shear velocity, v_s as measured on the dry rock, as well as dry density, ρ_{dry} ;

$$K_{dry} = \rho_{dry} v_p^2 - \frac{4}{3} \rho_{dry} v_s^2$$
(3)

Based on laboratory measurements of stress dependent sonic velocity, several authors have noted that β is a function of stress (e.g. Banthia et al., 1965; Todd and Simmons, 1972; Christensen and Wang, 1984; Engstrøm, 1992; Frempong et al., 2007) although in the ideal case β should be constant. Failure to satisfy the assumptions of Biot's (1941) theory, such as, drainage condition, linear elasticity and reversibility could be reasons for non-constant β . Several authors have found that β may be different for different physical properties. Teufel and Warpinski (1990) found different effective stress coefficient for velocity and for permeability. Berryman (1992) derived a set of effective stress coefficients for different physical properties of rocks, such as porosity, permeability. However, the effective stress that is relevant for compaction and subsidence is the effective stress coefficient for strain. This static effective stress coefficient *n* ideally should be determined from rock mechanics tests designed on the basis of the theoretical definition of Biot (1941).

Reservoir compaction is monitored by 4D seismic utilizing changes in sonic velocity and changing thickness of layers. In order to relate this deformation to changes in pore pressure, the effective stress coefficient must be known. So the question is whether we may use β calculated from well log data to estimate *n*? Numerous studies of elastic rock properties as Young's modulus, Poisson's ratio, bulk modulus and shear modulus, show significant difference between static and dynamic elastic properties (Simmons and Brace, 1965; King, 1969; Cheng and Johnston, 1981; Montmayeur and Graves, 1985; Jizba and Nur, 1990; Tutuncu and Sharma, 1992; Tutuncu et al., 1994; Plona and Cook, 1995; Yale et al., 1995;

Wang, 2000; Olsen et al., 2008b; Fjær, 2009). Most authors point to micro-cracks as a major cause of the discrepancy. Other causes include strain amplitude (Simmons and Brace, 1965; Cheng and Johnston, 1981; Plona and Cook, 1995), frequency (Simmons and Brace, 1965; Tutuncu and Sharma, 1992), viscoelasticity (Tutuncu and Sharma, 1992), inelasticity (Cheng and Johnston, 1981; Jizba and Nur, 1990) and stress path (Montmayeur and Graves, 1985; Yale et al., 1995; Fjær, 2009). Polna and Cook (1995) suggested that crack formation at grain contacts during mechanical loading could significantly deviate the static Young's modulus from the dynamic Young's modulus. Olsen et al. (2008a) suggested that the difference in drainage condition between a static and a dynamic experiment is a major source of difference between measured static and a static Young's modulus for saturated samples is to compare dynamic Young's modulus to the undrained static Young's modulus.

All these studies suggest that the stress dependence of the static effective stress coefficient *n* must be established in order to use 4D seismic data for monitoring reservoir compaction and changes in pore pressure. In addition, an investigation on how this stress dependent *n* is related to β would allow estimation of *n* from logging data. If it is possible to establish the relationship between β and *n*, the prediction of pore pressure will become easier and more accurate. In the present study, we measured *n* from mechanical loading tests and compared with β measured from elastic wave velocities.

Theoretically the effective stress coefficient is well studied (e.g. Geertsma, 1957; Nur and Byerlee, 1971; Todd and Simmons, 1972; Carroll and Katsube, 1983; Mavko and Jizba, 1991; Berryman, 1992; Dvorkin and Nur, 1993; Gurevich, 2004; Ciz et al., 2008). Pressure dependent dynamic effective stress coefficient β is measured by several authors (e. g. Banthia et al., 1965; Todd and Simmons, 1972; Christensen and Wang, 1985; Mavko and Jizba, 1991, Hornby 1996, Prasad and Manghnani, 1997; Frempong et al., 2007; Mavko and Vanorio 2010). In addition Geertsma (1957), Nur and Byerlee (1971), Frempong et al. (2007), Omdal et al. (2009) design experimental setup and conduct mechanical tests to measure the effective stress coefficient. Although, most studies are made on sandstones, Banthia et al. (1965) study Austin chalk and Omdal et al., (2009) study chalk from the Stevns outcrop, Denmark. For the 20% porous Austin chalk, Banthia et al. (1965) find that the dynamic effective stress coefficient varies from 0.70 to 0.60 in the differential stress range from 3.5 MPa to 14 MPa. Omdal et al. (2009) define two different static effective stress coefficients from hydrostatic loading tests; the elastic and the plastic. For the >40% porosity water saturated Stevns chalk, they find that the elastic static effective stress coefficient varies from 0.60 to 0.80 in the differential stress range between 0 MPa and 30 MPa. The plastic effective stress coefficient for the same calk ranges between 0.75 and 0.60 in the same stress range. The most important aspect of their finding is the opposite trend of elastic and plastic effective stress coefficient. While the elastic effective stress coefficient decreases with increasing effective stress the plastic effective stress coefficient decreases (Omdal et al., 2009).

Because the effective stress coefficient is described as a bulk property, most of its theoretical formulation and consequently the experimental determination is made under hydrostatic stress conditions (e.g. Nur and Byerlee, 1971; Carroll and Katsube, 1983; Dvorkin and Nur, 1993; Gurevich, 2004; Ciz et al., 2008; Mavko and Vanorio, 2010). However, the stress geometry in the subsurface is most unlikely to be hydrostatic. The first experimental determination of the effective stress coefficient is made by Geertsma (1957). He describes that in a reservoir the prevailing boundary condition is a constant vertical boundary stress and the absence of rock bulk deformations in the horizontal directions. This indicates that a static effective stress coefficient determined for uniaxial stress conditions will be more relevant in a reservoir compaction study.

In the present study, we derive α for one dimensional deformation from the original definition of Biot (1941). We further setup experiments for determining the stress dependent static effective stress coefficient *n* from an uniaxial stress condition. In addition we calculate the dynamic effective stress coefficient β from density and sonic velocities measured on core plugs. We compare *n* and β for chalks from two porosity groups; 30% and 40%. We then present a model based on the isoframe model (Fabricius, 2003) to illustrate the relationship between porosity and effective stress coefficient as a function of grain contact cement.

DATA

Two, one inch vertical plugs from the reservoir zone of Valhall Field, North Sea is investigated for determining the static effective stress coefficient (Table 1).

Table 1: Vertical chalk samples from Valhall field; length (l), diameter (d), porosity (ϕ), gas permeability (k_g), compressional velocity (v_p) and shear velocity (v_s). Velocity is measured at dry condition in the vertical direction.

Sample ID	/ (mm)	d (mm)	φ (%)	k _g (mD)	v _p (km/s)	v _s (km/s)
6AT4-3	13.2	24.9	32	1.1	3.12	1.95
6AT4-5	18.9	24.9	40	3.5	2.30	1.45

Density and stress dependent dry velocity data for 41, $1\frac{1}{2}$ " vertical core plugs from one vertical well and three deviated wells from the same field are also studied for stress dependency on β . Data of these core samples are collected at hydrostatic confined stress condition between 2 MPa and 35 MPa.

THEORY AND METHODS

Model based on grain contact cement



Figure 2: Iso-frame model (Fabricius, 2003). Calcite (compressional modulus M=111 GPa) and Brine (M=2.40 GPa) mixed in a rock by assuming a part (IF) of the solid to be in the solid frame and the remaining solid to be in suspension. Voigt (1910) defines the stiffest mixing. Critical porosity is considered as 0.7 (Fabricius, 2003) for the plot. If critical porosity is 1, IF=1 line conincide with the modified upper Hashin-Shtrikman bound (Hashin and Shtrikman, 1963; Mavko et al., 2009), and IF=0 is equal to the Reuss (1929) bound.

We use the isoframe model (Fabricius 2003) to quantify the amount of resistance pore fluid can offer against the overburden stress in a cemented rock frame. Isoframe modeling is a mixing procedure that allows the determination of a theoretical modulus, using an upper Hashin-Strikman bound (Hashin and Shtrikman, 1963) for mixing of a solid frame and a suspension (Figure 2). By changing the isoframe value (*IF*) the theoretical compressional modulus is set equal to the actual compressional modulus derived from compressional velocity data. Higher isoframe value indicates higher degree of grain to grain surface contact due to e.g. grain contact cementation. When large amounts of the surface area of the grains are in contact, pore fluids get less surface to react against the overburden stress. It makes the effective stress coefficient lower.

Dynamic effective stress coefficient β

The dynamic effective stress coefficient β is calculated by using Equation 2 and Equation 3, considering K_0 as the bulk modulus of pure calcite (Mavko et al., 2009). Sonic velocity is measured in dry samples up to 4 MPa hydrostatic pressure. As we use the same sample for static measurement, velocity data is not collected over 4 MPa in order to avoid damage to the sample.

Static effective stress coefficient n

During mechanical loading n is determined based on Biot's (1941) general theory of three-dimensional consolidation. We derive the equation for n under uniaxial stress conditions (Appendix 1).

$$n=1-\frac{\left(\frac{\partial e_{a}}{\partial P_{p}}\right)_{\sigma_{d}}}{\left(\frac{\partial e_{a}}{\partial \sigma_{d}}\right)_{P_{p}}}$$
(4)

where e_a is the axial strain in a one dimensional deformation, P_p is the pore pressure and σ_d is the differential stress.

This equation is in accordance with theoretical derivation of Todd and Simmons (1972) and as exemplified in the experimental data of Christensen and Wang (1985) for a hydrostatically confined system.

Translation of hydrostatic stress into equivalent uniaxial differential stress As static measurements are done at uniaxially confined stress condition and the dynamic measurements are done at hydrostatic stress condition. We calculate equivalent uniaxial differential stress σ_a for the hydrostatic measurements by using a translation factor as explained by Teeuw (1971):

$$\sigma_a = \frac{1}{3} \left(\frac{1+\nu}{1-\nu} \right) \sigma \tag{5}$$

Where, v is the Poisson's ratio and σ is the hydrostatic stress. v is calculated from compressional velocity, v_p and shear velocity, v_s as:

$$v = \frac{\left(v_p^2 - 2v_s^2\right)}{2\left(v_p^2 - v_s^2\right)}$$
(6)

Experimental setup



Figure 3: Schematic of the experimental setup. V and G indicate valves and pressure gauge respectively.

An experimental setup is designed so that the required conditions on which Equation 4 is derived can be fulfilled (Figure 3). The setup consists of a thick walled steel cell so that radial strain may be neglected and strain can be calculated from the axial deformation e_a only. Axial stress, σ_a , and pore pressure, P_p , are controlled by a valve system, so that $(\partial e_v / \partial P_p)$ at constant differential stress $(\sigma_a - P_p)$ as well as $(\partial e_v / \partial \sigma_d)$ at constant pore pressure can be measured. A constant stress rate of 2.78 kPa/s (10 MPa/h) was used during both loading and unloading. The theoretical strain-stress relationship is illustrated in Figure 4. The axial deformation is measured by external high accuracy LVDTs (Linear Voltage Deformation Transducers) and the load frame positioning system. The axial deformation measured by the load frame is corrected for the systems self-deflection (VIS – Virtual Infinite Stiffness correction).

Depth (m)	Pore	Hydrostatic	Overburden			
	pressure	pressure	stress			
	(MPa)	(MPa)	(MPa)			
2400	44.5	25.2	48.3			
2700	46.4	28.4	54.3			

Table 2: Valhall field pressure data (Andersen, 1995).

Possible effects from bedding and micro-cracks are minimized by repeated initial loading to a stress state which closely mimics the in situ conditions of the reservoir rocks. Vertical stress and strain in the reservoir are equivalent to axial stress and strain in the laboratory, as the experiments are conducted on vertically oriented core plugs. The axial stress, σ_a and pore pressure, P_p for the tests were designed to mimic the reservoir stress condition in Valhall field. We use 5 MPa differential stress at the beginning of the test, which represents the initial differential overburden stress condition in Valhall (Table 2). We load to maximally 50 MPa axial stress and anticipate that pore pressure can reach a minimum value, which is equal to the hydrostatic pressure (25 MPa), due to production.



Figure 4: Strain under stress during loading at constant differential stress, $P_d = (\sigma_a - P_p)$, and during loading at constant pore pressure, P_p . The coefficient *n* was calculated from the slopes of the curves (Equation 4).

Core samples are plugged (± 0.05 mm) to match the inside diameter of the cell, so that the sample would fit perfectly (no peripheral flow between the cell and the sample) inside the cell during saturation. Samples are dried at 60°C for 48 hours and then placed 24 hours at ambient temperature before placing them in the test cell. The test cell with the sample is then placed in the load frame and saturated with isopar oil. The volume of the chalk should increase a bit as it sucks oil into the pore space. As axial deformation is restricted by placing the top piston in fixed position the only possible deformation will occur in radial direction. If the sample fits perfectly into the cell, radial deformation will also be restricted and it will show a small increase in pore pressure as it sucks oil during the saturation process. The tests are completed in the following steps (Figure 5).



Figure 5: Strain-stress curve produced from the mechanical test as plotted in terms of axial stress, pore pressure and differential (axial - pore) stress for (a to c) a 40% porosity and 3.5 mD sample and (d to f) a 32% porosity and 1.1 mD sample. Steps indicated by number are described in the text.

- 1) Axial stress, σ_a is increased to 2 MPa keeping the pore pressure, σ_d at atmospheric.
- 2) By applying vacuum for 30 minutes air is sucked out of the system.
- 3) Saturating under atmospheric pressure for 24 hours with laboratory Isopar-L oil having viscosity 0.00141 Pa-s (1.41 cp) and density 0.765 g/cm³.
- 4) While keeping $\sigma_d = 0$, σ_a is increased to 9 MPa in an alternating loadingunloading-reloading manner to minimize the bedding effect.
- 5) Test for peripheral flow at 1, 2, 4 MPa pore pressure.
- 6) σ_a and P_p are increased simultaneously to 30 and 25 MPa respectively.
- 7) While loading at constant differential pressure of 5 MPa, σ_a and P_p are increased simultaneously to 50 and 45 MPa respectively. The stress is applied in cycles of 10 MPa loading and 5 MPa unloading to reduce further bedding effect.
- 8) P_p is decreased to 25 MPa at constant σ_a of 50 MPa.
- 9) While unloading at constant P_p of 25 MPa, σ_a is decreased from 50 MPa to 30 MPa.
- 10)While reloading at constant P_p of 25 MPa, σ_a is increased from 30 MPa to 50 MPa.
- 11)Unloading of both pore pressure and σ_a to atmospheric pressure.

Steps 7, 9 and 10 were used for calculation of n (Equation 8, Figure 6). Step 9 is followed in order to include the effect on n of water-flooding (axial stress decrease) and oil production (axial stress increase), respectively.



Figure 6: Sections of the curve of Figure. 5 used for calculation of *n*.

 $(\partial e_s / \partial \sigma_p)_{\sigma_d}$ is calculated from the tangent of the strain-stress curve under loading at constant differential pressure (Figure 6, step 7). Because the deformation is small and the trend is linear, we assume a common tangent from 5 MPa to 25 MPa differential stress (Figure 6).

 $(\partial e_a / \partial \sigma_d)_{P_p}$ is calculated from both unloading (Figure 5, 6; step 9) and loading curve under constant pore pressure (25 MPa) (Figure 5, 6; step 10). In this case tangents are drawn at one MPa stress intervals as strain under these conditions. (Figure 6).

The method is sensitive to a perfect contact between the test cell and the sample. If the contact is not perfect, then error in strain measurements will occur, as in this case, there will be radial strain so that the volumetric strain will not be measured from the LVDT reading. Furthermore, the two end surfaces of the sample should be exactly parallel and must fit perfectly with the piston and bottom porous plate. However, by following proper experimental procedure it is possible to overcome these problems.

The theory used for calculating the static effective stress coefficient assumes that there is no elastic hysteresis. This is only possible if the rock is perfectly elastic, which is rare in nature. In order to address the change in elasticity, the stress gradient is measured for very small (1 MPa) stress intervals. On this scale the hysteresis is so small that it can be neglected.

RESULTS



Figure 7: Dynamic effective stress coefficient β calculated from velocity data measured in dry chalk core plugs from Valhall field. Porosity of the samples varies between 10% and 40% as indicated by colors. Equivalent axial differential stress for the hydrostatic stress measurement is calculated by Equation 5. β shows dependency on the confining stress. For the same porosity, β decreases with increasing stress. Variation of β with stress is higher in the high porosity samples .The rate of decrease of β decrease for differential stress above 20 MPa.

The large dataset from the Valhall field show a significant variation in dynamic effective stress coefficient in a broad stress interval (Figure 7). The variations with stress of *n* and β for the studied samples are shown in Figure 8. We made a prediction of stress dependent β for each porosity group from the distribution in the large dataset (Figure 7) as indicated by the shaded region in Figure 8.



Figure 8: Comparison of *n* and β of the tested samples. Arrow indicates the order in which data is collected during the loading test. The open circles indicate *n* calculated from the unloading curve and the solid circles indicate *n* calculated from loading curve. The dynamic effective stress coefficient β for the same sample is indicated by the stars. Equivalent axial differential stress for the hydrostatic stress measurement is calculated by Equation 5. The shaded region is the expected range of β for respective porosity group (based on data presented in Figure 7).

The effective stress coefficient n varies during a loading or unloading operation (Figure 8). In a mechanical loading cycle, n increases with the increment of differential stress. By contrast, n also increases with the withdrawal of load in an unloading cycle.

DISCUSSION

Behavior of β

The effective stress coefficient of chalk is in several papers described as a function of porosity only (e.g. Krief et al., 1990; Engstrøm, 1995). However, this kind of relationship may not fully represent the behavior of β . Our results indicate that β is not (only) a porosity dependent coefficient. Laboratory (dynamic) measurements demonstrate that in the range of 30 MPa differential stress β can vary upto 10% (Figure 7) for high porosity reservoir chalk from Valhall. This observation is in accordance with Gommesen et al. (2007). They find β as to be a positive function of porosity with gradient defined by the cementation between grains contact.



Figure 9: Theoretical bounds for effective stress coefficient together with isoframe curves for a calcite (bulk modulus 75 GPa) and brine (bulk modulus 2.40 GPa) system. β calculated from core data sorted according to hydrostatic stress of the measurement (as indicated by color code). The effective stress coefficient *n* calculated from mechanical tests (black circles) show good agreement with β . Variation of n during a static test is indicated by the black bold line with the data point.

The variation of β can be illustrated by means of effective medium model (Fabricius 2003). It indicates that it is possible to have a range in β for the same porosity depending on the fraction of mineral in the solid frame (Figure 9). For chalk of constant porosity, β decreases as the cementation increases (Olsen et al., 2008). The degree of cementation is indicated by the isoframe values (Figure 9). For poorly cemented rocks (low isoframe value), β does not change significantly with porosity and remains close to unity, whereas for strongly cemented rocks, β decreases rapidly with decreasing porosity (Figure 9). The influence of cementation is more significant in the low porosity chalk. A 20% porosity chalk may have a β ranging between 0.60 and 0.92, depending on the cementation, whereas for 40% porosity chalk the variation may be less than 0.1 (Figure 9).

Contact cement precipitation between the grains depends on the diagenetic process of the chalk and therefore of the effective stress coefficient (Alam et al., 2010). Presence of fine clay may reduce the calcite grain contact and consequently the contact cement. This makes the frame weaker and β increases. However, increases in stress may result in elastic deformation of the grains and contact cement and therefore increasing the area of the grain contact. Simultaneously the effective stress coefficient decreases.

Behavior of n

Laboratory (static) measurements in this project indicate that n may change more than 10% for a probably insignificant porosity change of 0.5% (Figure 8).

The test results show that *n* increases significantly during the unloading cycle. This behavior is similar to that of β . The unloading cycle follows a rapid change in axial stress (step 8), which increases the effective stress and grain contact area expands. Therefore, especially for the higher porosity sample, the static effective stress coefficient *n* has lower value than the possible range of dynamic effective stress coefficient β (Figure 8). During the unloading process the grains tend to restore their original shape, thus contact area among the grains reduces and *n* increases. In addition, contact cement between the gains could break during this process as the cement develops at a later time during diagenesis, so that it is strained when the grains are relaxed and *vice versa*.

There is a sudden drop in n, when the direction of stress changes from unloading to loading. It could happen due to the rapid reversal of loading direction. The system could take some time to equilibrate and the stress state to be the same in the entire sample. However, this behavior is not fully understood. The coefficient n increases during the loading cycle (step 10). This behavior is opposite to the trend of β , and is unexpected. One possible reason for this increase in n is that the increment of axial stress could break some of the contact cement between the grains (irreversible deformation). This decreases the amount of grain to grain contact. By breaking the contact cement, the fraction of grain in suspension increase and isoframe value decrease (Figure 9). Thus, the load bearing capacity of the solid skeleton decreases and n increases.

During step 7 of the test, differential stress is constant while pore pressure increases. However, samples are strained slightly (Figure 6). If creep can be

disregarded during this elastic strain, an increasing effective stress may be inferred, which would indicate a decreasing coefficient n during pore pressure build up.

CONCLUSION

The dynamic effective stress coefficient, β as calculated from sonic data is not a constant value for chalk and ranges between 0.80 and 0.95 for the studied samples from the Valhall field. Our mechanical tests indicate that β predicts the effective stress coefficient, *n*, well for chalk with porosity near 30%, and acceptably for chalk with porosity near 40%. As it is evident that both dynamic and static effective stress coefficient is less than 1, the effective stress will always be higher than the differential stress.

For rapid change in stress it may be more relevant to use the effective stress coefficient, n, derived from mechanical tests rather than β . Our results indicate that for Valhall chalk n would increase as the reservoir depletes. Our results indicate that n could increase also during waterflooding due to the increase in pore pressure.

In the Valhall field, reservoir compaction and stress history of the rock are monitored by 4D seismic. The stress induced changes in velocity measured during 4D seismic monitoring includes porosity and compressibility alteration (Barkved et al., 2005). The findings of this project may be used to analyze the stress induced mechanical changes in the rocks due to pore pressure changes, which could assist in better understanding of 4D seismic response.

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APPENDIX 1

Derivation of static effective stress coefficient under uniaxial stress

Let us consider σ_x , σ_y and σ_z as the normal stress components parallel with the *x*, *y* and *z* coordinate axes respectively and the corresponding shear stress component as τ_x , τ_y and τ_z . Deformation corresponding to the stress components σ_x , σ_y , σ_z , τ_x , τ_y and τ_z are e_x , e_y , e_z , γ_x , γ_y , and γ_z respectively. Additionally, in a rock filled with pore fluid, θ is the increment in porosity due to an increment in fluid pressure, P_p .



Let us consider a uniaxial system in **Figure A1:** Distribution of stresses and compression, for which, $\sigma_x = \sigma_y = -\sigma_r$ and σ_z pore pressure in a fluid saturated rock. = $-\sigma_a$ (Figure A-1)

According to Terzaghi (1923), pore fluid pressure, P_p will act in the opposite direction of the principal stresses σ_x , σ_y and σ_z , hence, deformation equations as expressed by Biot (1941, Equation 2.4) becomes:

$$e_{x} = -\frac{\sigma_{x}}{E} + \frac{\nu}{E} \left(\sigma_{y} + \sigma_{z} \right) + \frac{P_{p}}{3H}, \qquad (A-1a)$$

$$e_{y} = -\frac{\sigma_{y}}{E} + \frac{\nu}{E} \left(\sigma_{z} + \sigma_{x} \right) + \frac{P_{p}}{3H}, \qquad (A-1b)$$

$$e_{z} = -\frac{\sigma_{z}}{E} + \frac{\nu}{E} \left(\sigma_{x} + \sigma_{y} \right) + \frac{P_{p}}{3H}, \qquad (A-1c)$$

Here we considered negative sign for compression, which change the signs of original Biot's (1941) derivation. Biot (1941) made the basic derivation based on tensile forces and described how to use these equations for soil case, where the stress is compressive and he changed the sign in the section 3 of his paper (Biot, 1941).

The radial component of the compressive force creates tensile stress in the axial direction. Therefore, strain component in the axial direction due to the radial

stress has opposite (positive) sign of the strain component due to the axial stress (equations A-1).

For uniaxial systems where the radial deformation is constrained, we get:

$$e_x = e_y = e_r = 0$$
 and $e_z = e_a$ (A-2)

From Equation A-1c,

$$e_{a} = -\frac{\sigma_{a}}{E} + \frac{\nu}{E} (\sigma_{r} + \sigma_{r}) + \frac{P_{p}}{3H},$$

$$e_{a} = -\frac{\sigma_{a}}{E} + \frac{\nu}{E} (2\sigma_{r}) + \frac{P_{p}}{3H}.$$
(A-3)

From Equation A-1a or Equation A-1b,

$$\sigma_r = \frac{\nu}{(1-\nu)}\sigma_a + \frac{1}{(1-\nu)}\frac{EP_p}{3H}.$$
 (A-4)

Putting value of σ_r from Equation A-4 in Equation A-3,

$$e_a = -\frac{\sigma_a}{E} + 2\frac{\nu}{E} \left(\frac{\nu}{(1-\nu)} \sigma_a + \frac{1}{(1-\nu)} \frac{EP_p}{3H} \right) + \frac{P_p}{3H},$$

$$\sigma_a = Me_a + \frac{E}{(1-2\nu)} \frac{P_p}{3H}.$$
 (A-5)

From the relationship among the elastic coefficients, $E=2\mu(1+\nu)$ and hence Equation A-5 becomes:

$$\sigma_a = M e_a + \frac{2(1+\nu)}{3(1-2\nu)} \frac{\mu}{H} P_p.$$
 (A-6)

As defined by Biot (1941), $\frac{2(1+\nu)}{3(1-2\nu)}\frac{\mu}{H} = \alpha$ is the effective stress coefficient for three-dimensional consolidation. This would indicate that α is the same for three-dimensional and confined uniaxial deformation. For uniaxial deformation we denoted this coefficient as *n*, therefore:

$$\sigma_a = Me_a + nP_p. \tag{A-7}$$

Differentiating Equation A-7 with respect to differential stress when pore pressure is constant:

$$\left(\frac{\partial e_a}{\partial \sigma_d}\right)_{P_p} = \frac{1}{M}.$$
 (A-8a)

Differentiating Equation A-7 with respect to pore pressure when differential stress is constant:

$$\left(\frac{\partial e_a}{\partial P_p}\right)_{\sigma_d} = \frac{1-n}{M}.$$
 (A-8b)

From Equation A-8a and Equation A-8b

$$n=1-\frac{\left(\frac{\partial e_{a}}{\partial P_{p}}\right)_{\sigma_{d}}}{\left(\frac{\partial e_{a}}{\partial \sigma_{d}}\right)_{P_{p}}}.$$
(A-9)

IV

Rock mechanical and petrophysical effects of CO₂ injection for enhanced oil recovery: chalk from South Arne field, North Sea

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Petrophysical and rock-mechanics effects of CO₂ injection for enhanced oil recovery: chalk from South Arne field, North Sea

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Keywords: Monitoring; Petrophysics; Reservoir geophysics; Rock physics; Velocity analysis.

ABSTRACT

Enhanced oil recovery by CO_2 injection (CO_2 -EOR) is a tertiary oil recovery process which has a great potential for being used at the same time as an effective technique for carbon dioxide capture and storage (CCS). Although CO₂-EOR has been used for several years, monitoring techniques for long time storage of CO_2 by this process are still under development. Especially there exists very limited information on chalk although there is a huge storage opportunity in the North Sea depleted chalk reservoirs. Chalk of the South Arne field in the North Sea is characterized by high porosity and high specific surface causing low permeability. A high porosity provides more room for CO₂ storage, while a high specific surface allows more surface area of the rock particles to come in contact with any reactive fluid that might be produced by CO₂ injection. From the South Arne field, we studied chalk from Ekofisk Formation having approximately 20% non-carbonate and Tor Formation which has less than 5% non-carbonate. We performed a series of laboratory experiments to reveal the changes in petrophysical and rock-mechanics properties of chalk due to the injection of CO₂ at supercritical state. We explored these changes with respect to the differences in porosity, specific surface, pore stiffness, wettability, mineralogy and mechanical failure. We observed 2-3% increase in porosity, minor smoothening of particle surface and consequently slight increase in permeability, a decrease in elastic stiffness as indicated by Biot's coefficient. However, no significant change in wettability was noticed. We found that the effect of CO₂ injection on both petrophysical and mechanical properties of chalk depend on carbonate content. Pure chalk with high carbonate content is relatively prone to mechanical weakening due to CO₂ injection, while no significant affect was observed in relatively impure chalk of Ekofisk Formation during the span of the experimental study. We noted that, in spite of mechanical weakening we expect only minor compaction because effective stress is decreased due to an increase in effective stress coefficient. Extensive time-lapse monitoring strategies are required during a CO_2 -EOR process for the measurement of changes in reservoir properties that may cause deformation of and leakage from a reservoir. Results of this study will provide data for designing future monitoring strategies based on 4D seismic.

INTRODUCTION

 CO_2 injection is a well established Enhanced Oil Recovery (EOR) method. The basic principle of this process is to inject CO_2 in a depleted reservoir to dissolve the remaining oil (miscible displacement) after traditional production. Recovery of oil can be increased by up to15% by using this technique (Gozalpour et al., 2005; Darvish et al., 2006; Ferguson et al., 2009; Shaffer, 2010). In addition, this process has a great potential for storing CO_2 , which could act as a remedy for increasing CO_2 concentration in the atmosphere; widely blamed for global warming (Bachu, 2000; Westrich et al., 2001; Pawar et al., 2004). On a global scale CO_2 injection could economically recover 39 to 48 billion barrels of oil from depleted reservoirs (Ferguson et al., 2009) while accommodating 8.1×10^{14} kg (810 Gt) of CO_2 in these reservoirs (Liteanu, 2009).

Enhanced Oil Recovery with CO_2 (CO_2 -EOR) in the North Sea is of particular interest. Markussen et al. (2002) modeled that additional 2.1 billion barrels of oil can be obtained from the North Sea reservoirs, while sequestering 680 Mt of CO_2 in 25 years. Due to the exploration and production activities in this region for more than four decades, reservoir capacity is well estimated and reservoir characteristics are well understood. Furthermore, safe storage capacity of these hydrocarbon reservoirs is historically established. Several North Sea chalk reservoirs are characterized by low permeability and high porosity. Injection of supercritical CO_2 increases mobility of the oil in these low permeable chalk and at the same time high porosity provides larger storage capacity. However, our current knowledge on the interaction between chalk and CO_2 and its influence on the reservoir characteristics for long time storage is limited.

Chalk is a sedimentary rock, developed from the diagenesis of pelagic calcareous ooze. Particles in calcareous ooze are primarily derived from the algae skeletons called coccospheres. The spherically shaped coccospheres are between 10 and 30
μ m in diameter and composed of 7-20 wheel shaped coccolith platelets of 2 to 20 μ m diameter and 0.5 to 2.5 μ m across (Scholle, 1977; D'Heur, 1984). North Sea chalks are predominantly composed of coccolith fragments or aggregates of coccolith platelets: entire coccospheres are relatively rare (Scholle, 1977). This makes chalk a very fine grained homogeneous rock with high specific surface area.

A high specific surface of particles means that the solid has large exposure to the fluid. Alteration in the pore fluids due to CO_2 injection may cause dissolution of the solid phase and/or precipitation of solids, so that the reservoir rock may change with respect to porosity, pore-geometry, permeability, wettability, stiffness and compaction behavior (Plummer and Busenberg, 1982; Wolcott et al., 1989; Wellman et al., 2003; Hawkes et al., 2005; Madland et al., 2006; Xu et al., 2007; Zuta and Fjelde, 2008). These changes may influence the overall productivity from the reservoir and the stability of the reservoir rock, sealing rock and wellbore.

CO₂ remains in supercritical condition in typical storage sites having high pressure (10 MPa - 30 MPa) and temperature (40°C - 130°C). In this condition, CO_2 has 40% - 70% less density than the surrounding pore fluid (Lemmon et al, 2005). This density contrast causes the buoyant CO_2 to migrate upwards and to create over pressure in the reservoir. In addition, possible weakening of chalk due to the chemical effect of CO₂ on calcite particles could weaken its mechanical properties and make it more vulnerable to compaction due to overburden stress or failure at well bores. Such failure could cause leaking of CO₂ from the reservoir. According to the Intergovernmental Panel of Climate Change (IPCC), a leakage must be less than 1% of the stored volume in 1000 years to meet the requirements for CO₂ storage (IPCC, 2005). Therefore, extensive time-lapse monitoring strategies are required during EOR for the measurement of changes in reservoir properties that may cause deformation of reservoir and leakage. Changes in chalk due to CO_2 injection can ideally be predicted by applying geophysical methods designed based on laboratory-determined petrophysical and rock-mechanics properties. However, little information has been published on petrophysical and rock-mechanics effect of injecting supercritical CO₂.

In order to address this issue, we performed a series of laboratory experiments to gather data to be used for reservoir modeling and provide a better understanding

of the interaction between chalk and CO_2 for future monitoring purposes. Porosity, permeability, carbonate content, specific surface, wettability, compressional and shear wave velocity, NMR T_2 relaxation and electrical resistivity. All parameters were measured before and after the CO_2 injection. Triaxial compression experiments were performed on waterflooded (reference) and water/ CO_2 injected cylindrical chalk cores and compiled in terms of strength envelopes to detect the effect of CO_2 on the mechanical properties of chalk.

MATERIAL

Chalk from the Ekofisk Formation of lower Paleogene age and the Tor Formation of upper Cretaceous age from the South Arne field of Danish North Sea was studied by means of core material collected from the wells SA-1 and Rigs-1 (Fig. 1). SA-1 is a deviated well and Rigs-1 is a vertical well. The Ekofisk and Tor formations are largely calcitic but have different silica and clay content. In general, the Ekofisk Formation rocks have high content (>12%) of silica and clay and the Tor Formation rocks have low (<5%) content of silica and clay (Røgen and Fabricius, 2002) (Fig. 2).



Figure 1: (a) Location map of South Arne Field, North Sea. (b) Position of the studied wells within the field, plotted on top of the chalk group depth structure map (Modified after Larsen, 1998).

Thirty six $1\frac{1}{2}$ inch (35 mm) vertical plugs of variable length were prepared by rotary drilling. Sixteen of them were used for porosity, permeability, sonic velocity, electrical resistivity and Nuclear Magnetic Resonance (NMR) transverse relaxation time (T_2) measurements. Twenty plugs were used for rock-

mechanics testing. Side trims of all 1¹/₂ inch samples were collected to prepare polished sections for backscattered electron (BSE) microscopy. An overview of the geological location of the studied samples is given in Table 1. Centimeter size chips were also collected from the core material from the wells SA-1 and Rigs-1 for measurement of carbonate content, specific surface and mineralogical composition.

Table 1: Studied geological interval and lab number of the samples for geophysical and rockmechanics tests. C, Q, K and S indicates calcite, quartz, kaolinite and smectite respectively as measured by X-ray diffractometry. The underlined samples were flooded with supercritical CO₂.

Well	Depth (m)	Formation	Minerals	Samples for geophysical tests	Samples for rock- mechanics tests
Rigs-1	2803.9	Ekofisk	C, Q, K		<u>RE-06A</u> , RE-08B, RE-09B, <u>RE-10A</u> , <u>RE-12B</u>
Rigs-1	2806.9	Ekofisk	C, Q, K		RE-14
Rigs-1	2813.0	Ekofisk	C, Q, K	RE-22A, <u>RE-23A</u> , <u>RE-24</u>	
Rigs-1	2816.1	Ekofisk	C, Q, K	<u>RE-26B2</u>	<u>RE-26B1</u> , RE-28A1, <u>RE-</u> <u>29</u> , RE-31
Rigs-1	2840.6	Tor	C, Q, K	<u>RT-01, RT-02</u>	
Rigs-1	2844.4	Tor	C, Q, K	RT-03	
SA-1	3319.8	Ekofisk	C, Q, S	SE-05A	
SA-1	3331.8	Ekofisk	C, Q, S	SE-02, SE-03	
SA-1	3381.7	Tor	C, Q, S, K*	<u>ST-23A</u> , ST-24A, <u>ST-24B</u> , <u>ST-26</u>	ST-25B
SA-1	3390.5	Tor	C, Q, S, K*		ST-20
SA-1	3399.7	Tor	C, Q, S, K*		<u>ST-16B</u> , ST-17B
SA-1	3408.7	Tor	C, Q, S, K*		ST-12B, <u>ST-13B</u>
SA-1	3418.8	Tor	C, Q, S		ST-01B, <u>ST-03B</u>
SA-1	3427.7	Tor	C, Q, S	** <u>ST-08A</u> , ** <u>ST-08B</u>	<u>ST-07</u>
SA-1	3437.8	Tor	C, Q, S		<u>ST-04B</u>

* Presence of trace only

** Used primarily as filter for the CO₂ flooding test.



Figure 2: Backscatter electron (BSE) micrographs of epoxy-impregnated and polished samples from the two studied formations of the wells SA-1 and Rigs-1: (a) before CO_2 injection and (b) after CO_2 injection. Dark is porosity and bright is calcite. Clay and quartz appear as grey as indicated with arrows. Ekofisk Formation: porosity: 32%, CaCO₃: 88%, gas permeability: 0.6 mD, sp. surface: 3.5 m²/g and Tor Formation: porosity: 26%, CaCO₃: 98.6%, gas permeability: 0.8 mD, sp. surface: 1.7 m²/g.

THEORY

Sound wave velocity was used as the central tool to study pore stiffness and its impact on the reservoir deformation behavior by means of effective stress coefficient. Electrical resistivity and NMR T_2 relaxation were utilized to detect changes in cementation and surface behavior. Results from triaxial testing were applied in modified Mohr-Coulomb failure criteria to investigate changes in mechanical properties of chalk.

Effective stress coefficient (Biot's coefficient), α

If CO₂ has affect on the stiffness of chalk, it will alter the effective stress state in a CO₂-EOR field. Effective stress (σ_{eff}) as defined by Biot (1941), is the difference between the overburden stress (σ_{ov}) and a fraction (effective stress coefficient, α) of the pore pressure (P_p);

$$\sigma_{eff} = \sigma_{ov} - \alpha P_p. \tag{1}$$

Overburden stress (σ_{ov}) due to the weight of the overlying sediment may be assumed constant for the span of the storage period. In contrast, pore pressure could increase due to injection of CO₂ at higher pressure as well as decrease due to pressure drawdown during production. Change in pore pressure will change the effective stress on the sediment and will be responsible for consequences due to CO₂ injection.

Pressure in the wetting phase works on the internal surface of the rock. The more the horizontal projection of surface of grains are in contact with the wetting fluid the more resistance the fluid can offer against the overburden stress. Due to deformation in a rock-mechanics and/or chemical process due to CO_2 injection, there is a possibility of increased or decreased grain contact (softening or hardening behavior). If this happens, the value of α will also change. For this reason, from elastic deformation of the rock we may estimate changes in α .



Figure 3: Theoretical bounds for effective stress coefficient for a calcite (bulk modulus 75 GPa) and brine (bulk modulus 2.40 GPa) system. Degree of cementation is indicated by the isoframe curves (*IF*) (Fabricius, 2003).

The variation of α can be illustrated by means of effective medium model (Fabricius, 2003). For chalk of constant porosity, α decreases as the cementation

increases (Olsen et al., 2008a). One of the ways of quantifying the degree of cementation is by the isoframe (*IF*) values (Fig. 3) (Fabricius, 2003). For poorly cemented rocks (low isoframe value), α does not change significantly with porosity and remains close to unity, whereas for strongly cemented rocks, α decreases rapidly with decreasing porosity (Fig. 3). Any chemical interaction of chalk with supercritical CO₂ will change the degree of cementation and α will move from one *IF* curve to another (Fig. 3). On the other hand if supercritical CO₂ reacts only with the particle surface and increase the porosity, α will move along the same *IF* curves as long as the degree of cementation remains unchanged.

 α is calculated from dry bulk modulus, K_{dry} and bulk modulus of the mineral frame, K_o :

$$\alpha = 1 - \frac{K_{dry}}{K_0}.$$
 (2)

 K_{dry} is calculated from the compressional velocity, V_p and shear velocity, V_s , as measured on the dry rock, as well as dry density, ρ_{dry} ;

$$K_{dry} = \rho_{dry} V_p^2 - \frac{4}{3} \rho_{dry} V_s^2.$$
 (3)

For V_p and V_s measurement on rocks saturated by a fluid, K_{dry} may be calculated by using Gassmann (1951) fluid substitution;

$$\frac{K_{sat}}{K_0 - K_{sat}} \approx \frac{K_{dry}}{K_0 - K_{dry}} + \frac{K_{fl}}{\phi(K_0 - K_{fl})},$$
 (4)

where K_{sat} is the bulk modulus for the saturated rock and K_{fl} is the modulus of the saturating fluid.

Archie's cementation factor, m

Archie's (1942) equation correlates resistivity of brine R_w with the resistivity of a rock saturated with brine R_o by defining a formation factor, F:

$$F = \frac{R_o}{R_w} \,. \tag{5}$$

The electrical current travels a longer path than the geometrical length of a rock. F indicates the degree of difficulty in electrical current flow due to the pore geometry. F is primarily controlled by porosity and specific surface, but the cementation exponent m determines the degree to which porosity, ϕ should be decreased, so that the pores could be considered as straight continuous channels. F is then (Archie, 1942):

$$F = \frac{1}{\phi^m}.$$
 (6)

The exponent *m* increases significantly with specific surface (Olsen et al., 2008a) which characterizes the pore geometry. Therefore, if CO_2 changes the pore geometry it would possibly change the cementation factor to be used for interpreting electrical resistivity data.

NMR transverse relaxation time, T_2

Transverse relaxation time, T_2 is the characteristic time that proton aligned by a magnetic field take to flip 90° after the magnetic field disappears. Relaxation of protons close to the solid surface is faster than of protons in the free flowing fluid (Kenyon, 1997). Transverse relaxation rate, $1/T_2$ in an *NMR* experiment is proportional to the surface to volume ratio (*S/V*) (Coates et al., 1999),

$$\frac{1}{T_2} = \rho \frac{S}{V} = \rho S_{\phi},\tag{7}$$

where, ρ is relaxivity and S_{ϕ} is the specific surface of pore space.

Protons in water relax faster in water-wet system than in an oil-wet system (Brown and Fatt, 1956; Williams, 1982, Hsu, 1992; Chen et al., 2006). Therefore, a change in wettability may result in a change in transverse relaxation time, T_2 .

Failure analysis in *p'-q* space

Compaction behavior of chalk can be analyzed in a p'-q space by correlating strength parameters measured at different boundary conditions (Fig. 4), where, p' is the mean effective stress:

$$p' = \frac{1}{3} (\sigma_1' + \sigma_2' + \sigma_3')$$
(8)

and q is the deviatoric stress:

$$q = \frac{1}{\sqrt{2}} \sqrt{(\sigma_1' - \sigma_2')^2 + (\sigma_2' - \sigma_3')^2 + (\sigma_1' - \sigma_3')^2}, \qquad (9)$$

where σ_1 , σ_2 and σ_3 are the normal principle stress components.



Figure 4: The region of elastic and plastic behavior and the failure lines are indicated in a p'-q space. In the region above the shear failure line chalk will fail. Pore collapse occurs at the transition from elastic to plastic behavior. Between the elastic and plastic state, rocks show residual strength as it strain even if the stress is unchanged. The traditional rock mechanical tests, hydrostatic compaction and uniaxial compaction are indicated by solid lines. The slope of a uniaxial compaction line decreases with increasing radial to axial stress ratio.

A failure criterion diagram in the p'-q space is illustrated in Fig. 4. The elastic area is restricted by a shear failure line and a pore collapse or yield surface. The shear failure line defines the possible states the material can sustain before it breaks. The yield surface separates elastic behavior from plastic behavior. After the yield surface a stiff-bonded rock behaves as a frictional material and appears as a plateau in the p'-q diagram, which is defined as residual strength. Inside the yield surface, deformation of the material is elastic. If CO₂ weakens the rock, these two lines will come closer to the origin.

When presenting the shear failure stresses in a p'-q plots, the angle of internal friction φ' and the effective cohesion c' can be derived as:

$$\sin(\varphi') = \frac{3M}{6+M} \text{ and} \tag{10}$$

$$c' = -a \tan \varphi', \tag{11}$$

where M (=q/p') is the slope of the shear failure line and *a* is the intersection of the shear failure line with the *p'*-axis.

METHODS

Sample preparation

Chips and side trims were cleaned for salt and hydrocarbons by soxhlet extraction. The samples were first refluxed by methanol to remove salts. Methanol was boiled at 110°C and the vapor was condensed by flowing water at 12°C. The absence of measurable chloride was checked by 0.03M AgNO₃ after stopping the process for three days, while the samples in the flask were immersed in methanol. After removing salts, the samples went through toluene refluxing for hydrocarbon removal. Toluene was boiled at 64.5°C and the vapor was condensed by flowing water at 12°C. This process for three days, with the samples in the samples in the samples in the vapor was condensed by flowing water at 12°C. This process for three days, with the samples immersed in toluene. Clean samples were dried in an oven at 55°C for two days.

All 1¹/₂ inch samples were first cleaned for salt and hydrocarbons by a cold flush cleaning method with a mixture of methanol and toluene. The plugs were mounted in a Hassler core holder and a confining pressure of 400 psi (2.75 MPa) was applied. The liquids were flushed through the sample with a positive displacement pump. Each step in a cleaning cycle may require a liquid throughput of 5-20 pore volumes or until the effluent is free of salt and colorless. Cleaned samples were dried in an oven at 55°C for two days.

General sample characterization

For chips and side trims, carbonate content was measured by titration with HCl and NaOH. The BET method (adsorption with nitrogen) was applied to determine the specific surface by using a Micrometritics Gemini III 2375

(Brunauer et al., 1938). Both powdered original sample and insoluble residue (IR) were analyzed by X-ray diffraction (XRD) using *Cu K-* α radiation with Ni filter by a Philips PW 1830 diffractometer. Carbonate was totally dissolved in an aqueous 2 N CH₃COOH solution at pH = 2.2 to separate the non-carbonate fraction (IR). Polished sections were prepared from epoxy-impregnated side trims. BSE images were recorded by a JEOL JSM 5900 LV electronic microscope at 1280×960 pixels resolution and at two different magnifications, 420×315 µm and 42.0×31.5 µm, to identify the textural changes due to CO₂ injection.

On cleaned and dried 1¹/₂ inch plugs, grain density and porosity were measured by helium porosimetry. Gas permeability was determined by using the Darcy's law for incompressible fluid flow with nitrogen gas inside a Hassler type core holder. The samples were then CT-scanned to screen for larger fossil fragments, fractures/fissures and other major in-homogeneities.

Saturating fluid

Simulated formation brine (HTF brine) was used as aqueous phase. Depending on the purpose (described later) South Arne crude oil (dead oil) or South Arne live oil (recombined oil) or Isopar-L was was used as hydrocarbon phase. Fluid properties are listed in Table 2.

Eluid	Densi	ity (g/cm ³)	Viscosity (cP)					
	15°C (atm.)	115°C (38 MPa)	15°C (atm.)	115°C (38 MPa)				
Simulated formation brine (HTF brine)	1.065	1.028 ^b	0.779	0.36 ^b				
South Arne stock tank oil	0.845	-	13.5	-				
South Arne live oil	-	0.63 ^c	-	0.25 ^c				
Isopar-L	0.779 ^c	-	1.29 ^c	-				
Supercritical CO ₂	-	0.71 ^c	-	0.06 ^c				
^a Supercritical CO ₂ in SA-1 live oil	-	0.67 ^c	-	0.21 ^c				

Table 2: Properties of the used fluids at ambient condition (15° C and 0.1 MPa) and at South Arne reservoir condition (115° C and 38 MPa), which was also used during CO₂ injection.

^a 30 (mol%) CO₂ at 115°C and 38 MPa.

^b Calculated by Batzle and Wang (1992) equations.

^c Yan and Stenby (2010).

Formation brine composition in the South Arne field is quite variable and a perfect match with the actual composition of the water in the Rigs-1 and SA-1 wells cannot be expected. For this study brine (HTF brine) was prepared on the

basis of water analysis from well SA-2 from the South Arne field (Table 3). The water composition was modified relative to the SA-2 analysis as follows:

1) The water analysis is not stoichiometric and to be used as a recipe some Cl⁻ were omitted.

2) Sr^{2+} and Ba^{2+} are omitted together with an appropriate amount of Cl⁻ to avoid precipitation of celestine, strontianite, barite and witherite.

3) Fe (total) was omitted because; in the experimental work it was not possible to control oxygen fugacity.

4) Al^{3+} was omitted because the amount is insignificant.

5) B^{3+} was omitted because of lack of experience with this component.

6) Si^{4+} was omitted because; in order to make it soluble in water it is necessary to add components that are not included in the analysis.

7) SO_4^{2-} was omitted to avoid precipitation of sulphate minerals.

An amount of $CaCO_3$ could precipitate from the solution during mixing. The water was filtered and the amount of precipitate was quantified.

Element	SA-2 Water	S	Simulated formation brine (HTF brine)											
	analysis (mg/l)	Compound	Compound g/l	Concentration mg/l	Concentration mol/l									
Na⁺	31021	NaCl	78.847	31016	1.3491									
		NaHCO₃	0.018	5	0.0002									
K^{+}	522	KCI	0.995	522	0.0134									
Mg ²⁺	665	MgCl ₂ .6H ₂ O	5.562	665	0.0274									
Ca ²⁺	5667	CaCl ₂ .2H ₂ O	20.788	5667	0.1414									
Sr ²⁺	461	-	-	-	-									
Ba ²⁺	627	-	-	-	-									
Fe(total)	30	-	-	-	-									
Al ³⁺	2	-	-	-	-									
B ³⁺	106	-	-	-	-									
Si ⁴⁺	31	-	-	-	-									
Cl	64040	-	-	60270	1.7000									
HCO ₃ ⁻	500	-	-	13	0.0002									
SO4 ²⁻	17	-	-	-	-									

Table 3: Composition of synthetic brine: salinity 90423 ppm and resistivity 0.077 Ω m at 25°C.

Irreducible water saturation to be used during CO₂ injection

In a water wet system, at irreducible water saturation all the particle surface exposed to pores (S_{ϕ}) will be covered by a film of water. The samples collected for testing vary with respect to porosity and permeability (Fig. 5), so in order to obtain a common water film thickness in pores during CO₂ injection, a common water saturation for all samples cannot be applied. We estimate suitable water saturations by using the pseudo water film thickness model of Larsen and Fabricius (2004). From logging data and conventional core analysis data we calculate the specific surface of pores;



Figure 5: Water saturation from log analysis compared to the water saturation recommended for CO₂ flooding, as well as resulting calculated pseudo water film thickness (PWFT); (a) for Rigs-1 well, (b) SA-1 well. Porosity and permeability used for PWFT calculation is given in (i), (ii) and (iii). Large black dots are measurements taken in this project. Small circles and dots are core data collected from Geological Survey of Denmark and Greenland (GEUS) core lab database. Permeability indicated by filled data points is measured in the vertical direction whereas unfilled data points represent measurements in the horizontal direction.

$$S_{\phi} = \sqrt{\frac{c\phi}{k_l}} , \qquad (12)$$

where ϕ is porosity and k_l is liquid permeability. When gas permeability (k_g) data is available k_l can be calculated as (Mortensen et al., 1998);

$$k_l = 0.25k_g (\text{mD})^{1.083} (\text{mD})$$
 (13)

for North Sea chalk and the factor c may be approximated as a function of porosity (Mortensen et al., 1998):

$$c(\phi) = \left[4\cos\left\{\frac{1}{3}\arccos(2\phi - 1) + \frac{4}{3}\pi\right\} + 4 \right]^{-1}.$$
 (14)

Pseudo water film thickness (*PWFT*) is then calculated from S_{ϕ} and water saturation at irreducible condition, S_{wir} , by (Larsen and Fabricius, 2004);

$$PWFT = \sqrt{\frac{S_{wir}}{S_{\phi}}} .$$
 (15)

Larsen and Fabricius (2004) found that PWFT is not constant but decreases with increasing capillary pressure. Water saturation and PWFT for Rigs-1 and SA-1 are presented in Fig. 5. We assume that the water saturation of SA-1 and Rigs-1 are irreducible and that the generally higher PWFT in Rigs-1 is the result of lower capillary pressure in that well. So we selected a common PWFT of approximately 20 nm for all samples and S_{wir} was calculated for individual samples corresponding to this PWFT.

Injection rate required to avoid worm holes resulting from CO₂ injection.

Previous laboratory test series on carbonates experienced the forming of wormholes, making the interpretation of test results difficult (e.g. Hoefner and Fogler, 1989; Egerman et al., 2006 Lombard et al., 2010). Thus, to avoid wormholes, we estimated a suitably low CO_2 injection rate.

Transport of fluid in a reactive porous medium can result in dissolution of the solid phase. The geometric pattern of dissolution is controlled by flow rate and rate of reaction (Egerman et al., 2005). Where transport of the fluid is the limiting factor, compact dissolution takes place. Where rate of reaction is the limiting factor, uniform dissolution throughout the pore space dominates. Where both factors play a significant role, worm holes may arise (Fig. 6).



In order to facilitate interpretation of geophysical data after CO_2 injection, uniform dissolution is required. The reactive transport may be described in terms of the Peclet number (*Pe*) and the Damköhler number (*Da*). *Pe*, describes the time for diffusion relative to time for convection and *Da* describes time for convection relative to time for dissolution. Time for diffusion relative to time for dissolution is thus described by the product *PeDa*.

For simplicity and to be on the safe side we assumed injection of a strong acid. *Pe* and *PeDa* was calculated as functions of injection rate to find a suitable injection rate which will not create wormholes. According to this interpretation, injection rates should be below 6 m/s (10 ml/hr for a $1\frac{1}{2}$ inch plug).

Initial brine saturation (S_w-I)

All samples were first saturated with HTF brine or diluted HTF brine aiming at 100% saturation. Diluted HTF brine was used for Rigs-1, Ekofisk samples for rock-mechanics testing as the evaporation method was used to achieve desired irreducible water saturation calculated by the *PWFT* method. The evaporation method is more effective for low permeability chalk (Springer et al., 2003).

A vacuum procedure was used for initial brine saturation. Samples were placed in desiccators and vacuum were created by a water pump while brine was poured into the desiccators gradually until the samples were covered with brine. To increase degree of saturation, while these samples were immersed in brine they were pressurized in a pressure chamber with elevated pressure of 1600 psi (11 MPa) for 3 days. Afterwards the degree of saturation was tested by the Archimedes method. The samples were subsequently subjected to primary drainage, water flooding and CO_2 injection.

Achieving desired saturation before CO₂ injection *Geophysical test set*

For the geophysical tests one group of samples were CO_2 injected at irreducible water saturated condition and another group of samples were CO_2 injected at residual oil saturated condition (Table 4).

Table 4: Test design for geophysical measurements. Grey boxes indicate intermediate stages of measurement taken on a sample. Black boxes indicate final test with a sample.

Condition	Dry-l	S _w -I			-	S _{wir}			S _{or}			S _{CO2}			Dry-F			-	S _w -F			_	
Sample	Velocity Resistivity NMR	Thin section Velocity	Resistivity	Thin section	Velocity	Resistivity	Thin section	Velocity	Resistivity	NMR	Thin section	Velocity	Resistivity	NMR	Thin section	Velocity	Resistivity	NMR	Thin section	Velocity	Resistivity	NMR	Thin section
RE-22A																							
RT-03																							
SE-03					-																		
ST-24A																							
RE-24																							
RT-01																							
SE-05A																							
ST-24B																							
RE-23A																							
RT-02																							
SE-02																							
ST-23A																							
RE-26B2																							
ST-26																							

To obtain irreducible water saturation (S_{wir}) the following procedure was followed. Brine saturated samples were mounted in a core holder and were heated at 80°C for 2 days to establish uniform reservoir temperature. Holding the

sample at 18 barg (1.8 MPa) sleeve pressure, at least 1.9 pore volume of South Arne Crude oil at room temperature (23°C) was then flushed through the samples at a rate of less than 0.5 ml/h to achieve an uniform distribution of the oil phase throughout the sample. Samples were then aged at 80°C for 24 days at 18 barg (1.8 MPa) sleeve pressure. Afterwards, samples were flushed with at least 2.3 pore volume of oil at a rate of less than 0.5 ml/h at a temperature of 23°C and sleeve pressure of 18 barg (1.8 MPa). By this operation any gas evolved during the ageing should be removed from the pores. Archimedes test was then done in oil to calculate oil saturation.

To obtain residual oil saturation by waterflooding (S_{or}), the following procedure was followed: Mounting in a core holder the samples at S_{wir} were heated at 80°C for 2 days. The samples were then flushed with degassed HTF brine. The oil production from each core holder was collected. Differential pressure over samples was aimed not to surpass 5 bar (0.5 MPa). The flushing of each sample was completed with brine flow for 1 day at 2 ml/h, if allowed by the differential pressure. Archimedes test was done in HTF brine to calculate brine saturation.

Rock-mechanics test set

In reference samples S_{wir} and S_{or} were achieved by following the same procedure as for the geophysical test samples

Samples for CO_2 injection were brought to an irreducible water saturation condition before placing in a reservoir condition rig, where both waterflooding and CO_2 injection were performed. For these samples S_{wir} was achieved by dilution-evaporation method to generate a uniform brine distribution in a short period of time (Springer et al., 2003). By this method samples were first saturated with diluted HTF brine. Water was then removed from the diluted brine by evaporation to obtain normal HTF brine salinity and desired PWFT. The remaining pore space was filled by Isopar-L oil.

CO₂ injection

The injection experiments were conducted in a reservoir condition rig utilizing a Hassler-type core holder for 1.5" (37.5 mm) plugs with a floating end piece, a number of pressure cylinders for the experimental fluids, two acoustic separators for quantifying the fluid production, a differential pressure transducer for measuring the pressure difference across the sample, a densitometer, and a high

pressure pump system for generating confining pressure, flow and pore fluid pressure. Details of the experimental setup is published by Olsen (2010). A series of samples were placed in a core holder. Plugs are mounted with increasing permeability towards the outlet end of the core holder to form a composite core. A good fit between the individual samples is aimed to assure good capillary contact. The core holder with core plugs was mounted in a vertical position and CO₂ injection was performed vertically from the bottom of the stacked samples towards the top. The injection experiments were conducted at 380 bara (38 MPa) pore pressure, 500 bara (50 MPa) hydrostatic confining pressure and a temperature of 115°C. Three sets of injection experiments were made (1) geophysical test samples, (2) rock-mechanics test samples from SA-1 Tor Formation and (3) rock-mechanics test samples from Rigs-1 Ekofisk Formation.

Geophysical test set

The objective of CO_2 injection was to identify the changes in chalk when CO_2 is injected into an already waterflooded field and when CO_2 is injected from the beginning of production. Therefore a group of irreducible water saturated and a group of residual water saturated (waterflooded) samples were placed in the rig. In addition filter samples were placed at the inlet and at the outlet in order to minimize possible back-flow and saturation end effects.

Arrangement of samples

(inlet) ST-08B » ST-24B » RE-24 » RT-01 » RE-23A » ST-23A » RT-02 » ST-08A (outlet).

After mounting the samples in the core holder, the core holder was mounted in the reservoir condition rig. Temperature, fluid pressure and hydrostatic confining pressure were increased simultaneously until reservoir pressure conditions were achieved. Samples were held at this condition for one week. The composite core was then injected with 352.5 ml (2.83 PV) supercritical CO_2 at a rate of 2 ml/h.

Rock-mechanics test set

The intention of these injection tests is to mimic waterflooding followed by CO_2 injection in chalk. The two experiments used the same fluids: 1) a live crude oil prepared by recombination of samples of separator gas and separator oil, 2) HTF brine and 3) supercritical CO_2 of purity 99.99%. The only difference between the injection experiment on SA-1 Tor Formation samples and Rigs-1 Ekofisk Formation samples was the injection rates; which was 2.0 ml/h and 0.6 ml/h, respectively, due to the difference in permeability.

Arrangement for SA-1 Tor Formation samples (inlet) ST-16B » ST-04B » ST-03B » ST-13B » ST-07 » ST-26 (outlet).

Arrangement for Rigs-1 Ekofisk Formation samples (inlet) RE-29 » RE-26B2 » RE-10A » RE-06A » RE-12B » RE-26B1 (outlet).

For establishing reservoir conditions, laboratory oil (Isopar-L) was replaced by injecting 3 pore volumes of live reservoir oil into the samples and aging them for three weeks at this condition. In the waterflooding phase the samples were flooded by HTF brine until oil production stopped. The cores were then injected with supercritical CO_2 until production of oil stopped.

After the CO_2 injection, the samples were flooded with HTF brine to remove as much CO_2 as possible. Finally the samples were depressurized, cooled, and dismounted from the rig. At the end of CO_2 injection the samples were stored in HTF brine before geophysical and triaxial testing.

Geophysical test design

Three groups of samples were selected for sonic velocity, electrical resistivity and NMR measurements. Each group contains four samples representing each of the studied intervals: SA-1 Ekofisk Formation (SE), SA-1 Tor Formation (ST), Rigs-1 Ekofisk Formation (RE) and Rigs-1 Tor Formation (RT). The test plan was designed so that sonic velocity and electrical resistivity (where possible) could be recorded at initial dry conditions (*Dry-I*), initial brine saturated (S_w -*I*), irreducible water saturated (S_{wir}), residual oil saturated (S_{or}), after supercritical CO₂ injected at reservoir condition (S_{CO2}), cleaned-dry after CO₂ injection (*Dry-F*), and brine re-saturated after CO₂ injection (S_w -*F*). In addition, one sample from each group (ST and RE) of rock-mechanics tests was included in the geophysical tests (Table 4).

Simulated formation brine (HTF brine) and South Arne crude oil were used as water and oil phase respectively for all samples. Due to low permeability (<0.1 mD), SE samples were removed from the process after the S_w -I condition. Among the three groups, Group-1 samples were kept at brine saturated condition

 $(S_w$ -I) and used for reference NMR signal in the wettability study. CO₂ was injected into Group-2 samples at S_{or} condition and into Group-3 samples at S_{wir} condition. NMR T_2 relaxation time was measured in all CO₂ injected samples before they were cleaned for salt and dried. Porosity and permeability were measured at this final condition to quantify the effect of CO₂ injection on these properties. After sonic velocity measurement in dry condition, these samples were re-saturated with brine. Sonic velocity and electrical resistivity measurement were measured at this condition (S_w -F) and compared with S_w -I condition.

Sonic velocity and electrical resistivity measurements

Stress in the horizontal direction in a reservoir is a fraction of the vertical stress. Therefore, a uniaxial confined compression is the most suitable condition in order to mimic the actual reservoir stress on rock. The relationship between radial stress (σ_r) and axial stress (σ_a) can be expressed by means of Poisson's ratio (v) (Teeuw, 1971):

$$\frac{\sigma_r}{\sigma_a} = \left(\frac{v}{1-v}\right)^{\frac{1}{n}}.$$
(16)

For linear elastic media, n = 1 (Teeuw, 1971). For South Arne SA-1 and Rigs-1 Poisson's ratio was calculated from sonic velocity measured under uniaxial unconfined compression:



(17)

Figure 7: Poisson's ratio of South Arne field as calculated from sonic velocity measured under uniaxial unconfined condition (16). Dashed line indicates the value use in this project.

where, V_p is the compressional wave velocity and V_s is the shear wave velocity. Calculated Poisson's ratio ranges mostly between 0.20 and 0.30 (Fig. 7). However, in order for simplicity it was decided to apply a general $v \approx 0.25$. For this v:

$$\sigma_r = 0.33\sigma_a. \tag{18}$$

A generalized radial to axial stress ratio also ease establishing a better control over the radial stress, as the pump for controlling radial stress was semiautomatic. The pump requires adjusting manually with the change in stress level. By using a constant stress ratio for all samples it is possible to control the pump based on experience so that the desired ratio between radial and axial stress can be maintained continuously.



Figure 8: Experimental setup for sonic velocity and resistivity measurements.

Measurements were performed by placing the sample between the two pistons of a loading frame and inside a triaxial cell (Fig. 8). Maximally 4 MPa axial stress was applied in loading/reloading cycles while pore pressure was kept atmospheric. Each test contains four cycles: (i) loading to 3 MPa axial stress, (ii) unloading to 1 MPa axial stress, (iii) Reloading to 4MPa axial stress, and (iv) unloading to atmospheric condition. In all cycles the radial stress was controlled to satisfy equation (18). Reservoir rocks are subjected to both vertical and lateral stress as well as high pore pressure (overpressure) in the North Sea chalk reservoirs. To simulate reservoir stress in a laboratory experiment requires the application of the differential stress (total stress minus pore pressure) instead of the actual stresses (Teeuw, 1971). The effective vertical stress in South Arne is between 10 MPa and 20 MPa. However, the velocity variation in North Sea chalk samples was found to be less than 3% between 4 and 11 MPa (Borre and Fabricius, 2001). Therefore, we used 4 MPa as maximum stress in order to avoid damaging the sample which was used repetitively (Table 4).

Compressional wave velocity V_p and shear wave velocity V_s were measured by recording the travel time of a transmitted ultrasonic wave at 200 KHz through a sample of known length.

Experimental setup for electrical resistivity measurement is shown in Fig. 8. Electrical resistance of the samples was measured at 23°C simultaneously with velocity, from a variable resistor connected in series with the sample in a 1 kHz AC circuit of 1 volt power supply. As current flows through the sample and the variable resistor is equal $(i_1=i_2)$:

$$\frac{V_{\text{sample}}}{R_{\text{sample}}} = \frac{V_{\text{supply}} - V_{\text{sample}}}{R_{\text{variable resistor}}} \,.$$
(19)

The variable resistor was adjusted by looking at the oscilloscope, so that the voltage drop across the sample becomes half of the supply voltage. At this condition the resistivity set in the variable resistor gives the resistivity of the sample:

$$R_{\text{sample}} = R_{\text{variable resistor}} \,. \tag{20}$$

Low frequency and supply voltage was selected so that the phase angle shift remains close to zero.

Data were collected at 1 MPa stress intervals from 1 to 4 MPa, for both sonic velocity and electrical resistivity measurement.

NMR T₂ relaxation time measurements

Transverse (spin-spin) relaxation time, T_2 was measured by standard CPMG (Carr-Purcell-Meiboom-Gill) pulse sequence by using a resonance instruments Maran spectrometer at two steps with different parameter setup due to the use of two different labs.

1.) At initial brine saturated condition taking one representative sample from each of the studied formations of both wells (Table 4, group 1).

2.) All CO_2 injected samples for petrophysical analysis (Table 4). Measurement was also repeated in the samples measured at step 1 with the setup of step 2.

Setup for step 1 measurements:

Experiments were made at 35 °C with Larmor frequency of 2.12 MHz and low magnetic field, B_0 . Number of echoes collected was 8000 with 300 scan. Echo spacing (τ) which is the time between successive rephrasing (P180) pulses of 200 microseconds was chosen.

Setup for step 2 measurements:

Experiments were made at 35°C with Larmor frequency of 1.83 MHz and magnetic field, B_0 , as 0.044T. Number of echoes collected was 8192 with 128 scan. Echo spacing (τ) which is the time between successive rephrasing (P180) pulses of 200 microseconds was chosen.

The relaxation time (T_2) distribution was obtained with the DXP programmed from Resonance Instruments. With the short echo spacing and low applied magnetic field (B_0) in both steps, the T_2 relaxation is dominated by surface relaxation (Kleinberg et al., 1993) and the contribution from diffusion in T_2 relaxation time can be neglected (Hürlimann, 1998).

Final sample characterization

After finishing the designed geophysical tests the samples were cleaned for brine and dried. These samples were then characterized by measuring carbonate content, specific surface of both crushed sample and insoluble residue and by Backscatter Electron microscopy of thin sections.

Rock-mechanics test design

The triaxial tests were carried out in a conventional high-pressure Hoek cell (Fig. 9). Confining pressure was supplied by a high-pressure actuator, and the actuator pressure and volume change were recorded. The axial deformation was measured by external LVDTs (Linear Voltage Deformation Transducer) and the load frame positioning system. The axial deformations measured by the load frame were corrected for the systems self-deflection (VIS – Virtual Infinite Stiffness correction) and are mainly used for checking the deformations measured by the

LVDTs. Local axial and radial deformations were measured by 4-6 strain gauges glued directly onto the test sample. A schematic representation of the test setup is shown in Fig. 9. Volumetric strain was calculated from the expelled fluid on a precision balance. Measures were taken to minimize evaporation from the balance (sealed container, oil layer covering the water surface).



Figure 9: Schematic of setup for rock-mechanics test. Deformation was measured by both Linear Voltage Deformation Transducer (LVDT) and Strain Gauges (SG)

Ten test samples were prepared from well SA-1 Tor Formation chalk, and ten test samples were prepared from the Rigs-1 Ekofisk Formation chalk (Table 5). All samples were initially saturated to irreducible water saturated condition. Afterwards, for each formation, 5 samples were first waterflooded and then CO_2 injected at reservoir conditions before rock-mechanics testing. The remaining 5 samples were rock-mechanics tested immediately after waterflooding, providing a reference when evaluating the mechanical effect of CO_2 injection after waterflooding.

Each test set comprises 5 test types providing onset pore collapse stresses, shear failure strength and elastic moduli (Table 5, Fig. 10). In addition, some test types also quantify the time dependent properties (Table 5).

Test type 1

Three main test phases were performed: (1-A) Hydrostatic loading to onset pore collapse; (1-B) Loading to onset pore collapse with stress ratio 0.6; (1-C) Compression phase: loading to failure with 4 MPa confining pressure (Fig. 10). Two creep phases were performed during the hydrostatic phase to test whether

CO_2 affects the time dependent parameters and as a support for pore collapse determination.

Table 5: Stress path for rock-mechanics tests. Each of the five test types contains one reference sample and one CO_2 injected sample. HS=hydrostatic test phase; SR=stress-ratio test phase; UA=uniaxial test phase; (SG)=uniaxial condition controlled by strain gauges.

			Yi	eld determinat	ion	Compression Creep				
Test set	Test type	Sample		\rightarrow –	\rightarrow –	\rightarrow (MPa)	Stress at creep (MPa)			
	1	RE-14	(A) HS	(B) SR 0.6		(C) 4	20			
e	2	RE-08B	(A) SR 0.27			None ¹⁾	20, 70 ¹⁾			
enc	3	RE-09B	(A) SR 0.30			(B) 1	20, 105, 131, 155			
efer	4	RE-28A1	(A) SR 0.35	(B) SR 0.35	(C) SR 0.35	(D) 8	None			
Ř	5	RE-31	(A) SR 0.8	(B) SR 0.5		(C) 25	None			
	1	RE-26B1	(A) HS	(B) SR 0.6		(C) 4	20			
dec	2	RE-06A	(A) UA (SG)			(B) 1 ²⁾	20, 72, 103			
00	3	RE-12B	(A) SR 0.30			(B) 1	20, 110, 130			
$0_2 f$	4	RE-29	(A) SR 0.35	(B) SR 0.35	(C) SR 0.35	(D) 8	None			
ŏ	5	RE-10A	(A) SR 0.8	(B) SR 0.5		(C) 25	None			
	1	ST-01B	(A) HS	(B)SR 0.6		(C) 4	10, 20			
e	2	ST-12B	(A) UA (SG)			(B) 4	10, 20, 30, 76, 98			
enc	3	ST-20	(A) UA (SG)			(B) 1	10, 20, 95, 115			
efei	4	ST-17B	(A) SR 0.35	(B) SR 0.35	(C) SR 0.35	(D) 8	10			
Ř	5	ST-25B	(A) SR 0.8	(B) SR 0.5		(C) 25	None			
	1	ST-03B	(A) HS	(B) SR 0.6		(C) 4	10, 20			
dec	2	ST-07	(A) SR 0.33			(B) 4	10, 20, 30, 62, 73			
00	3	ST-16B	(A) SR 0.31			(B) 1	10, 20, 79, 95			
0^{2}	4	ST-13B	(A) SR 0.35	(B) SR 0.35	(C) SR 0.35	(D) 8	None			
ŏ	5	ST-04B	(A) SR 0.8	(B) SR 0.5	_	(C) 25	None			

1.) Sample failed before compression phase

2.) Confining pressure altered to 1 MPa to provide a better determination of failure line

Test type 2

Two main test phases were performed: (2-A) Uniaxial loading to onset pore collapse (uniaxial condition controlled by radial strain gauges); (2-B) Compression phase: loading to failure with 4 MPa confining pressure (Fig. 10). 1-3 creep phases were performed during the uniaxial compaction phase, one creep phase at uniaxial pore collapse and one creep phase after loading to virgin curve.



Figure 10: Stress paths for rock-mechanics tests plotted in a p'-q plan with onset yield surface and shear failure line. Five types of test are indicated by colors. The arrows indicate the stress path the test sample experienced during the test. Details of individual tests are presented in table 5.

Test type 3

Two main test phases were performed: (3-A) Uniaxial loading to onset pore collapse (uniaxial condition controlled by radial strain gauges); (3-B) Compression phase: loading to failure with 1 MPa confining pressure (Fig. 10). 1-2 creep phases were performed during the uniaxial compaction phase, one creep phase at uniaxial pore collapse and 1-2 creep phases after loading to virgin curve.

Test type 4

Four main test phases were performed: (4-A), (4-B) and (4-C) are three successive stress ratio loadings to onset pore collapse; all with stress ratio = 0.35; and one compression phase (4-D): loading to failure with 8 MPa confining pressure (Fig. 10). No creep phases were performed except in sample ST-17B.

Test type 5

Three main test phases were performed: (5-A) loading to onset pore collapse with stress ratio 0.8; (5-B) Loading to onset pore collapse with stress ratio 0.5; (5-C) Compression phase: loading to failure with 25 MPa confining pressure (Fig. 10). No creep phases were performed.

Information from the different mechanical test types are combined by stress states at failure or for the pore collapse (yield) in a p'-q plot.

Elastic parameters

The bulk modulus (*K*) was calculated based on expelled fluid (volumetric strain) and mean effective stress (p') produced from uniaxial loading. On the p'-volumetric strain curve *K* is determined as the tangent at half the p'_{vi} value.

The modulus of elasticity was determined on the basis of LVDT measurements (E^*) and strain gauge measurements (E) during the compression test phase.

Poisson's ratio (v) was determined from radial and axial strain gauge measurements at the onset of the compression phase.

The modulus of uniaxial compaction was calculated from LVDT (M^*) and strain gauge (M) measurements produced from uniaxial loading. On the σ_a -vertical strain curve M is determined as the tangent at half the $\sigma_{a,vi}$ value.

The coefficient of earth pressure at rest, K_0 is determined as the lowest σ_3/σ_1 value measured during uniaxial compaction. K_0 is also determined in cases where compaction is controlled by fixed stress ratio if the compaction development is close to the uniaxial development.

RESULTS

Sample characterization

Rigs-1 and SA-1 Ekofisk Formation samples contain up to 25% and 20% noncarbonate fraction respectively. By contrast Tor Formation samples from Rigs-1 and SA-1 contains less than 5% and 2% non-carbonate respectively (Table 6). Quartz is the dominant non-carbonate mineral in both wells. Clay minerals in the Rigs-1 samples are predominantly kaolinite whereas in SA-1 smectite dominates. Distribution of non-carbonates is recognizable in BSE images at large magnification and pores are found to be partially filled with clay in samples from Ekofisk Formation of both wells (Fig. 2a). The Ekofisk Formation also contains considerable amounts of preserved large hollow microfossils and has carbonate wackstone or mudstone texture. The Tor Formation samples by contrast typically contain a homogeneous matrix of calcareous nannofossil debris and have carbonate wackstone or mudstone texture.

Sample	Diameter	Length	Grain	Porosity		Gas		Carbo	nate	Sp. su	rface	Sp. surface		
	(mm)	(mm)	density	(V/	√)	Perme	ability	cont	ent	Cha	ılk	IR (m ² (m)		
			(g/m [°])	Defere	Aftor	(mL)) After	(%) After	(m²/	g) After	(m²/	(g)	
				веюге	Aller	Delore	Aller	Delote	Aller	Delote	Aitei	Delote	Aller	
RE-22A	37.3	30.9	2.71	0.33	-	1.1	-	88	-	3.8	-	12	-	
RT-03	36.8	31.3	2.71	0.42	-	4.8	-	97	-	1.9	-	10	-	
SE-03	37.4	45.4	2.71	0.18	-	0.04	-	78	-	6.4	-	35	-	
ST-24A	37.4	43.7	2.72	0.26	-	0.8		98	-	1.7	-	20	-	
RE-24	37.3	38.9	2.72	0.36	0.37	0.9	0.8	88	90	3.6	3.6	12	16	
RT-01	37.0	29.7	2.71	0.39	0.41	4.4	8.2	95	97	2.1	1.6	9	13	
SE-05A	37.5	30.7	2.72	0.26	-	0.1	-	81	-	5.2	-	23	-	
ST-24B	37.4	34.0	2.72	0.25	0.26	0.8	0.9	98	97	1.7	1.0	20	26	
RE-23A	37.2	26.5	2.72	0.32	0.33	0.6	1.3	88	88	3.5	3.2	12	14	
RT-02	37.1	24.8	2.72	0.35	0.36	2.3	8.2	95	97	2.1	1.3	9	11	
SE-02	37.5	20.8	2.71	0.16	-	0.02	-	78	-	6.4	-	35	-	
ST-23A	37.5	27.0	2.72	0.26	0.28	0.8	1.9	99	97	1.7	1.7	20	25	
RE-26B2	37.5	44.3	2.71	0.29	-	0.5	-	90	-	2.9	-	11	-	
ST-26	37.5	72.7	2.71	0.28	0.29	1.1	0.4	99	97	1.6	1.5	20	26	
ST-08A	36.8	30.0	2.71	0.32	0.35	3.2	4.7	100	94	1.7	1.2	19	9	
ST-08B	37.2	40.5	2.71	0.31	0.32	2.6	2.2	100	95	1.6	1.5	19	10	
RE-14	37.4	74.8	2.701	0.31	-	0.5	-	78	-	4.7	-	8	-	
RE-08B	37.4	74.9	2.698	0.32	-	0.5	-	76	-	3.9	-	10	-	
RE-09B	37.4	74.7	2.694	0.30	-	0.5	-	79	-	3.6	-	10	-	
RE-28A1	36.9	74.7	2.704	0.29	-	0.8	-	90	-	2.9	-	11	-	
RE-31	37.3	69.4	2.707	0.29	-	0.6	-	89	-	3.2	-	11	-	
RE-26B1	37.5	72.8	2.71	0.31	0.32	0.5		90	-	2.9	-	11	-	
RE-06A	37.5	75.3	2.70	0.32	0.33	0.5	-	76	-	3.9	-	10	-	
RE-12B	37.6	75.2	2.69	0.30	0.34	0.5	-	79	-	3.6	-	10	-	
RE-29	37.4	75.1	2.71	0.28	0.29	0.4	-	89	-	3.2	-	11	-	
RE-10A	37.5	75.2	2.70	0.31	0.31	0.5	-	79	-	3.6	-	10	-	
ST-01B	38.2	74.7	2.71	0.30	-	1.8	-	99	-	1.7	-	15	-	
ST-12B	37.0	75.0	2.714	0.31	-	1.6	-	99	-	1.9	-	14	-	
ST-20	37.4	75.2	2.712	0.28	-	1.6	-	98	-	2.1	-	31	-	
ST-17B	37.3	75.2	2.713	0.29	-	1.1	-	99	-	1.8	-	13	-	
ST-25B	37.4	75.1	2.713	0.28	-	1.0	-	99	-	1.6	-	20	-	
ST-03B	37.5	75.5	2.71	0.29	0.32	1.7		99		1.7	-	15		
ST-07	37.1	74.9	2.72	0.31	0.29	2.7	-	100	-	1.6	-	19	-	
ST-16B	37.5	75.2	2.72	0.28	0.29	1.2	-	99	-	1.8	-	13	-	
ST-13B	37.2	75.2	2.71	0.31	0.28	2.2	-	100	-	1.9	-	14	-	
ST-04B	37.5	74.9	2.71	0.28	0.31	1.3	-	99	-	1.6	-	15	-	

Table 6: Physical properties of the studied samples before and after CO₂ injection.

Saturation

Brine saturation achieved at different stages of the geophysical and rockmechanics tests is shown in Table 7. It is apparent from the brine saturation at S_{CO2} condition that supercritical CO₂ injection allows to extract more oil than waterflooding.

	Geop	ohysica	l analy	rsis			Rock-mechanics analysis								
Sample	S _w -I	S _{wir}	Sor	S_{CO2}	S_w - F		Sample	S _w -I	S _{wir}	Sor	S_{CO2}	S _w -F			
RE-22A	0.98	-	-	-	-		RE-08B	-	0.46	0.69	-	-			
RT-03	0.96	-	-	-	-		RE-09B	-	0.45	0.71	-	-			
SE-03	0.98	-	-	-	-		RE-14	-	0.45	0.70	-	-			
ST-24A	0.98	-	-	-	-		RE-28A1	-	0.30	0.69	-	-			
RE-24	0.99	0.32	0.68	0.94	0.97	÷	RE-31	-	0.31	0.64	-	-			
RT-01	0.99	0.20	0.80	0.86	0.95	-	RE-06A	-	0.35	_	0.93	_			
SE-05A	0.97	-	-	-	-		RE-10A	-	0.44	-	0.95	-			
ST-24B	0.98	0.30	0.70	0.82	0.93		RE-12B	-	0.45	-	0.96	-			
RE-23A	0.98	0.28	-	0.69	0.90	÷	RE-26B1	-	0.30	-	0.96	-			
RT-02	0.98	0.17	-	0.83	0.96		RE-29	-	0.27	-	0.89	-			
SE-02	0.93	-	-	-	-		ST-01B	-	0.32	0.70	-	-			
ST-23A	0.94	0.18	-	0.51	0.89		ST-12B	-	0.57	0.57	-	-			
							ST-17B	-	0.25	0.57	-	-			
RE-26B2	0.99	0.28	-	0.93	-		ST-20	-	0.34	0.58	-	-			
						-	ST-25B	-	0.38	0.63	-	-			
ST-26	1.00	-	-	0.84	0.93	÷	ST-03B		0.15		0.92				
						-	ST-04B	-	0.15	-	0.93	_			
ST-08A	1.00	-	-	0.98	0.98		ST-07	-	0.14	-	0.94	-			
ST-08B	1.00	-	-	0.98	0.98		ST-13B	-	0.14	-	0.91	-			
					-		ST-16B	-	0.15	-	0.95	-			

Table 7: Brine saturation achieved at different stages of the geophysical and rock-mechanics tests.

Petrophysical properties

Average porosity of Rigs-1 Ekofisk, Rigs-1 Tor, SA-1 Ekofisk and SA-1 Tor is 30%, 35%, 20% and 30% respectively (Fig. 5, Table 6). Relation between porosity and permeability is influenced by the non carbonate content as specific surface of the bulk is mostly determined by it. Due to high specific surface of Ekofisk Formation chalk, permeability is lower than Tor Formation chalk (Fig. 11a). Kozeny permeability (k_k) calculated from the specific surface ($k_k = c\phi^3/S^2$) is less than the measured permeability. This is expected, as some fractures may open during the core retrieval process which may increase the permeability measured in core plugs. In addition, during crushing of chalk in preparation for the specific surface measurement (BET method) some grain contacts are exposed, which will be added to the measured specific surface and reduce Kozeny permeability. However, the consistent increasing trend indicates homogeneity of the tested samples (Fig. 11b).



Figure 11: (a) Variation of porosity-permeability relationship according to the specific surface (BET method). Liquid (equivalent to Klinkenberg corrected) permeability was calculated from air permeability by using equation (13). (b) Relationship between liquid permeability and permeability calculated from porosity and specific surface (by BET method) by using Kozeny's equation. Unfilled markers represent Ekofisk Formation and filled markers represent Tor Formation. Black markers indicate before CO_2 injection and grey markers indicate after CO_2 injection.

Due to supercritical CO_2 injection an increase in porosity of 1% to 2% was observed in Ekofisk Formation samples, while the increase in Tor Formation samples is 2% to 3% (Fig. 12a). In most cases an increase in permeability was also observed (Fig. 12b, c).



Figure 12: Change in physical properties due to CO₂ injection, (a) porosity, (b) gas permeability, (c) equivalent liquid permeability calculated from porosity and specific surface by Kozeny's equation. Filled data points represent Tor Formation and unfilled data points represent Ekofisk Formation.

Table 8: Compressional and shear wave velocity as well as electrical resistivity at different experimental conditions. Data presented here were taken at 3 MPa axial stress and 1 MPa confining stress because it is the maximum stress level in a reloading cycle (minimum bedding effect under our experimental condition). Pore pressure was atmospheric for all tests.

	Compressional wave velocity (km/s)							Shear wave velocity (km/s)							Resistivity (ohm-m)				
Sample	Dry-I	S _w -I	S _{wir}	Sor	S _{CO2}	Dry-F	S _w -F	Dry-I	S _w -I	S _{wir}	Sor	S _{CO2}	Dry-F	S _w -F	S _w -I	S _{wir}	Sor	S _{CO2}	S _w -F
RE-22A	3.20	3.17	-	-	-	-	-	1.95	1.60	-	-	-	-	-	0.9	-	-	-	-
RT-03	1.98	2.43	-	-	-	-	-	1.26	1.48	-	-	-	-	-	0.4	-	-	-	-
SE-03	2.80	3.32	-	-	-	-	-	1.89	1.77	-	-	-	-	-	4.6	-	-	-	-
ST-24A	3.68	3.67	-	-	-	-	-	2.23	1.97	-	-	-	-	-	1.7	-	-	-	-
RE-24	2.80	2.86	2.75	2.82	2.74	2.59	2.78	1.84	1.43	1.40	1.47	1.48	1.77	1.35	0.7	7.7	3.2	0.8	1.0
RT-01	2.70	2.81	2.60	2.79	2.70	2.41	2.73	1.68	1.65	1.58	1.54	1.59	1.57	1.65	0.6	17.6	1.4	0.7	0.7
SE-05A	3.10	3.01	-	-	-	-	-	2.07	1.63	-	-	-	-	-	1.5	-	-	-	-
ST-24B	4.11	4.12	3.91	3.99	3.83	3.75	3.87	2.42	2.20	2.21	2.22	2.02	2.39	2.26	1.0	14.9	1.3	1.5	1.6
RE-23A	3.29	3.28	3.07	-	3.05	2.97	3.09	1.97	1.64	1.68	-	1.54	1.81	1.68	0.5	10.5	-	1.3	1.0
RT-02	3.37	3.40	3.19	-	3.18	3.09	3.29	2.02	1.70	1.66	-	1.64	1.75	1.66	0.7	16.2	-	0.9	0.9
SE-02	2.99	3.39	-	-	-	-	-	1.99	1.54	-	-	-	-	-	3.9	-	-	-	-
ST-23A	3.59	3.82	3.61	-	3.47	3.22	3.58	2.31	1.90	1.85	-	1.70	1.90	1.86	1.1	22.2	-	2.1	1.8
RE-26B2	-	3.30	3.26	-	3.24	-	-	-	1.77	1.75	-	1.76	-	-	2.2	12.5	-	1.1	-
ST-26	3.55	3.54	-	-	3.41	3.30	3.46	2.14	1.84		-	1.76	2.02	1.79	-	-	-	-	1.3
ST-08A	3.04	3.13	-	-	2.99	2.51	2.97	1.91	1.66	-	-	1.52	1.97	1.70	0.8	-		0.9	0.9
ST-08B	2.84	3.02	-	-	2.86	2.55	2.90	1.80	1.48	-	-	1.43	1.71	1.45	-	-	-	-	-
RE-14A	-	3.28	-	-	-	-	-	-	1.72	-	-	-	-	-	1.6	-	-	-	-
RE-08B	3.52	3.28	-	-	-	-	-	2.06	1.59	-	-	-	-	-	1.6	-	-	-	-
RE-09B	3.49	3.39	-	-	-	-	-	2.05	1.85	-	-	-	-	-	1.7	-	-	-	-
RE-28A1	-	3.30	-	-	-	-	-	-	1.77	-	-	-	-	-	2.4	-	-	-	-
RE-31	-	3.29	-	-	-	-	-	-	1.65	-	-	-	-	-	2.4	-	-	-	-
RE-26B1	-	3.21	3.11	-	-	-	-	-	1.66	1.64	-	-	-	-	2.1	11.4	-	-	-
RE-06A	3.63	3.10	3.16	-	-	-	-	2.16	1.57	1.67	-	-	-	-	1.6	6.8	-	-	-
RE-12B	3.85	3.43	3.35	-	-	-	-	2.29	1.85	1.73	-	-	-	-	1.7	5.5	-	-	-
RE-29	3.63	3.33	3.23	-	-	-	-	2.20	1.74	1.79	-	-	-	-	2.6	13.1	-	-	-
RE-10A	3.77	3.34	3.30	-	-	-	-	2.34	1.80	1.82	-	-	-	-	1.6	5.3	-	-	-
ST-03B	3.35	-	-	-	-	-	-	2.02	-	-	-	-	-	-	-	-	-	-	-
ST-07	3.13	-	-	-	-	-	-	1.93	-	-	-	-	-	-	-	-	-	-	-
ST-16B	3.46	-	-	-	-	-	-	2.11	-	-	-	-	-	-	-	-	-	-	-
ST-13B	3.12	-	-	-	-	-	-	1.94	-	-	-	-	-	-	-	-	-	-	-
ST-04B	3.76	-	-	-	-	-	-	2.20	-	-	-	-	-	-	-	-	-	-	-

N.B. No Sonic velocity measurement were made in ST reference samples for rock-mechanics tests

Geophysical properties

Compressional wave velocity, shear wave velocity and electrical resistivity measured at different stages of the experimental procedure are presented in Table 8 and Fig. 13a. Shear wave velocity is significantly lower in saturated samples as compared to the dry samples. There is a minor increase in compressional wave velocity in the saturated Tor Formation samples and notable increase in SA-1 Ekofisk Formation samples. Unexpectedly a decrease is observed in compressional wave velocity of the Rigs-1 Ekofisk samples. There is a possibility of water weakening in these samples due to high content of kaolinite. The effect of brine saturation is better understood from the V_p / V_s plots (Fig. 13b). In contrast, no marked effect of replacing brine with hydrocarbon was observed. Only SA-1 Tor Formation indicates an increase in V_p/V_s after CO₂ injection.



Figure 13: (a) Measured velocities at different stages of experimental procedure as defined in Table 4 and Table 5. Filled markers represent compressional wave velocity and open markers indicate shear wave velocity. (b) Ratio between compressional and shear wave velocity. Experimental stages are indicated by colors in the legend.

In order to estimate the effect of CO_2 injection on the stiffness of the chalk frame, Biot's coefficient was calculated from V_p and V_s and density (equations (2), (3) and (4)) measured at different stages of the experimental procedure (Fig. 14). Flooding with supercritical CO_2 leads to a decrease in frame stiffness of Tor Formation chalk as indicated from the decrease in compressional modulus (Fig. 15a) and increase in Biot's coefficient (Fig. 15b) Biot's coefficient increases most for samples with low Biot's coefficient (from below 0.8 to above 0.8) (Fig. 15b). For samples with high Biot's coefficient of both Ekofisk Formation and Tor Formation this effect is relatively small.



Figure 14: Biot's coefficient calculated from velocity and bulk density at different stages of the experimental procedure as defined in Table 4 and Table 5. Experimental stages are indicated by colors in the legend.



Figure 15: Effect of CO_2 injection on stiffness (a) compressional modulus calculated from sonic velocity and bulk density, (b) Biot's coefficient and (c) degree of cementation as indicated by the change of isoframe values. Black data points are immediately after CO_2 injection and grey data points are after re-saturation with formation brine. Circle, diamond, triangle and rectangle indicate Rigs-1 Ekofisk, Rigs-1 Tor, SA-1 Ekofisk and SA-1 Tor Formation respectively.

In general, Archie's cementation factor shows a decrease after CO_2 injection (Fig. 16a). The factor indicates the ease of electrical current flow through the sample. After CO_2 injection, the Tor Formation samples fall below the cementation factor trend of North Sea chalk as defined by Olsen et al. (2008a) and follows the trend of some of the Ekofisk Formation chalk which is more likely to be fractured (Fig. 16b). This may be due to the opening of micro-fractures as the samples has gone through several test phases where vacuum was applied, e.g. saturation, CO_2 injection where pore pressure and confining stress were applied, as well as velocity and resistivity measurements where axial stress and confining stress were applied.



Figure 16: (a) Effect of CO2 injection on the cementation factor as calculated from electrical resistivity by using equations (5) and (6). (b) Relationship between cementation factor and effective specific surface of the bulk (S= $\phi \times S\phi$) (12). Circle, diamond, triangle and rectangle indicate Rigs-1 Ekofisk, Rigs-1 Tor, SA-1 Ekofisk and SA-1 Tor Formation respectively. Black data points represent initial brine saturated condition and grey data points are after resaturation with formation brine. Note: Which brine was used during re-saturation after CO2 injection and cleaning was not noted. However, the brine was one of the brines for which resistivity was 0.22 Ω m, 0.13 Ω m or 0.077 Ω m. 0.13 Ω m was used in this calculation as 0.22 Ω m and 0.077 Ω m gives value of cementation factor below 1.5 and above 2.2 respectively, which is unrealistic for chalk (Olsen et al., 2008a).

Normalized T_2 peaks do not move in time scale after CO₂ injection irrespective to the state at which CO₂ was injected (Fig. 17b). It indicates that there is no significant effect of CO₂ injection on the wettability of the calcite surface.



CO₂ injected at residual oil saturated condition

Figure 17: NMR transverse relaxation time (T_2) distribution normalized to helium porosity at (a) initial brine saturated condition with higher scanning interval, (b) initial brine saturated condition along with after CO₂ injection at irreducible water saturated condition and residual water saturated condition with lower scanning interval. Left peaks in the figures (a) represent clay bound and right peak is for calcite bound water. In figures (b) clay bound peaks were not recorded due the use of different scanning parameters in two different laboratories. For reference, same initial brine saturated (S_w -I) samples were used in both sets of experiments. The peaks in (b) does not show any significant movement along the time scale which indicates that the calcite surface does not change wettability due to CO₂ injection.

Table 9: Failure and elastic parameters derived from rock-mechanics tests. $\sigma_{a,yi}$ and $\sigma_{r,yi}$ are the axial and radial stresses at onset pore collapse. $\sigma_{a,f}$ and $\sigma_{r,f}$ are the axial and radial effective stresses at shear failure and $\sigma_{a,res}$ and $\sigma_{r,res}$ are the corresponding set of residual stresses, respectively, during the shear failure had occurred. Elastic parameters marked by an * indicates measurement based on LVDT reading and without an * indicates measurement based on strain gauges. v is Poisson's ratio, K is bulk modulus, E is Young's modulus and K_0 is coefficient of earth pressure at rest.

	-	Pore collapse stress Shear						Residual Elastic parameter							
		-			failur	е	stren	gth							
Test set	Sample	<i>σ_{a, yi}</i> MPa	<i>σ_{r, yi}</i> MPa	Stress path	<i>σ_{a,f}</i> MPa	<i>o_{r,f}</i> MPa	$\sigma_{\!\!a,res}$ MPa	<i>σ_{r, res}</i> MPa	V	<i>K</i> GPa	E* GPa	<i>E</i> GPa	M* GPa	M GPa	Ko
	RE-14 RE-14	55 57	55 34.2	HS SR 0.6	41.8	4	24.2	4	0.33	6.0	6.6	8.7	-	-	-
rence	RE-08B RE-09B RE-28A1	63 85 62	17 25.5 21.7	SR 0.27 SR 0.30 SR 0.35	^a 31.5	a 1	^a 8.1	a 1	^a 0.21	3.6 5.8	^a 1.9	^a 2.2	5.2 ^d 8.0 ^d	17.8 [°] 18.5°	¹ 0.27 ^d 10.26
Refe	RE-28A1 RE-28A1 RE-31	83 94 74	29.1 32.8	SR 0.35 SR 0.35 SR 0.8	59.5	8	37.5	8	0.26	4.3	8.3	10.4	7.8 ^f	15.4 ^f	0.35 ^f
	RE-31	74 74	37 37	SR 0.5	88.5	25	87.6	25	0.23	5.5	11.6	15.5	-	-	-
	RE-26B1 RE-26B1	58 58	58 34.7	HS SR 0.6	49.8	4	25.4	4	0.18	6.1	7.4	10.5	-	-	-
CO ₂ injected	RE-06A 50 RE-12B 105 RE-29 55	13 31 19.3	^b UA SR 0.30 SR 0.35	26.3 31	1 1	6.5 10.1	1 1	e	3.0 5.0	2.7 2.9	e e	3.7 6.9 ^d	e 13.8 ^c	0.2 10.3 ^d	
	RE-29 RE-29	69 86	24.2 30.1	SR 0.35 SR 0.35	53.9	8	35	8	0.3	4.0	8.4	11.6	7.1 ^f	15.6 ^f	0.35 ^f
	RE-10A RE-10A	63 73	50.4 36.4	SR 0.8 SR 0.5	106	25	-	-	0.23	6.4	12.2	17.1	-	-	-
	ST-01B 59.9° ST-01B 68	[°] 59.9 [°] 40.8	HS SR 0.6	48.3	4	29.8	4	0.25	9.0	8.1	11.6	-	-	-	
rence	ST-12B ST-20 ST-17B	60 75 56 4 ⁰	21.7 34.9 19.8°	^b UA ^b UA SR 0.35	40.3 21.7	4 1.1	23 10.7	4 1.1	0.21 0.29	4.6 6.3	4.0 2.4	4.6 e	7.2 10.1 ⁹	11.7 17.0 ⁹	0.32 0.35
Refe	ST-17B ST-17B	70 85	24.5 29.7	SR 0.35 SR 0.35	56.7	8	38.7	8	d	5.3	7.1	6.5	8.8	18.0	0.35 ^f
	ST-25B ST-25B	75 80	40	SR 0.8 SR 0.5	80	25		-	0.25	7.0	12.2	15.0	-	-	-
	ST-03B ST-03B	58.3 [°] 65	[°] 58.2 [°] 39	HS SR 0.6	47.4	4	23.2	4	0.23	7.9	8.5	11.8	-	-	-
njected	ST-07 ST-16B ST-13B	60 70 50	19.5 21.7 17.5	SR 0.30 SR 0.31 SR 0.35	35.3 26.7	4 1	21.4 10.5	4 1	^е 0.24	3.8 3.8	6.2 3.1	е 3.5	5.8 ^h 5.5 ⁱ	13.6 ^r 12.3 ⁱ	0.33 ^h 0.25
CO ₂ in	ST-13B 55 ST-13B 55 ST-13B 59	19.2 20.6	SR 0.35 SR 0.35	44	8	34	8	0.29	3.9	8.1	10.5	6.5 ^f	15.6 ^f	0.35 ^f	
	ST-04B	80	40	SR 0.8 SR 0.5	80	25	-	-	0.28	6.9	13.7	16.5	-	-	-

^a No compression phase due to early failure of test sample. ^b Uniaxial condition maintained on basis of strain gauges. ^c Minimum value, onset of pore collapse not reached. ^d Radial strain gauges failure. ^e Axial strain gauges failure. ^f Stress ratio maintained at approximate K_0 . ^g K^* is not determined in stress-strain region with K_0 =0.35, but rather K_0 =0.48 due to increasing K_0 when controlling the uniaxial boundary condition in the compaction phase. ^h Uniaxial boundary conditions not accomplished by control of strain gauges. The test is performed with a fixed stress ratio of 0.33. ⁱ Uniaxial boundary conditions accomplished by control of strain gauges to approximately 30 MPa axial stress. The rest of the test is performed with a fixed stress ratio of 0.31.





Figure 18: The p'-q plots of reference (black) and CO₂ flooded set of samples (grey) reveal the effect of injection of supercritical CO₂ on the mechanical strength of (a) Ekofisk Formation and (b) Tor Formation chalk. Circles indicate compaction strength and stars indicate shear strength. Pore collapse stress for second or third cycle with same stress ratio is indicated by squares with a cross. The dotted lines indicate the changes in effective stress due to a change in Biot's coefficient, α . The effective stress was calculated based on normal overburden condition (without overpressure) and considering a constant bulk density of the overburden sediment as 2.2 g/m³ and constant fluid density of 1.0 g/cm³.



Figure 19: Comparison of reference samples and CO_2 injected samples: (a) uniaxial pore collapse stress and (b) compressional modulus calculated from strain gauge measurements during compaction under uniaxial condition. Radial to axial stress ratio was maintained approximately at 0.3 for uniaxial condition, depending on the Poisson's ratio in order to simulate reservoir stress state. Filled squares represent SA-1 Tor Formation and unfilled circles indicate Rigs-1 Ekofisk Formation.
Time dependent properties

For the hydrostatic and uniaxial compaction tests, creep phases were carried out in the elastic and elasto-plastic stress regime. An overview of the selected stress levels and the creep parameters ε_s (%/log scale of time) and t_0 (primary consolidation time) are given in Table 10.



Figure 20: Strain per log cycle, ε_s plotted against (a), (b) mean effective stress and (c), (d) effective axial stress for (a), (c) Ekofisk Formation and (b), (d) Tor Formation. Reference samples and CO₂ injected samples are indicated by black and grey lines respectively. Initial porosities are shown.

Comparison of creep data from reference and CO_2 injecting tests shows no clear effect of supercritical CO_2 on the creep properties (Fig. 20). Comparison between the two test pairs from Ekofisk Formation though, shows that ε_s decreases as a result of CO_2 injection. However, the test pair, sample RE-09B vs. sample RE-12B shows no effect, except at very high stresses above 100 MPa (Table 10).

Table 10: Creep stress σa (axial) and σr (radial), creep parameters, (ϵs and to) and boundary conditions for the tests. HS=hydrostatic test phase; SR=stress-ratio test phase; UA=uniaxial test phase. "Uniaxial" signifies a test where area constancy is maintained by radial strain gauges; in case of radial strain gauge malfunction, the test is continued with a fixed stress ratio approximating constant area conditions.

Test Type	Sample	σ_a MPa	σ_r MPa	$\varepsilon_{\rm s}$ %/logscale	t ₀ min	Boundary condition
Reference	RE-14 RE-08B RE-08B	19.9 19.9 70.5	20 4.2 19	0.019 0.036 0.81	80 200 150	HS UA SR=0.27
	RE-09B RE-09B RE-09B RE-09B RE-09B RE-31	19.9 105.4 131.2 154.9	5.3 31.6 39.4 46.5	0.019 0.37 1.98 2.94	- 25 150 140 550 -	UA SR=0.30 SR=0.30 SR=0.30
CO ₂ injected	RE-26B1 RE-06A RE-06A RE-12B RE-12B RE-12B RE-12B RE-29 RE-10A	20 19.9 72.4 103.3 19.9 109.9 129.9 - -	20 4.2 20.8 40.1 6.3 32.6 38.6 -	a 0.021 0.26 0.63 0.021 0.34 1 -	a 90 100 80 150 100 110 - -	HS UA UA UA SR=0.30 SR=0.30 - -
Reference	ST-01B ST-01B ST-12B ST-12B ST-12B ST-12B ST-12B ST-20 ST-20 ST-20 ST-20 ST-20 ST-20 ST-20 ST-20 ST-20 ST-25B	9.9 19.9 9.9 29.9 75.5 98.4 9.7 20 95.1 115.1 - -	9.9 19.9 3.6 7.5 10 34.4 44 3.1 10 45.5 60.2	-8 -6 0.013 0.023 0.024 1.11 2.1 0.015 0.01 0.55 1.46	5 5 12 40 60 200 165 70 100 140 260 -	HS HS UA UA UA UA UA UA SR=0.52 -
CO ₂ injected	ST-03B ST-03B ST-04B ST-07 ST-07 ST-07 ST-07 ST-07 ST-13B ST-16B ST-16B ST-16B ST-16B	9.9 20 - 9.9 20 29.9 61.7 72.7 - 10 19.9 79 95.5	9.9 20 - 3.2 6.5 9.8 20.1 23.7 - 3 5.1 24.5 29.6	0.022 0.016 - 0.02 0.025 0.038 0.28 1.15 - 0.018 0.016 0.72 2.4	70 21 - 35 55 100 130 300 - 55 35 270 100	HS HS SR=0.33 SR=0.33 SR=0.33 SR=0.33 SR=0.33 UA UA SR=0.31 SR=0.31

¹⁾ Fluctuating axial deformation rate during creep

impedes ε_s and t_0 determination

DISCUSSION

Influence of mineralogy of chalk

It was observed that Ekofisk Formation chalk is generally less affected by the CO_2 injection process compared to Tor Formation chalk. It may be due to the high content of silicates and clay which inhibit calcite dissolution (Zuddas and Mucci, 1998; Zhang et al., 2005). Another reason may be less exposure to CO_2 during the experiment. Distribution of non-calcite particles inside the pore space of calcite matrix (Fig. 2) contribute to the high specific surface and small pore size of Ekofisk Formation. NMR transverse relaxation time, T_2 is smaller in Ekofisk Formation (Fig. 17), which indicates smaller pore size (Kenyon, 1997). Smaller pore size is being the primary cause for low permeability, which restricts the flow of CO_2 inside pore space. Therefore less CO_2 per unit surface area is available in Ekofisk Formation and the chalk may for this reason experience less calcite dissolution.

Fluid flow

Supercritical CO_2 injection changes the viscosity and density of the resultant fluid by mixing with the oil (Teja and Rice, 1981) and increase the sweep efficiency. Due to the very high specific surface in Ekofisk Formation most of the oil remains immobile during the waterflooding phase. However, CO_2 injection decreases the kinematic viscosity. Therefore more oil became mobile in Ekofisk Formation samples during the CO_2 injection phase which was immobile during the waterflooding phase.

Waterflooding produced up to 75% of oil in place in Tor Formation (Olsen, 2010) and up to 65% in Ekofisk Formation (Olsen, 2011). Supercritical CO_2 injection followed by waterflooding produced up to 20% additional oil in Tor Formation and 30% additional oil from Ekofisk Formation chalk and approximately 5% residual oil saturation was achieved (Olsen, 2010; Olsen, 2011).

Porosity

Porosity shows an overall increasing trend after CO_2 injection (Fig. 12a). On the other hand a decrease in carbonate content was observed. This primarily suggests dissolution of calcite particles due to CO_2 injection. This is also supported by lower specific surface, which is probably a result of smoothening of calcite particles after CO_2 injection. However, dissolution features are difficult to point

out from BSE images (Fig. 2). It may be due to the small (2% to 3%) increase in porosity or may be due to the other features as fracturing is involved in the porosity increment.

The lower electrical resistivity after CO₂ injection suggests that there is a possibility of opening micro-cracks due to sample preparation and measurement procedures. As a result, Archie's cementation factor, *m* calculated from the electrical resistivity data after CO₂ injection falls considerably below the trend line of *m* and the effective specific surface area S_{eff} (*m*=0.09ln S_{eff} +1.97) defined by Olsen et al. (2008a) for North Sea chalk.

Permeability and specific surface

A consistent decrease in specific surface of bulk samples is noticed after CO_2 injection (Table 6). This results in a higher permeability after CO_2 injection as calculated by Kozeny's equation (Fig. 12c). Measured permeability in CO_2 injected samples is also in agreement with calculated permeability (Fig. 12b). Lower measured permeability in two samples after CO_2 injection may be insignificant or may be due to precipitation of fines produced by calcite dissolution. Permeability increase is in Tor Formation higher than Ekofisk Formation. As mentioned above, this may be due to different degrees of dissolution. Within Tor Formation larger permeability increase in Rigs-1 samples may have occurred due to the higher porosity than SA-1 samples, because higher porosity accommodates more fluid to react with the particle surface.

An increase in specific surface of the non-carbonate fraction was observed after CO_2 injection (Table 6). This effect is unexpected and may need further verification.

Failure strength

Flooding with supercritical CO_2 does not seem to influence the strength properties significantly (Fig. 18a). Generally, CO_2 flooded chalks from Tor Formation tend to fail at slightly lower stresses than reference (waterflooded) samples, and the magnitude of the angle of internal friction of Tor Formation samples may approach that of the Ekofisk Formation samples after CO_2 injection (Fig. 18b).

Fig. 18 and Fig. 19 suggest that pore collapse occurs at lower effective stress in samples which have been injected with CO_2 both for Ekofisk Formation and Tor Formation. This tendency seems rather insignificant at hydrostatic stress level but following the yield surface towards the shear failure line this tendency may become more pronounced. However, the difference between the two yield surfaces may be within the uncertainty range.

Stiffness

An increase in Biot's coefficient is an indication of decreasing contact cement between particles which is observed by the movement of Biot's coefficient from higher *IF* region to lower *IF* region in Fig. 15c. A decrease in cementation is indicated by lowering *IF* values and signifies a week porous structure and consequently less stiff rock.



Figure 21: Critical frequency, $f_c = (\phi \eta) / (2\pi \rho_{fl} k)$; calculated from porosity (ϕ), liquid permeability (k), fluid density (ρ_{fl}) and viscosity (η) as an indicator of stiffness. Triangle, square with cross, diamond and circle indicates that the rock is saturated with air (dry), South Arne live oil, HTF brine and 30 percent (volume) CO₂ dissolved in oil respectively. Properties of air is considered ambient condition and properties of fluid considered at reservoir condition (Table 2). Grey data points are Ekofisk Formation sample and black data points are Tor Formation samples.

The stiffness of a sedimentary rock can be influenced by the pore fluid. Andreassen and Fabricius (2010) showed that failure in rocks occurs at lower stresses if it is saturated with fluids having lower kinematic viscosity. The fluid effect on the stiffness of rocks can be characterized by Biot's (1956a, b) critical frequency, $f_c = (\phi \eta)/(2\pi \rho_{fl} k)$ which is calculated from porosity (ϕ), liquid permeability (k), fluid density (ρ_{fl}) and viscosity (η). The higher the critical frequency the stiffer is the rock (Andreassen and Fabricius, 2010). The effect is more prominent in low permeability rocks as chalk, as fluid flow is highly controlled by the specific surface due to smaller effective pore radius (Fabricius et al., 2010).

Fig. 21 shows that the studied samples indeed are less stiff at fluid saturated condition compared to dry condition. Due to lower permeability, Ekofisk Formation samples show less fluid effect compared to Tor Formation samples. Samples saturated with live oil with 30% dissolved CO₂ show least stiffness at reservoir condition among the fluid (HTF brine and live oil) saturated samples due to lower kinematic viscosity (η/ρ_{fl}). This suggests that possible weakening in chalk may not only be due to chemical interaction but also due to fluid effects resulting from altered viscosity and density.

Effective stress

Decrease in stiffness due to the increase of Biot's coefficient could raise a concern on the stability of the reservoir. However, equation (1) suggests that effective stress on a reservoir would decrease if there is no change in pore pressure. It means that, although the rock becomes less stiff after CO_2 injection it also becomes subjected to a smaller effective stress.

An increase in Biot's coefficient signifies that the rock will fail at lower effective stress as it becomes less stiff. As illustration of this phenomenon, we considered an initial average Biot's coefficient of 0.90 for Ekofisk Formation samples and of 0.85 for Tor Formation samples (Fig. 14) and constructed initial failure curves using different uniaxial conditions (σ_2/σ_1) (Fig. 18). We further calculated failure curve for a lower and a higher Biot's coefficient considering a normal overburden condition, where the axial stress (σ_1) arises from the weight of the sediment and where the pore pressure (P_f) is hydrostatic (no overpressure). Our calculation shows that, if both σ_1 and P_f remain unchanged, the failure curve moves closer towards the origin when α increases and vice versa.

Static and dynamic behavior

Reservoir compaction is monitored by 4D seismic utilizing changes in sonic velocity and changing thickness of reservoir layers. Changing thickness in reservoirs (static) is due to both elastic and plastic deformations as shown in rock-mechanics tests in this study. In contrast, sound wave propagation (dynamic) characterizes purely elastic behavior as demonstrated in geophysical tests in this study. Compressional modulus, the most relevant parameter for a

compaction study shows significant difference between static and dynamic values (Fig. 22). Although strain gauge measurements are close to the dynamic compressional modulus, LVDT measurements indicates that the samples are less stiff. The strain gauge measures deformation over an interval of 1 cm of the sample and is less affected by the apparatus setup, but may not be representative for the whole sample if it is inhomogeneous. On the other hand, while LVDT measures over the entire length of the sample it may be affected by instrument setup, bedding and skew in the sample (Olsen et al., 2008b). Therefore, investigation is required to find out the reasons for this discrepancy, relevancy of using static or dynamic data and the relationship between static and dynamic values.

Numerous studies show significant difference between static and dynamic elastic properties (e.g. Simmons and Brace, 1965; Jizba and Nur, 1990; Tutuncu et al., 1994; Fjær, 2009). One reason is that the strain amplitude in sonic velocity measurement is very low compared to the strain amplitude of rock-mechanics tests (Simmons and Brace, 1965; Cheng and Johnston, 1981; Plona and Cook, 1995). Olsen et al. (2008b) suggested that the difference in drainage condition between a static and a dynamic experiment is a major source of difference between measured static and dynamic properties. If fluids in pore space are unable to escape during compression the rock will appear stiffer.



Figure 22: Compressional modulus of the studied chalk (a) before CO_2 injection (reference samples for static data) and (b) after CO_2 injection (CO_2 injected samples for static data). Black markers indicate dynamic data calculated from sonic velocity and bulk density and grey markers indicate static data measured by strain gauge or LVDT. Filled data points are Tor Formation samples and unfilled data points are Ekofisk Formation samples. Marker shape (square, circle, triangle and diamond) used for each procedure and experimental step is indicated by arrows.

CONCLUSION

Injection of supercritical CO_2 leads to an increase in porosity. A decrease in Specific surface area of the particles indicates that a reaction between CO_2 enriched water and particles takes place which smoothens the particle surface. Accordingly, a partial effect on permeability was also seen. A positive effect is also observed from the decrease in stiffness, as indicated by Biot's coefficient. No significant effect on wettability as indicated by NMR T_2 relaxation time was observed.

Rock-mechanics testing indicates that in 30% porosity chalk from the South Arne field injection of supercritical CO₂ has no significant effect on shear strength and compaction properties, while there is probably a slight decrease in stiffness properties.

For both the Tor and Ekofisk formations, flooding with CO_2 after waterflooding does not seem to moderately affect the shear strength parameters (internal friction angle and effective cohesion). For the Tor formation, the elastic deformation parameters seem to be affected (reduced) after CO_2 flooding. For the Ekofisk formation, the effect on the elastic moduli is not significant. The time dependent properties for both Tor and Ekofisk formation does not seem to be affected by CO_2 flooding in the relevant stress regime.

The change in both petrophysical and rock-mechanics properties is insignificant in Ekofisk formation, compared to the changes in Tor Formation, most probably due to the little contact cement in Ekofisk Formation in the first place.

Our data suggest that, although supercritical CO_2 injection decreases the stiffness of chalk, the effective stress acting on the reservoir also decreases. However, due to the decrease in stiffness CO_2 injected chalk could fail at lower stresses than the original reservoir rock would have failed. Therefore a combined rock-physical and rock-mechanical model is required for failure prediction and reservoir monitoring.

4D seismic monitoring utilizes sonic velocity and change in reservoir thickness (strain) so that stiffness and effective stress can be calculated. These data can be used for pore pressure prediction. From the change (decrease) in pore pressure, it may be possible to monitor any leakage form the reservoir. However, in order to

predict pore pressure change in the stiffness of rock, effective stress as indicated by Biot's coefficient must be taken into consideration. The findings of this project may also be used to analyze stress induced mechanical changes in the rocks due to pore pressure changes.

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V

Surface charge of calcite and its influence on the electrical conductivity in chalk

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Surface charge of calcite and its influence on the electrical conductivity in chalk. Mohammad Monzurul Alam*, Rajib Ahsan, Abdul Karim Shaik and Ida Lykke Fabricius. Department of Environmental Engineering, Technical University of Denmark.

Summary

Excess conductivity arising from Cation Exchange Capacity (*CEC*) could play a significant role in quantification of hydrocarbons in North Sea chalk. We studied Ekofisk and Tor Formation chalk samples from the South Arne field of the North Sea. *CEC* of synthetic calcite was measured to be between 13 μ Eq/m² and 16 μ Eq/m², whereas, calculated *CEC* of Ekofisk Formation chalk varies between 3 μ Eq/m² and 6 μ Eq/m². We estimated relative proportion of clay surface and calcite surface by Nuclear Magnetic Resonance (*NMR*). Our data indicate that the North Chalk has excess conductivity and that a part of this is contributed by the calcite surface in addition to excess conductivity due to clay.

Introduction

Electrical conductivity in reservoir rocks provides us with information on hydrocarbon saturation (Archie, 1942) because hydrocarbons are non-conductive. The major source of electrical conductivity is the presence of ions as Na^+ and Cl^- in formation water. In addition, clay conducts electrical charge along its surface due to its Cation Exchange Capacity (*CEC*) (Hill and Milburn, 1956; Waxman and Smits, 1968; Clavier, 1984). In presence of water, silicate layers in clay become negatively charged and positive current-conducting ions (Wyllie, 1960) adsorbs to the clay surface. Due to high specific surface of clay, conductivity arising from *CEC* could contribute a significant part in the overall conductivity in clay bearing reservoir rocks.

Most of the North Sea chalk formations contain some amount of clay (Røgen et al., 2005). While influence of *CEC* on the conductivity of sand is well studied, its importance on chalk has only received little attention (Fabricius et al., 2005). Chalks are composed of calcite grains of silt size and consequently it has high specific surface.

The surfaces of calcite in chalk are primarily rhombohedral crystal surfaces. In the calcite atomic structure, calcium atoms are octahedrally coordinated by oxygen from six different CO_3 groups. Net charge on the unreacted crystal surfaces is zero. In presence of water, electrical charges form in the interface between the calcite surface and water. Several authors reported that in a pure aqueous suspension of calcite, the potential determining ions (*PDI*s) on the

surface are Ca^{2+} and CO_3^{2-} (e.g. Yarar and Kitchener, 1970; Thompson et al., 1989). Studies on wettibility alteration in chalk demonstrated that this Ca^{2+} ions on the calcite surface could be exchanged by other ions, e.g. Mg^{2+} (Korsnes et al., 2006; Strand et al., 2006; Zhang et al., 2007).

We studied the exchangeability property of Ca^{2+} ions from calcite surface and its relation to excess electrical conductivity. Ca^{2+} ions from the surface of synthetic chalk were replaced by Mg^{2+} ions to estimate the amount of exchangeable ions. Nuclear Magnetic Resonance (*NMR*) technique was used to quantify the contribution from the non-calcite and from the calcite fraction to the overall specific surface of chalk. Specific surface of the individual components were then compared with the excess conductivity of the chalk in order to identify the component which contribute most to the overall excess conductivity.

Methods and theory

Excess conductivity from CEC

As a clay surface becomes negatively charged in a typical aqueous environment, a diffuse layer is formed near the clay surface where Na^+ ion concentration exceeds Cl ion concentration. Clavier et al. (1984) showed that at salinity over 0.4 mol/L, a stable layer of thickness x_H is achieved which transmit electric charge. The apparent excess conductivity due to this layer can be calculated by,

$$C_x = \frac{\beta Q_v}{1 - V_o^H Q_v} \tag{1}$$

Where, β is the counterion equivalent conductivity [2.50 (S/m)/(meq/cm³) for the Na⁺ ion (Clavier et al., 1984)], Q_{ν} is counterion concentration in pore space and V_Q^H is the volume of clay water per unit counterion.

Excess conductivity may be calculated from *CEC* of the chalk grains, CEC_{rock} and specific surface for bulk volume, *S*, by rearranging the formula of Clavier et al. (1984),

$$C_{x} = \frac{\beta \times CEC_{rock} \times SSA \times \rho_{g} \times (1-\phi)}{\phi - S \times x_{H}}$$
(2)

where, ρ_g is the grain density and ϕ is porosity. SSA is the specific surface area measured by BET method. *CEC_{rock}*, for the North Sea chalk may be expressed as,

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$$CEC_{rack} = \begin{cases} CEC_{ir} \times IR \frac{SSA_{ir}}{SSA} + \\ CEC_{calcite} \times \left(1 - IR \times \frac{SSA_{ir}}{SSA}\right) \end{cases} \times (1 - \phi)$$
(3)

Where, CEC_{ir} and $CEC_{calcite}$ are the CEC of non-carbonates and the calcite part of the chalk respectively. *IR* is the fraction of irreducible residue by weight (*IR*=1-CaCO₃ fraction).

CEC of *IR* was estimated by replacing the exchangeable bases by *Ba* using *BaCl₂*. *CEC* of calcite was estimated by adsorbing Mg^{2^+} ions onto the calcite surface and replacing Ca^{2^+} ions.



Exchangeable Ca2+ ions

Two synthetic calcites, *CCL* (low specific surface area, $0.24\pm0.05 \text{ m}^2/\text{g}$) and *CCH* (high specific surface area, $11.0\pm0.2 \text{ m}^2/\text{g}$) were used to study the effect of grain size on the ion exchange capacity of calcite. Synthetic calcites were washed for more than 50 hours with a Mg^{2+} containing (50 ppm) solution to displace Ca^{2+} from the calcite surface until Ca^{2+} ions concentration in the solution

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became stable. The initial concentration of Mg^{2+} ions is less than 5% of the concentration in sea water. The concentration is so low that it according to Berner (1975) has insignificant effect on calcite solubility. The Mg^{2+} containing solution was prepared from equilibrated calcite solution, so that, it cannot cause net dissolution of calcite.



Figure 2: *NMR* transverse relaxation of brine saturated chalk, normalized to helium porosity. Solid lines indicate T_2 distribution and dotted lines are cumulative T_2 . Peaks at earlier time represent clay bound water whereas the later peaks represent calcite-bound water.

Concentrations of Ca^{2+} and Mg^{2+} were measured at time intervals by Atomic Adsorption Spectroscopy. The longer the Mg^{2+} containing solution is allowed to come in contact with calcite surface, the more Ca^{2+} goes into the solution and the more Mg^{2+} ions adsorbs on the surface, until it approaches equilibrium (Figure 1).

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Table 1: Overview of the physical properties of the studied samples.

Sample	Well	Formation	Major clay	Cabonate content (%)	Gas Permeability (mD)	Bulk Sp. surface (m ² /g)	Total porosity	Small pores (Clay)	Larger pores (Calcite)	CEC (µEq/m²)	Excess conductivity, C _x (S/m)	Attenuation coefficient Q _P
SE-03	SA-1	Ekofisk	Smectite	78	0.04	6	0.18	0.07	0.11	6	1.0	11
ST-24A	SA-1	Tor	Smectite	98	0.8	1.7	0.26	0.09	0.17	2.5	0.1	29
RE-22A	Rigs-1	Ekofisk	Kaolinite	88	1.1	4	0.33	0.14	0.18	4	0.2	31
RT-03	Rigs-1	Tor	Kaolinite	97	4.8	1.9	0.42	0.16	0.26	2.5	0.05	-

Clay bound and calcite bound pore water from NMR Relaxation of protons close to the solid surface is faster than of protons in the free flowing fluid (Kenyon, 1997). Therefore, if the interface of solid and fluid is conductive due to a layer of conducting ions, a relationship between relaxation rate and excess conductivity is to be expected. Transverse relaxation rate, $1/T_2$ in a NMR experiment is proportional to the surface to volume ratio (*S/V*) (Coates et al., 1999),

$$\frac{1}{T_2} = \rho \frac{S}{V} = \rho S_{\phi} \tag{4}$$

where, ρ is relaxivity and S_{ϕ} is the specific surface for pore space.

NMR T_2 distribution curves (Figure 2) were used to quantify the small pores in the clay and larger pores bounded by calcite, which are used to estimate surface contribution from the clay and the calcite part of the chalk. Due to the high specific surface of chalk and consequent high *S/V*, free flowing fluid peaks are not found. We defined the peak with low relaxation time (T_2) as representing non-calcite mineral bound brine and the peak with longer relaxation time as representing calcite bound brine.

Data

We used chalk samples from SA-1 and Rigs-1 wells of the North Sea South Arne field. Samples represent the Ekofisk and Tor formations, which are mineralogically different.

Results and discussion

In the synthetic calcite experiment, amount of adsorbed Mg^{2^+} ions corresponds to 8 (±0.5) µEq/m² (4 µmole/m²) and 6.5 (±0.5) µEq/m² (3 µmole/m²) for CCL and CCH respectively (Figure 3). At the same time the increase in Ca^{2^+} ions in the solution were, 16 (±0.5) µEq/m² (8 µmole/m²) and 13 (±0.5) µEq/m² (6 µmole/m²) for CCL and CCH respectively. The surface area per Ca^{2^+} ion on the crystal faces of calcite is 0.204 nm² on {10<u>1</u>4} corresponding to maximum monolayer adsorption density 8.14 µmole/m² (Madsen, 2002). As our data is within this

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CEC of the insoluble residue of SA-1 Ekofisk and Rig-1 Ekofisk formation was found to be between 7 μ Eq/m² and 10 μ Eq/m². In Tor Formation CEC of the insoluble residue was found to be 9 - 17 μ Eq/m² and 8 - 9 μ Eq/m² for SA-1 and Rigs-1 respectively. Excess conductivity calculated by Eq. 2 is 1 S/m for SA1-Ekofisk, 0.2 S/m for Rigs-1 Ekofisk and 0.1 S/m for both SA-1 Tor and Rigs-1 Tor Formation. Due to the higher non-carbonate content in Ekofisk Formation (Table 1) excess conductivity is higher than the relatively clean chalk of Tor Formation.

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Although it is widely described in literature that excess conductivity is only due to the *CEC* of clay, we found that calcite dominates in determining excess conductivity in chalk. Plots of excess conductivity versus non-calcite specific surface and versus total specific surface show no significant relationship (Figure 4a, 4c). Excess conductivity rather increases with the increase of calcite specific surface in the total pore space (Figure 4b). However, if the chalk contains high amount of smectite clay (as in sample SE-03) excess conductivity could be significantly higher than the excess conductivity due to calcite (Figure 2b).

Attenuation of acoustic wave occurs due to the friction at the interface between solid and fluid (Biot, 1956). Friction arises from relative motion between solid and viscous fluid. If a stable monolayer of electrical current conducting ions is present on the surface of the solid, it could be possible to see on the attenuation behavior of rock saturated with viscous fluid. Similar to the excess conductivity, attenuation coefficient of the studied samples also shows dependence on calcite surface rather than clay or total surface (Figure 4d, 4e, 4f). This provides the possibility to estimated excess conductivity of chalk from attenuation of acoustic wave.

Conclusions

We found that calcite grains have considerable *CEC*. Due to the small grain size of calcite in chalk, excess conductivity in chalk is controlled by the calcite surface rather than by the clay specific surface. Excess conductivity of chalk consequently has a positive linear relationship with the specific surface of calcite. The *NMR* tool can be used to calculate calcite specific surface in chalk and from the average value of calcite *CEC* it is possible to predict excess conductivity. As electrical conductivity is the central factor in Archie's equation, excess conductivity due to both clay and calcite should be properly utilized for accurate fluid saturation calculation.

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EDITED REFERENCES

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VI

NMR as a Tool for Estimation of Excess Conductivity in Chalk

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Poster presented in 72nd EAGE Conference and Exhibition, Barcelona, Spain 14-17 June 2010



Introduction

Nuclear Magnetic Resonance (*NMR*) characterizes the surface to volume ratio of the pore space in a fluid saturated rock. The *NMR* transverse relaxation time (T_2) is inversely proportional to the equivalent pore radius. Chalk is a homogeneous rock primarily composed of calcitic particles of silt size and consequent high specific surface area (Scholle, 1977). Presence of clay and sub micron-size quartz makes the surface to volume ratio even higher.

Smectitic clay has the ability to transport electrical current by its adsorbed cat-ions quantified as Cation Exchange Capacity (*CEC*). Most of the North Sea chalk contain some amont of clay, primarily smectite or kaolinite (Røgen et al., 2005). We found that calcite also has *CEC*. Excess conductivity arising from *CEC* could play a significant role in quantification of hydrocarbons in North Sea chalk. We demonstrate the use of T_2 as an indicator of excess conductivity, so that NMR logs could be applied to determine excess conductivity in chalk.

Methods and Theory

Relaxation of protons close to the solid surface is faster than of the protons in the free flowing fluid (Kenyon, 1997). In presence of ions, a diffuse layer of cations is formed near the clay or calcite surface which conducts electric current (Clavier et al. 1984). Therefore, if the interface of solid and fluid is conductive a relationship between relaxation rate and excess conductivity is to be expected.



Figure 1 NMR transverse relaxation of brine saturated chalk, normalized to helium porosity. T_2 distribution is indicated by solid lines whereas dotted lines are cumulative T_2 . Each left peak represents clay bound water whereas the right peaks represent calcite-bound water.

Transverse relaxation rate, l/T_2 is proportional to the surface to volume ratio S/V (Coates et al., 1999),

$$\frac{1}{T_2} = \rho \frac{S}{V} = \rho S_{\phi} \tag{1}$$

where, ρ is relaxivity and S_{ϕ} is the specific surface for pore space.

Excess conductivity may be calculated from *CEC* of the rock grains, CEC_{rock} and specific surface for bulk volume, *S*, by rearranging the formula by Clavier et al. (1984),

$$C_{x} = \frac{\frac{\beta \times CEC_{rock} \cdot \rho_{g} (1-\phi)}{\phi}}{1-Sx_{H}}$$
(2)

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where, β is the counterion equivalent conductivity, ρ_g is the grain density and x_H the thickness of the diffuse double layer.

We used chalk samples from SA-1 and Rigs-1 wells of the North Sea South Arne field. Samples represent the Ekofisk and Tor formations. NMR T_2 distribution curves were used to quantify the small pores in the clay and larger pores bounded by calcite (Figure 1).

Result and Discussion

Due to the high specific surface of chalk and consequent high S/V, we may assume that there is no free flowing fluid. We defined the peak with faster relaxation time as representing non-calcite mineral bound brine and the peak with slower relaxation time as representing calcite bound brine.



Figure 2 Excess conductivity as a function of (a) non-calcite specific surface, (b) calcite specific surface and (c) total specific surface, each with respect to the total porosity. Excess conductivity due to the calcite CEC is indicated by the solid line in (b).

Although we found that CEC of the insoluble residue is higher than the CEC of calcite, we also found that calcite dominates in determining excess conductivity in chalk. Plots of excess conductivity versus non-calcite specific surface and versus total specific surface show no significant relationship (Figure 2a, 2c). Excess conductivity rather increases with the increase of calcite specific surface in the total pore space (Figure 2b). However, if the chalk contains high amount of smectite clay (as in sample SE-03) excess conductivity could be significantly higher than the excess conductivity due to calcite (Figure 2b).

Conclusion

We found that calcite grains have considerable CEC. Interestingly, excess conductivity in chalk is controlled by the calcite surface rather than by the clay specific surface. Excess conductivity of chalk consequently has positive linear relationship with the specific surface of calcite. The NMR tool could thus potentially be used to calculate calcite specific surface in chalk and from the average value of calcite CEC it is possible to predict excess conductivity.

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VII

9 Appendix

The appendix contains the following experimental details

- CT scan images of the studied samples
- BSE images of the studied samples, before and after CO₂ injection.
- Strain-stress diagrams.
- Compressional wave velocity (V_p) at different stresses
- Shear wave velocity (V_p) at different stresses
- Electrical resistivity at different stresses
- X-ray diffractograms
- GEUS CO₂ injection report



Figure A VII-1: CT scan images of the studied samples.



Continued



Figure A VII-2: BSE images of the Rigs 1 studied interval before CO₂ injection.



Continued



Continued



Figure A VII-3: BSE images of the SA-1 studied interval before CO₂ injection.



Continued



RE-26B2



Continued


Figure A VII-4: BSE images of the all studied $1\frac{1}{2}$ inch samples after CO₂ injection.









VII-11





VII-12













VII-15





Experimental stage is indicated in each figure. A typical experiment consist of (1) loading to 3 MPa, (2) unloading down to 1 MPa, (3) reloading to 4 MPa and (4) unloading to atmospheric condition.





Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	inal u	nloadin	g
RE-22A	3.13	3.14	3.20	3.20	3.14	3.15	-	-	-	-	-	-	3.13
RT-03	1.83	1.84	1.93	1.98	1.94	1.93	-	-	-	-	-	-	-
SE-03	2.81	2.64	2.66	2.80	-	-	-	-	-	-	-	-	-
ST-24A	3.45	3.56	3.65	3.68	-	-	-	-	-	-	-	-	-
RE-24	2.76	2.76	2.80	2.80	2.80	2.80	-	-	-	_	-	-	2.76
RT-01	2.63	2.63	2.67	2.70	2.66	2.63	2.67	2.70	2.70	2.69	2.67	2.63	2.63
SE-05A	-	-	3.10	3.10	-	-	-	-	-	-	-	-	-
ST-24B	4.02	4.11	4.08	4.11	4.11	4.11	-	-	-	-	-	-	-
RE-23A	3.29	3.29	3.29	3.29	3.29	3.29	-	-	-	-	-	-	3.27
RT-02	-	3.37	3.37	3.37	3.36	3.36	-	-	-	-	-	-	3.31
SE-02	2.34	2.63	2.84	2.93	2.93	2.73	2.88	2.99	3.00	3.14	3.07	2.87	2.66
ST-23A	-	-	-	3.59	-	-	-	-	-	-	-	-	-
RE-26B2	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-26	3.48	3.51	3.51	3.55	3.53	3.51	3.53	3.55	3.57	3.55	3.53	3.52	3.47
ST-08A	2.95	2.99	3.00	3.05	3.00	3.00	3.00	3.04	3.05	3.05	3.04	3.00	3.00
ST-08B	2.81	2.77	2.80	2.83	2.80	2.77	2.80	2.84	2.90	2.88	2.80	2.79	2.80
RE-06A	3.62	3.62	3.63	3.63	3.63	3.63	3.63	3.63	3.64	3.63	3.62	3.62	3.63
RE-08B	3.49	3.49	3.49	3.51	3.50	3.49	3.49	3.52	3.52	3.52	3.52	3.51	3.49
RE-09B	3.49	3.56	3.50	3.49	3.49	3.49	3.48	3.49	3.50	3.51	3.48	3.45	3.30
RE-10A	3.78	3.78	3.76	3.77	3.81	3.76	3.77	3.77	3.78	3.80	3.78	3.75	3.77
RE-12B	3.81	3.85	3.85	3.85	3.85	3.85	3.85	3.85	3.85	3.85	3.86	3.87	3.81
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	3.42	3.52	3.56	3.63	3.66	3.61	3.62	3.63	3.63	3.63	3.63	3.61	3.51
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	3.08	3.18	3.25	3.28	3.35	3.10	3.19	3.35	3.36	3.33	3.18	3.18	3.11
ST-04B	3.76	3.76	3.76	3.76	3.76	3.75	3.76	3.76	3.76	3.76	3.76	3.76	3.72
ST-07	3.07	3.08	3.09	3.12	3.13	3.11	3.10	3.13	3.15	3.14	3.10	3.10	3.03
ST-13B	3.09	3.09	3.09	3.09	3.09	3.07	3.09	3.12	3.13	3.11	3.12	3.07	2.97
ST-16B	3.43	3.45	3.45	3.46	3.46	3.44	3.43	3.46	3.47	3.46	3.44	3.43	3.43

Table A VII-1: Compressional wave velocity (V_p) (km/s) at different axial stresses, measured at initial dry condition (*Dry-I*).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	Final u	nloadin	g
RE-22A	3.12	3.16	3.16	3.17	3.17	3.14	3.16	3.17	3.20	3.17	3.17	3.13	3.11
RT-03	2.27	2.31	2.37	2.42	2.40	2.35	2.39	2.43	2.48	2.44	2.41	2.35	2.30
SE-03	3.21	3.23	3.29	3.32	3.31	3.26	3.31	3.32	3.35	3.32	3.30	3.26	3.24
ST-24A	3.69	3.70	3.70	3.68	3.61	3.66	3.70	3.67	3.68	3.64	3.64	3.64	3.64
RE-24	2.77	2.81	2.83	2.87	2.86	2.82	2.85	2.86	2.91	2.89	2.86	2.83	2.78
RT-01	2.77	2.78	2.80	2.81	2.80	2.77	2.80	2.81	2.84	2.82	2.78	2.76	2.74
SE-05A	2.98	3.02	3.02	3.04	3.05	2.98	3.02	3.01	3.04	3.04	2.95	2.81	2.74
ST-24B	4.01	4.05	4.12	4.14	4.12	4.12	4.12	4.12	4.15	4.14	4.13	4.13	4.06
RE-23A	3.23	3.23	3.28	3.28	3.29	3.24	3.28	3.28	3.31	3.27	3.24	3.23	3.22
RT-02	3.35	3.40	3.40	3.44	3.40	3.40	3.39	3.40	3.41	3.37	3.38	3.35	3.32
SE-02	3.26	3.26	3.39	3.39	3.36	3.36	3.39	3.39	3.39	3.40	3.39	3.35	3.31
ST-23A	3.75	3.75	3.79	3.80	3.82	3.77	3.80	3.82	3.85	3.85	3.83	3.78	3.77
RE-26B2	3.28	3.28	3.29	3.30	3.28	3.28	3.30	3.30	3.35	3.30	3.29	3.27	3.26
ST-26	3.47	3.48	3.52	3.55	3.53	3.52	3.53	3.54	3.56	3.55	3.53	3.52	3.52
ST-08A	3.04	3.02	3.07	3.12	3.08	2.72	3.09	3.13	3.13	3.84	3.80	3.06	3.00
ST-08B	2.86	2.87	2.90	2.98	2.94	2.90	2.93	3.02	3.03	3.03	2.96	2.90	2.87
RE-06A	3.17	3.21	3.21	3.07	3.05	3.04	3.06	3.10	3.10	3.10	3.03	3.02	2.96
RE-08B	3.26	3.25	3.28	3.29	3.28	3.25	3.28	3.28	3.28	3.29	3.28	3.27	3.23
RE-09B	3.36	3.34	3.38	3.40	3.39	3.37	3.38	3.39	3.41	3.39	3.37	3.34	3.34
RE-10A	3.33	3.33	3.33	3.34	3.34	3.33	3.33	3.34	3.35	3.35	3.32	3.32	3.32
RE-12B	3.42	3.41	3.41	3.43	3.43	3.40	3.43	3.43	3.43	3.43	3.42	3.41	3.41
RE-14A	3.24	3.25	3.27	3.28	3.28	3.25	3.28	3.28	3.30	3.29	3.28	3.25	3.25
RE-26B1	3.17	3.16	3.19	3.21	3.20	3.18	3.20	3.21	3.23	3.21	3.19	3.19	3.16
RE-28A1	3.25	3.25	3.28	3.29	3.28	3.27	3.28	3.30	3.31	3.30	3.28	3.27	3.25
RE-29	3.25	3.25	3.30	3.31	3.31	3.28	3.31	3.33	3.34	3.34	3.32	3.30	3.27
RE-31	3.26	3.27	3.28	3.29	3.29	3.27	3.29	3.29	3.30	3.31	3.29	3.26	3.25
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-2: Compressional wave velocity (V_p) (km/s) at different axial stresses, measured at initial water saturated condition (S_w-I) .

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	Final u	nloadin	g
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-24	2.74	2.76	2.74	2.75	2.74	2.74	2.73	2.75	2.76	2.75	2.75	2.72	2.72
RT-01	2.60	2.59	2.60	2.61	2.60	2.60	2.60	2.60	2.62	2.62	2.58	2.60	2.56
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24B	3.90	3.91	3.93	3.93	3.92	3.88	3.91	3.91	3.90	3.92	3.92	3.92	3.90
RE-23A	3.04	3.06	3.07	3.09	2.95	2.92	3.02	3.07	3.08	3.01	2.92	2.92	2.92
RT-02	3.16	3.21	3.19	3.20	3.21	3.19	3.19	3.19	3.20	3.19	3.20	3.19	3.18
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-23A	3.58	3.58	3.59	3.60	3.61	3.58	3.61	3.61	3.59	3.59	3.58	3.55	3.55
RE-26B2	3.19	3.21	3.22	3.20	3.23	3.21	3.23	3.26	3.26	3.24	3.23	3.22	3.18
ST-26	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-08A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-06A	3.11	3.13	3.14	3.16	3.14	3.13	3.14	3.16	3.16	3.17	3.14	3.12	3.12
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-10A	3.23	3.26	3.27	3.28	3.26	3.26	3.28	3.30	3.30	3.29	3.26	3.27	3.26
RE-12B	3.30	3.33	3.33	3.35	3.35	3.33	3.34	3.35	3.35	3.35	3.34	3.33	3.32
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B1	3.05	3.07	3.09	3.11	3.09	3.07	3.08	3.11	3.12	3.11	3.09	3.06	3.05
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	3.14	3.16	3.19	3.22	3.21	3.18	3.21	3.23	3.22	3.22	3.21	3.19	3.16
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-3: Compressional wave velocity (V_p) (km/s) at different axial stresses, measured at irreducible water saturated condition (S_{wir}) .

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	Final u	nloadin	g
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-24	2.74	2.76	2.79	2.82	2.80	2.78	2.80	2.82	2.82	2.81	2.80	2.78	2.76
RT-01	2.73	2.74	2.78	2.79	2.79	2.74	2.78	2.79	2.85	2.79	2.79	2.74	2.71
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24B	3.98	3.99	3.98	3.99	3.99	3.98	3.99	3.99	3.99	3.99	3.99	3.98	3.98
RE-23A		-	-	-	-	-	-	-	-	-	-	-	-
RT-02	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-23A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B2		-	-	-	-	-	-	-	-	-	-	-	-
ST-26	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-08A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-06A	_	-	-	-	-	-	-	-	-	_	-	-	-
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-4: Compressional wave velocity (V_p) (km/s) at different axial stresses, measured at residual oil saturated condition (S_{or}) .

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	-inal u	nloadin	g
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-24	2.61	2.63	2.66	2.74	2.70	2.62	2.68	2.74	2.77	2.75	2.73	2.62	2.59
RT-01	2.60	2.59	2.62	2.65	2.65	2.60	2.65	2.70	2.73	2.70	2.65	2.59	2.60
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24B	3.74	3.75	3.79	3.83	3.82	3.76	3.79	3.83	3.84	3.83	3.80	3.76	3.76
RE-23A	2.99	2.98	2.99	3.02	3.02	2.99	3.02	3.05	3.09	3.13	3.05	2.98	2.97
RT-02	3.17	3.17	3.17	3.18	3.17	3.16	3.17	3.18	3.21	3.21	3.18	3.14	3.12
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-23A	3.40	3.41	3.33	3.45	3.47	3.43	3.46	3.47	3.53	3.52	3.50	3.46	3.44
RE-26B2	3.19	3.20	3.20	3.27	3.21	3.20	3.21	3.24	3.27	3.26	3.23	3.20	3.19
ST-26	3.31	3.31	3.34	3.34	3.40	3.31	3.40	3.41	3.41	3.41	3.41	3.40	3.36
ST-08A	2.68	2.68	2.79	2.99	2.91	2.71	2.90	2.99	2.99	2.98	2.96	2.69	2.68
ST-08B	2.67	2.75	2.80	2.84	2.81	2.76	2.81	2.86	2.86	2.84	2.80	2.79	2.64
RE-06A	_	-	-	-	-	-	_	-	-	-	-	-	-
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-14A	_	-	-	-	-	-	_	-	-	-	-	-	-
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-5: Compressional wave velocity (V_p) (km/s) at different axial stresses, measured after CO₂ inction (S_{CO2}).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	-inal u	nloadin	g
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-24	2.42	2.48	2.55	2.58	2.56	2.54	2.56	2.59	2.61	2.59	2.58	2.54	2.49
RT-01	2.07	2.19	2.32	2.40	2.34	2.25	2.34	2.41	2.45	2.43	2.36	2.28	2.12
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24B	3.18	3.18	3.50	3.75	3.55	3.44	3.52	3.75	3.75	3.74	3.50	3.44	3.19
RE-23A	2.61	2.79	2.92	2.95	2.91	2.91	2.95	2.97	2.97	2.96	2.93	2.84	2.82
RT-02	3.16	3.17	3.17	3.17	3.17	3.16	3.17	3.09	3.21	3.20	3.17	3.14	3.12
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-23A	2.48	2.66	3.23	3.22	3.23	2.74	3.22	3.22	3.22	3.22	3.21	2.74	2.49
RE-26B2	_	-	-	-	-	-	_	-	-	_	-	-	-
ST-26	3.00	3.14	3.26	3.29	3.26	3.14	3.25	3.30	3.30	3.30	3.25	3.03	3.01
ST-08A	2.08	2.10	2.27	2.44	2.32	2.21	2.45	2.51	2.54	2.51	2.47	2.22	2.09
ST-08B	2.32	2.39	2.42	2.54	2.53	2.40	2.53	2.55	2.60	2.58	2.55	2.41	2.40
RE-06A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-6: Compressional wave velocity (V_p) (km/s) at different axial stresses, measured at dry condition after CO₂ injection (*Dry-F*).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	-inal u	nloadin	g
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-24	2.69	2.69	2.72	2.78	2.73	2.71	2.73	2.78	2.83	2.82	2.74	2.69	2.67
RT-01	2.63	2.69	2.70	2.73	2.70	2.70	2.70	2.73	2.74	2.75	2.70	2.69	2.61
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24B	3.83	3.85	3.87	3.87	3.87	3.84	3.87	3.87	3.88	3.87	3.87	3.84	3.80
RE-23A	3.02	3.02	3.08	3.09	3.08	3.02	3.08	3.09	3.19	3.09	3.09	3.01	3.00
RT-02	3.21	3.22	3.28	3.28	3.28	3.29	3.29	3.29	3.29	3.29	3.28	3.27	3.17
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-23A	3.58	3.58	3.58	3.58	3.57	3.58	3.56	3.58	3.58	3.58	3.57	3.56	3.56
RE-26B2	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-26	3.38	3.40	3.42	3.46	3.43	3.39	3.44	3.46	3.47	3.46	3.43	3.36	3.35
ST-08A	3.34	3.36	2.94	2.97	2.97	2.81	2.94	2.97	3.02	2.97	2.95	2.80	2.75
ST-08B	2.73	2.83	2.87	2.90	2.89	2.85	2.88	2.90	2.96	2.93	2.91	2.83	2.74
RE-06A	_	-	-	-	-	-	_	-	-	_	-	-	-
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-7: Compressional wave velocity (V_p) (km/s) at different axial stresses, measured at water saturated condition after CO₂ injection (S_w -F).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	-inal u	nloadin	g
RE-22A	1.89	1.91	1.94	1.95	1.93	1.93	-	-	-	-	-	-	1.91
RT-03	1.22	1.23	1.24	1.26	1.26	1.25	-	-	-	-	-	-	-
SE-03	1.82	1.83	1.86	1.89	-	-	-	-	-	-	-	-	-
ST-24A	2.05	2.07	2.09	2.23	-	-	-	-	-	-	-	-	-
RE-24	1.71	1.71	1.71	1.84	1.72	1.71	-	-	-	-	-	-	1.71
RT-01	1.61	1.62	1.67	1.68	1.67	1.63	1.67	1.68	1.69	1.68	1.68	1.63	1.62
SE-05A	-	-	2.07	2.07	-	-	-	-	-	-	-	-	-
ST-24B	2.37	2.41	2.42	2.42	2.43	2.42	-	-	-	-	-	-	-
RE-23A	1.94	1.95	1.97	1.97	1.97	1.96	-	-	-	-	-	-	1.95
RT-02	-	2.01	2.01	2.02	2.02	2.02	-	-	-	-	-	-	2.00
SE-02	1.70	1.79	1.90	1.98	1.93	1.85	1.92	1.99	2.02	2.00	1.96	1.87	1.77
ST-23A	-	-	-	2.31	-	-	-	-	-	-	-	-	-
RE-26B2	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-26	2.11	2.12	2.13	2.14	2.13	2.12	2.13	2.14	2.14	2.14	2.13	2.12	2.09
ST-08A	1.84	1.85	1.88	1.90	1.90	1.89	1.89	1.91	1.92	1.91	1.90	1.88	1.87
ST-08B	1.73	1.74	1.77	1.79	1.77	1.75	1.77	1.80	1.81	1.80	1.78	1.75	1.73
RE-06A	2.15	2.15	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16
RE-08B	2.03	2.05	2.06	2.06	2.06	2.05	2.06	2.06	2.06	2.06	2.06	2.05	2.05
RE-09B	1.98	1.99	2.00	2.00	2.00	1.99	2.00	2.05	2.01	2.00	2.00	1.99	1.98
RE-10A	2.42	2.22	2.23	2.23	2.23	2.22	2.23	2.34	2.24	2.23	2.23	2.23	2.21
RE-12B	2.27	2.28	2.28	2.29	2.28	2.28	2.29	2.29	2.29	2.29	2.29	2.28	2.27
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	1.94	2.15	2.18	2.20	2.19	2.17	2.19	2.20	2.20	2.20	2.20	2.19	1.95
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	1.94	1.96	1.97	1.99	1.98	1.97	1.98	2.02	1.99	1.99	1.98	1.98	1.93
ST-04B	2.18	2.19	2.19	2.20	2.19	2.19	2.19	2.20	2.20	2.20	2.20	2.19	2.18
ST-07	1.90	1.91	1.91	1.92	1.92	1.91	1.92	1.93	1.93	1.93	1.92	1.91	1.91
ST-13B	1.92	1.93	1.94	1.94	1.94	1.94	1.94	1.94	1.95	1.94	1.94	1.94	1.91
ST-16B	2.10	2.10	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.10

Table A VII-8: Shear wave velocity (V_s) (km/s) at different axial stresses, measured at initial dry condition (*Dry-I*).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	Final u	nloadin	g
RE-22A	1.55	1.54	1.58	1.60	1.58	1.57	1.59	1.60	1.60	1.60	1.59	1.58	1.56
RT-03	1.36	1.40	1.41	1.42	1.42	1.40	1.44	1.48	1.50	1.46	1.42	1.40	1.38
SE-03	1.75	1.75	1.76	1.77	1.77	1.76	1.77	1.77	1.78	1.78	1.77	1.76	1.76
ST-24A	1.93	1.94	1.95	1.96	1.94	1.95	1.99	1.97	1.97	1.98	1.97	1.96	1.96
RE-24	1.40	1.41	1.43	1.42	1.42	1.42	1.43	1.43	1.44	1.44	1.43	1.42	1.42
RT-01	1.65	1.64	1.64	1.64	1.63	1.63	1.63	1.65	1.66	1.66	1.63	1.64	1.63
SE-05A	1.67	1.67	1.63	1.64	1.66	1.66	1.63	1.63	1.65	1.64	1.64	1.62	1.57
ST-24B	2.16	2.17	2.19	2.24	2.19	2.20	2.20	2.20	2.20	2.20	2.20	2.20	2.20
RE-23A	1.61	1.62	1.63	1.64	1.63	1.63	1.63	1.64	1.64	1.64	1.64	1.63	1.62
RT-02	1.70	1.70	1.71	1.71	1.71	1.70	1.71	1.70	1.70	1.70	1.69	1.68	1.67
SE-02	1.54	1.53	1.55	1.54	1.55	1.55	1.55	1.54	1.54	1.57	1.56	1.55	1.55
ST-23A	1.89	1.89	1.90	1.90	1.90	1.89	1.90	1.90	1.91	1.91	1.90	1.89	1.89
RE-26B2	1.74	1.74	1.74	1.75	1.75	1.74	1.75	1.77	1.78	1.77	1.75	1.74	1.74
ST-26	1.80	1.80	1.82	1.83	1.83	1.81	1.83	1.84	1.84	1.84	1.83	1.82	1.82
ST-08A	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.61	1.74	2.02
ST-08B	1.39	1.40	1.43	1.47	1.45	1.41	1.45	1.48	1.51	1.50	1.46	1.42	1.40
RE-06A	1.55	1.56	1.56	1.57	1.57	1.55	1.56	1.57	1.57	1.57	1.57	1.55	1.54
RE-08B	1.63	1.62	1.60	1.60	1.59	1.58	1.59	1.59	1.58	1.59	1.59	1.59	1.58
RE-09B	1.84	1.75	1.81	1.84	1.85	1.85	1.85	1.85	1.84	1.85	1.85	1.86	1.84
RE-10A	1.80	1.80	1.80	1.80	1.79	1.79	1.79	1.80	1.80	1.80	1.80	1.80	1.79
RE-12B	1.82	1.82	1.83	1.84	1.83	1.82	1.83	1.85	1.85	1.85	1.83	1.82	1.82
RE-14A	1.71	1.71	1.72	1.72	1.72	1.71	1.72	1.72	1.73	1.72	1.72	1.71	1.71
RE-26B1	1.68	1.66	1.65	1.66	1.66	1.65	1.66	1.66	1.67	1.67	1.66	1.65	1.65
RE-28A1	1.76	1.75	1.76	1.77	1.75	1.75	1.75	1.77	1.78	1.77	1.76	1.75	1.75
RE-29	1.72	1.72	1.72	1.74	1.73	1.74	1.72	1.74	1.74	1.73	1.73	1.72	1.72
RE-31	1.64	1.64	1.63	1.64	1.63	1.63	1.64	1.65	1.65	1.64	1.64	1.63	1.65
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-9: Shear wave velocity (V_s) (km/s) at different axial stresses, measured at initial water saturated condition (S_w -I).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	-inal u	nloadin	g
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-24	1.38	1.38	1.39	1.40	1.39	1.37	1.39	1.40	1.40	1.40	1.39	1.36	1.35
RT-01	1.58	1.57	1.57	1.58	1.56	1.57	1.57	1.58	1.59	1.59	1.55	1.55	1.53
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24B	2.19	2.20	2.20	2.21	2.20	2.19	2.21	2.21	2.21	2.21	2.20	2.19	2.18
RE-23A	1.68	1.67	1.68	1.68	1.69	1.68	1.68	1.68	1.68	1.69	1.70	1.70	1.70
RT-02	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.67	1.66	1.67	1.67	1.67
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-23A	1.83	1.85	1.85	1.86	1.85	1.84	1.85	1.85	1.86	1.85	1.88	1.86	1.86
RE-26B2	1.71	1.72	1.74	1.75	1.74	1.72	1.74	1.75	1.76	1.76	1.74	1.72	1.70
ST-26	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-08A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-06A	1.66	1.67	1.66	1.66	1.66	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-10A	1.73	1.77	1.81	1.82	1.81	1.80	1.81	1.82	1.83	1.82	1.81	1.79	1.78
RE-12B	1.73	1.73	1.73	1.73	1.74	1.74	1.74	1.73	1.73	1.73	1.74	1.74	1.73
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B1	1.63	1.63	1.65	1.64	1.64	1.64	1.64	1.64	1.64	1.64	1.64	1.63	1.63
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	1.74	1.75	1.77	1.79	1.78	1.76	1.78	1.79	1.81	1.80	1.79	1.76	1.74
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-10: Shear wave velocity (V_s) (km/s) at different axial stresses, measured at irreducible water saturated condition (S_{wir}) .

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unlo	ading	R	eloadir	ng	F	-inal u	nloadin	ıg
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-24	1.73	1.74	1.75	1.77	1.76	1.75	1.76	1.47	1.78	1.77	1.76	1.74	1.73
RT-01	1.53	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.55	1.54	1.55	1.52	1.50
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24B	2.20	2.23	2.22	2.22	2.23	2.24	2.23	2.22	2.22	2.22	2.23	2.24	2.23
RE-23A	-	-	-	-	-	-	-	-	-	-	-	-	-
RT-02	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-23A	-	-	-	-	_	-	-	-	-	-	-	-	-
RE-26B2		-	-	-	_	-	_	-	-	_	-	-	-
ST-26		-	-	-	-	-	-	-	-	-	-	-	-
ST-08A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-06A	_	-	-	-	-	-	-	-	-	-	-	-	-
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-11: Shear wave velocity (V_s) (km/s) at different axial stresses, measured at residual oil saturated condition (S_{or}) .

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	F	Final u	nloadin	g
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-24	1.72	1.72	1.73	1.75	1.72	1.71	1.73	1.48	1.77	1.76	1.74	1.70	1.72
RT-01	1.56	1.54	1.56	1.59	1.57	1.54	1.57	1.59	1.61	1.60	1.56	1.54	1.55
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-24B	2.03	2.03	2.02	2.00	2.00	1.99	2.01	2.02	2.00	1.99	1.99	1.99	1.96
RE-23A	1.54	1.53	1.54	1.54	1.54	1.55	1.55	1.54	1.54	1.54	1.54	1.54	1.54
RT-02	1.61	1.64	1.63	1.64	1.63	1.63	1.63	1.64	1.64	1.64	1.63	1.62	1.61
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-23A	1.70	1.70	1.68	1.70	1.70	1.70	1.70	1.70	1.73	1.72	1.71	1.70	1.71
RE-26B2	1.76	1.77	1.77	1.77	1.76	1.76	1.76	1.76	1.77	1.77	1.76	1.76	1.75
ST-26	1.69	1.71	1.72	1.75	1.73	1.70	1.72	1.76	1.78	1.76	1.73	1.70	1.68
ST-08A	1.48	1.48	1.50	1.52	1.52	1.50	1.50	1.52	1.54	1.53	1.51	1.49	1.49
ST-08B	1.39	1.39	1.41	1.42	1.41	1.40	1.41	1.43	1.44	1.43	1.42	1.40	1.39
RE-06A	_	-	-	-	-	-	_	-	-	_	-	-	-
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A VII-12: Shear wave velocity (V_s) (km/s) at different axial stresses, measured after CO₂ injection (S_{CO2}).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5	
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	Final unloading				
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-	
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-	
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-24	1.71	1.72	1.75	1.77	1.76	1.74	1.76	1.77	1.78	1.78	1.77	1.75	1.73	
RT-01	1.49	1.52	1.54	1.56	1.56	1.52	1.55	1.57	1.59	1.58	1.56	1.49	1.47	
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-24B	1.92	2.00	2.38	2.39	2.40	2.01	2.39	2.39	2.35	2.38	2.40	2.01	1.99	
RE-23A	1.94	1.98	1.99	2.00	1.99	1.92	1.99	1.81	2.01	2.01	1.99	2.00	1.99	
RT-02	1.61	1.63	1.63	1.64	1.63	1.63	1.63	1.75	1.64	1.64	1.62	1.62	1.61	
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-23A	1.78	1.82	1.89	1.91	1.89	1.84	1.88	1.90	1.92	1.91	1.88	1.84	1.79	
RE-26B2	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-26	1.97	1.99	2.02	2.02	2.02	1.99	2.02	2.02	2.02	2.02	2.03	1.99	1.97	
ST-08A	1.84	1.77	1.85	1.95	1.89	1.82	1.89	1.97	2.03	2.00	1.94	1.83	1.81	
ST-08B	1.51	1.54	1.65	1.70	1.67	1.59	1.67	1.71	1.74	1.72	1.68	1.60	1.56	
RE-06A	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-	

Table A VII-13: Shear wave velocity (V_s) (km/s) at different axial stresses, measured at dry condition after CO₂ injection (*Dry-F*).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5		
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	Final unloading					
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-		
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-24	1.32	1.31	1.34	1.35	1.35	1.33	1.34	1.35	1.36	1.36	1.35	1.32	1.30		
RT-01	1.57	1.61	1.62	1.64	1.63	1.60	1.62	1.65	1.67	1.66	1.63	1.60	1.58		
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-24B	2.25	2.25	2.25	2.26	2.25	2.23	2.25	2.26	2.27	2.26	2.25	2.23	2.23		
RE-23A	1.65	1.65	1.67	1.68	1.67	1.66	1.67	1.68	1.69	1.69	1.67	1.65	1.63		
RT-02	1.65	1.65	1.66	1.66	1.66	1.65	1.66	1.66	1.67	1.66	1.66	1.65	1.65		
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-23A	1.83	1.83	1.84	1.86	1.85	1.85	1.84	1.86	1.87	1.86	1.85	1.85	1.83		
RE-26B2	_	-	-	-	-	-	-	-	-	-	-	-	-		
ST-26	1.76	1.76	1.77	1.78	1.78	1.76	1.78	1.79	1.80	1.79	1.78	1.76	1.76		
ST-08A	1.70	1.70	1.66	1.69	1.67	1.64	1.67	1.70	1.71	1.70	1.69	1.66	1.63		
ST-08B	1.44	1.42	1.43	1.45	1.44	1.41	1.44	1.45	1.47	1.46	1.44	1.41	1.40		
RE-06A	_	-	-	-	-	-	-	-	-	_	-	-	-		
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-		

Table A VII-14: Shear wave velocity (V_s) (km/s) at different axial stresses, measured at water saturated condition after CO₂ injection (S_w -F).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5	
Sample	First loading				Unloa	ading	R	eloadir	ng	Final unloading				
RE-22A	0.75	0.72	0.77	0.91	0.93	0.90	0.82	0.86	0.88	0.89	0.89	0.76	0.71	
RT-03	0.40	0.40	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.40	0.40	0.40	
SE-03	2.64	3.14	3.31	3.34	4.40	4.23	4.33	4.60	3.36	3.31	3.27	3.02	1.81	
ST-24A	1.01	1.07	1.14	1.69	1.54	1.18	1.64	1.67	1.66	1.61	1.69	1.10	1.02	
RE-24	0.62	0.63	0.65	0.65	0.66	0.67	0.65	0.65	0.65	0.66	0.67	0.67	0.67	
RT-01	0.55	0.53	0.54	0.53	0.54	0.54	0.55	0.55	0.55	0.56	0.57	0.57	0.56	
SE-05A	1.30	1.32	1.40	1.49	1.59	1.70	1.56	1.53	1.54	1.59	1.65	1.77	1.73	
ST-24B	1.04	1.05	1.02	1.04	1.03	1.03	1.03	1.00	1.04	1.04	1.05	1.05	1.04	
RE-23A	0.49	0.46	0.48	0.50	0.50	0.50	0.52	0.52	0.53	0.56	0.57	0.58	0.59	
RT-02	0.67	0.67	0.68	0.70	0.70	0.70	0.71	0.72	0.76	0.80	0.79	0.75	0.70	
SE-02	3.77	3.49	3.79	3.96	3.87	3.74	3.82	3.90	3.98	3.94	3.88	3.78	3.73	
ST-23A	1.03	1.06	1.04	1.05	1.06	1.06	1.07	1.09	1.10	1.10	1.10	1.10	1.11	
RE-26B2	2.23	2.23	2.22	2.22	2.22	2.18	2.21	2.21	2.28	2.26	2.26	2.20	2.23	
ST-26	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-08A	0.84	0.85	0.85	0.85	0.82	0.82	0.82	0.83	0.83	0.83	0.82	0.82	0.83	
ST-08B	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-06A	1.61	1.58	1.57	1.57	1.58	1.61	1.58	1.58	1.60	1.60	1.58	1.60	1.58	
RE-08B	1.53	1.52	1.53	1.53	1.58	1.58	1.58	1.58	1.58	1.58	1.58	1.55	1.53	
RE-09B	1.86	1.83	1.71	1.71	1.79	1.80	1.73	1.73	1.73	1.73	1.79	1.80	1.74	
RE-10A	1.60	1.58	1.58	1.60	1.60	1.58	1.58	1.58	1.60	1.60	1.58	1.58	1.58	
RE-12B	1.60	1.60	1.66	1.65	1.65	1.65	1.65	1.66	1.66	1.67	1.66	1.66	1.65	
RE-14A	1.55	1.57	1.57	1.57	1.58	1.55	1.56	1.57	1.57	1.57	1.57	1.56	1.56	
RE-26B1	2.04	2.04	2.04	2.04	2.04	2.04	2.04	2.07	2.07	2.05	2.04	2.03	2.02	
RE-28A1	2.46	2.46	2.48	2.45	2.42	2.40	2.45	2.45	2.48	2.46	2.45	2.40	2.39	
RE-29	2.54	2.52	2.58	2.64	2.63	2.52	2.63	2.63	2.60	2.61	2.61	2.57	2.58	
RE-31	2.31	2.39	2.46	2.47	2.42	2.38	2.44	2.44	2.46	2.42	2.42	2.38	2.39	
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-	

Table A VII-15: Electrical resistivity (Ω -m) at different axial stresses, measured at initial water saturated condition (S_w -I).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5	
Sample	- - -	First lo	bading		Unloa	Unloading Reloading				Final unloading				
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-	
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-	
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-24	11.1	9.7	8.4	7.7	7.9	8.6	8.0	7.7	7.4	7.3	7.7	8.3	8.9	
RT-01	22.2	19.9	18.7	18.0	18.1	18.4	17.6	17.6	16.6	16.6	16.6	17.2	17.8	
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-24B	19.6	17.4	15.7	14.7	14.7	15.9	15.5	14.9	14.3	14.4	14.9	15.8	17.0	
RE-23A	14.4	12.7	11.6	10.4	10.9	11.9	11.7	10.5	10.0	10.1	10.4	11.2	12.0	
RT-02	23.8	21.9	17.3	17.1	15.5	17.1	16.2	16.2	14.3	14.6	15.0	16.2	18.2	
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-23A	34.9	29.7	26.1	21.9	22.2	25.7	24.6	22.2	19.7	19.7	20.9	24.1	27.0	
RE-26B2	15.6	14.8	13.5	12.7	12.3	13.5	13.1	12.5	12.2	12.4	12.7	13.2	13.8	
ST-26	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-08A	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-08B	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-06A	7.6	7.4	7.0	6.8	6.9	7.0	6.8	6.8	6.6	6.7	6.8	7.0	7.1	
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-10A	6.4	5.9	5.5	5.4	5.4	5.5	5.4	5.3	5.1	5.2	5.2	5.3	-	
RE-12B	6.5	6.1	5.7	5.4	5.5	5.8	5.6	5.5	5.3	5.3	5.4	5.6	5.9	
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-26B1	13.7	12.8	11.9	11.4	11.5	12.0	11.7	11.4	11.1	11.2	11.4	11.8	12.3	
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-	
RE-29	16.1	14.7	13.5	13.0	13.2	13.7	13.3	13.1	12.9	13.0	13.1	13.5	14.1	
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-	
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-	

Table A VII-16: Electrical resistivity (Ω -m) at different axial stresses, measured at irreducible water saturated condition (S_{wir}).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5		
Sample	First loading				Unloa	ading	R	eloadir	ng	Final unloading					
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-		
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-24	2.91	3.04	3.36	3.41	3.22	3.00	3.14	3.21	3.28	3.27	3.14	2.98	3.00		
RT-01	1.36	1.39	1.45	1.45	1.43	1.40	1.43	1.45	1.46	1.42	1.42	1.46	1.45		
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-24B	1.40	1.36	1.32	1.34	1.33	1.33	1.33	1.34	1.34	1.33	1.32	1.33	1.34		
RE-23A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RT-02	-	-	-	-	-	-	-	-	-	-	-	-	-		
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-23A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-26B2	_	-	-	-	-	-	-	-	-	-	-	-	-		
ST-26	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-08A	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-08B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-06A	_	-	-	-	-	-	-	-	-	-	-	-	-		
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-		

Table A VII-17: Electrical resistivity (Ω -m) at different axial stresses, measured at residual oil saturated condition (S_{or}).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5		
Sample		First lo	bading		Unlo	ading	R	eloadir	ng	Final unloading					
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-		
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-24	0.74	0.74	0.79	0.84	0.80	0.77	0.78	0.84	0.86	0.85	0.83	0.77	0.78		
RT-01	0.64	0.64	0.67	0.68	0.66	0.64	0.65	0.66	0.68	0.67	0.65	0.63	0.63		
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-24B	1.43	1.44	1.52	1.57	1.53	1.45	1.48	1.55	1.58	1.55	1.49	1.45	1.45		
RE-23A	1.02	1.03	1.33	1.35	1.29	1.03	1.07	1.25	1.28	1.27	1.18	1.02	1.02		
RT-02	0.84	0.85	0.87	0.90	0.87	0.84	0.86	0.88	0.91	0.89	0.86	0.83	0.83		
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-23A	2.03	2.06	2.04	2.05	2.06	2.06	2.07	2.09	2.10	2.10	2.10	2.10	2.11		
RE-26B2	1.02	1.03	1.07	1.14	1.09	1.06	1.06	1.12	1.15	1.14	1.09	1.05	1.05		
ST-26	1.24	1.24	1.30	1.32	1.30	1.27	1.29	1.32	1.34	1.32	1.30	1.29	1.32		
ST-08A	0.85	0.87	0.96	0.97	0.88	0.87	0.87	0.93	0.95	0.92	0.87	0.87	0.86		
ST-08B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-06A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-		

Table A VII-18: Electrical resistivity (Ω -m) at different axial stresses, measured after CO₂ injection (S_{CO2}).

Axial stress	0.5	1	2	3	2	1	2	3	4	3	2	1	0.5		
Sample		First lo	bading		Unloa	ading	R	eloadir	ng	Final unloading					
RE-22A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RT-03	-	-	-	-	-	-	-	-	-	-	-	-	-		
SE-03	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-24A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-24	0.78	0.80	1.02	1.03	1.03	0.87	0.98	1.00	1.00	1.00	0.99	0.83	0.79		
RT-01	0.68	0.68	0.83	0.88	0.78	0.67	0.67	0.78	0.79	0.76	0.68	0.67	0.67		
SE-05A	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-24B	1.42	1.44	1.65	1.70	1.68	1.47	1.62	1.65	1.67	1.66	1.60	1.42	1.40		
RE-23A	1.02	1.03	1.05	1.14	1.06	1.02	1.04	1.10	1.28	1.15	1.04	1.00	0.98		
RT-02	0.91	0.90	0.90	0.89	0.88	0.88	0.88	0.89	0.89	0.89	0.89	0.88	0.88		
SE-02	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-23A	1.50	1.53	1.84	1.90	1.89	1.78	1.85	1.88	1.88	1.88	1.87	1.79	1.42		
RE-26B2	_	-	-	-	-	-	_	-	-	_	-	-	-		
ST-26	1.03	1.12	1.25	1.25	1.22	1.05	1.14	1.19	1.19	1.19	1.14	1.04	1.03		
ST-08A	0.89	0.90	0.99	1.01	0.92	0.89	0.89	0.94	0.95	0.94	0.89	0.87	0.87		
ST-08B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-06A	-	-	-	-	-	-	-	-	-	_	-	-	-		
RE-08B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-09B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-10A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-12B	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-14A	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-26B1	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-28A1	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-29	-	-	-	-	-	-	-	-	-	-	-	-	-		
RE-31	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-03B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-04B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-07	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-13B	-	-	-	-	-	-	-	-	-	-	-	-	-		
ST-16B	-	-	-	-	-	-	-	-	-	-	-	-	-		

Table A VII-19: Electrical resistivity (Ω -m) at different axial stresses, measured at water saturated condition after CO₂ injection (S_w -F).





Figure A VII-14: X-ray diffractograms of sample taken from 2807 m depth of Rigs-1 well.



Figure A VII-15: X-ray diffractograms of sample taken from 2813 m depth of Rigs-1 well.



Figure A VII-16: X-ray diffractograms of sample taken from 2816 m depth of Rigs-1 well.



Figure A VII-17: X-ray diffractograms of sample taken from 2841 m depth of Rigs-1 well.



Figure A VII-18: X-ray diffractograms of sample taken from 2844 m depth of Rigs-1 well.



Figure A VII-19: X-ray diffractograms of sample taken from 2841 m depth of SA-1 well.



Figure A VII-20: X-ray diffractograms of sample taken from 2841 m depth of SA-1 well.


Figure A VII-21: X-ray diffractograms of sample taken from 2841 m depth of SA-1 well.



Figure A VII-22: X-ray diffractograms of sample taken from 2841 m depth of SA-1 well.



Figure A VII-23: X-ray diffractograms of sample taken from 2841 m depth of SA-1 well.



Figure A VII-24: X-ray diffractograms of sample taken from 2841 m depth of SA-1 well.



Figure A VII-25: X-ray diffractograms of sample taken from 2841 m depth of SA-1 well.



Figure A VII-26: X-ray diffractograms of sample taken from 2841 m depth of SA-1 well.



Figure A VII-27: X-ray diffractograms of sample taken from 2841 m depth of SA-1 well.

Geological Survey of Denmark and Greenland (GEUS)

Confidential report

CO₂-flooding for DTU Environment: Experiment FS-3

GEUS Core Laboratory Report KLAB 45/2010 Dan Olsen 21. May 2010

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1. Summary

A CO₂ flooding experiment was conducted on a composite 1.5" plug sample composed of 8 chalk samples and 5 greensand samples. The aim of the work was to flush the samples with CO₂ at the conditions P_{fluid} =380 bar, P_{conf} =500 bar, and temperature=115°. These conditions are identical to the conditions used in the project "Oil Recovery through CO₂ Injection" financed by the Danish National Advanced Technology Foundation. The present work is a continuation of work done in the project "Oil Recovery through CO₂ Injection".

The experimental procedure that was defined before the work was followed. The main result was that the rock samples was flooded with 2.8 pore volumes of CO_2 at reservoir conditions, and the saturated with formation water.

At two instances during the work technical failures occurred where the net overburden stress exceeded the nominal value of 120 bar. During the first failure the net overburden stress reached approximately 220 bar, which caused a reduction in sample length of 0.5 mm or 0.12%. Assuming isotropic compaction this is equivalent to a porosity reduction of 1.15%. The second failure caused in increase in NOB to 209 bar. The associated change in sample length was only determined after flooding the sample with CO_2 , where the combined effect of the NOB increase and the CO_2 -flooding was a length reduction of 0.15 mm, which is considered insignificant.

After CO₂-flooding the samples were delivered to DTU Environment.

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2. Introduction

This report presents the CO_2 -flooding work conducted by GEUS for DTU Environment in the spring 2010. The work is a continuation of work done in the project "Oil Recovery through CO_2 Injection" financed by the Danish National Advanced Technology Foundation in the period 2007 to 2010. The latter project will be referred to as "the HTF project".

The work was initially specified in an e-mail with a quotation from Dan Olsen (GEUS) on 23rd February 2009 that was accepted by Mohammad Monzurul Alam (DTU Environment) in an e-mail on 29th September 2009. The work was planned at a meeting at GEUS on 6th October 2009 by Mohammad Monzurul Alam (DTU Environment), Ida Fabricius (DTU Environment), and Dan Olsen (GEUS) where an experimental procedure (version 1) was agreed. Minor changes to the experimental procedure were agreed upon several times, the final version of the procedure being version 4 from 12th March 2010, which is given in Table 5.1. Step 12 of the procedure "Perform CCAL if possible" remains to be done. This step is optional, and will be performed if requested.

The work of GEUS consisted of a flooding experiment that is shortly referred to as experiment FS-3. The aim of the experiment was to perform CO_2 -flooding of a number of rock samples. Preparation of the samples was not included in the work. The reservoir condition part of the experimental work was conducted from 9th March 2010 to 14th April 2010.

The CO_2 -flooded sample that was the main result of the work was delivered to Mohammad Monzurul Alam on 16^{th} April 2010.

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3. Equipment

The flooding experiments were conducted in a reservoir condition rig at GEUS that utilized a Hassler-type core holder for 1.5" plug samples and a high pressure pump system. The core holder accepts samples up to a maximum length of 46 cm.

In addition the reservoir rig comprises a number of pressure cylinders, pressure transducers and other equipment that are situated inside a large thermostated oven (Fig. 3.1). The oven provides temperature control with a stability significantly better than 1 °C. The reservoir condition rig has specifications that allow experimental work at fluid pressures up to 690 bar and temperature up to 121 °C. The rig is equipped with a densitometer that measures the density of the fluid produced from the core sample at reservoir conditions.



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4. Fluids and experimental conditions

The experimental conditions for experiment FS-3 are summarised in Table 4.1. The temperature and fluid pressure conditions were selected to be identical with the conditions used in the HTF project.

All experimental data are corrected for the thermal expansion of the pressure medium that took place when the pressure medium flowed from the high-pressure pump that was situated at 23 °C, into the oven, and conversely corrected for thermal contraction when the pressure medium flowed from the oven back to the pump. The flow-rates of the high-pressure pumps are at convenient occasions checked versus the reading of the separator at reservoir conditions. The latest check was on 9th December 2009 where the flow-rate given by the pump (2.103 m/h) was found to deviate less than 2% from the flow-rate given by the separator (2.140 ml/h). The check was performed at the same conditions as the current experiment, i.e. 380 bar fluid pressure and 115 °C.

The water used in the FS-3 experiment was simulated formation water identical with the water used in the HTF project. Table 4.2 presents the composition and some other parameters for the simulated formation water.

Some of the rock samples in experiment FS-3 were partially saturated with degassed crude oil from the South Arne Field. The degassed crude oil was originally supplied by Dong Energy A/S within the HTF project. The CO₂ used for the experiments had a purity of 99.99 %.

Experiment id.	FS-3
Sample type	Composite 1.5" plug
Temperature	115 °C
Fluid pressure	380 bara
Hydrostatic confining pressure	500 bara

Water id.	HTF brine
Density @ 1 atm and 22 °C	1.065 g/ml
Density @ 380 bar and 115 °C	1.025 g/ml
a ⁺	31021 mg/l
-+	522 mg/l
$4g^{++}$	665 mg/l
a ⁺⁺	5667 mg/l
-	60270 mg/l
CO ₂ -	13 mg/l
alinity	9.2 wgt%

5. Experiment FS-3

5.1. Experiment set-up

The experimental procedure for experiment FS-3 is presented in Table 5.1.

Table 5.1. Experimental procedure for experiment FS-3, v.4, GEUS, 12. March 2010

- 1. Photography of individual plugs.
- 2. Mount a composite core in a core holder. Plugs of similar lithology and saturation state are mounted with increasing permeability towards the outlet end of the core holder.
- 3. Establish reservoir conditions: $P_{conf} = 500$ bara, $P_{fluid} = 380$ bara, T = 115 °C.
- 4. Equilibration at reservoir conditions for 1 week.
- Flood the core with CO₂ at a rate of 2 ml/h. (rate subject to change). Logging of produced fluid volumes, T, flow-rate, P_{conf}, P_{fluid}, ΔP. Target for amount of injected CO₂ is 355 ml at reservoir conditions, equivalent to 2.5 pore volumes.
- 6. Flush the core with approximately 1.5 pore volume of HTF brine.
- 7. Depressurize and cool down rig. Dismount the core.
- 8. Photography of individual plugs.
- 9. Saturate the core with HTF brine by the vacuum & pressure technique.
- 10. Ship the samples to DTU-ER.
- 11. Await samples to be returned from DTU-ER.
- 12. Perform CCAL including Dean Stark analysis, if possible.

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5.2. Sample characterization and sample mounting

Experiment FS-3 was conducted with a composite sample that consisted of thirteen individual 1.5" plug samples. Eight of the samples were samples of chalk and five of the samples were samples of greensand, cf. Table 5.2. Porosity and gas permeability (kg) for the chalk samples were determined by GEUS as part of the HTF project. Porosity and gas permeability for the greensand samples were supplied by Zakir Hossain, DTU Environment.

The thirteen sub-samples were mounted in the core holder in the sequence indicated by the first column of Table 5.2. The five greensand samples were positioned at the inlet end of the core holder. In flow sequence after the greensand samples followed a chalk sample, ST-08B, that acted as a filter towards possible fines migration originating from the sandstone samples. Then followed three chalk samples that contained water and residual crude oil (ST-24B, RE-24, RT-01) and three chalk samples that contained residual water and crude oil (RE-23A, ST-23A, RT-02). Finally, at the outlet of the core holder, chalk sample ST-08A was positioned as a filter towards possible back-flow into the core holder, and also served to contain possible saturation end effects. The core holder was mounted in a vertical position, and both the CO₂-flooding and the following brine flooding took place from the bottom towards the top of the core holder. The core holder was equipped with a floating end piece, which allowed determination of changes in the sample length during the experiment, cf. section 5.6.

5.3. Initial experiment set-up

After mounting the samples in the core holder, the core holder was mounted in the GEUS reservoir condition rig. The fluid pressure and the hydrostatic confining pressure were increased simultaneously until the reservoir pressure conditions, $P_{fluid}=380$ bar and $P_{conf}=500$ bar, were reached, cf. Fig. 5.1. During the pressure ramping, the difference between

Table 5.2 Experiment FS-3, initial sample characterization.Arrow indicates flow direction from bottom towards top of core.											
	Sample	Lithology	Diameter	Length	Geom.vol.	Por	Pore vol	kg	Saturation		
	id.		(mm)	(mm)	(ml)	(%)	(ml)	(mD)	state		
Out	let end										
	ST-08A	Chalk	36.83	30.04	32.00	32.3	10.34	3.16	Sw 100%		
	RT-02	Chalk	37.08	24.83	26.81	35.0	9.38	2.30	Swir		
	ST-23A	Chalk	37.49	27.02	29.83	26.2	7.81	0.83	Swir		
	RE-23A	Chalk	37.19	26.52	28.81	32.0	9.22	0.67	Swir		
	RT-01	Chalk	37.03	29.70	31.99	38.9	12.44	4.38	Sor		
	RE-24	Chalk	37.31	38.86	42.49	35.9	15.25	0.88	Sor		
	ST-24B	Chalk	37.35	34.03	37.28	24.8	9.25	0.78	Sor		
	ST-08B	Chalk	37.18	39.32	42.69	31.0	13.23	2.64	Sw 100%		
	1-4	Greensand	37.00	29.83	32.07	37.3	11.96	530	Sw 100%		
	1-141	Greensand	37.00	33.75	36.29	34.9	12.66	360	Sw 100%		
	1A-141	Greensand	37.00	29.20	31.40	30.1	9.45	230	Sw 100%		
	1-139	Greensand	37.00	33.30	35.80	34.2	12.25	210	Sw 100%		
	1A-142	Greensand	37.00	31.64	34.02	29.3	9.97	160	Sw 100%		
Inlet end											
Arithmetic mean value			37.11			32.45		115.82			
Har	monic mear	n value						2.01			
Cumulative value				408.04	441.48		143.22				

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the fluid pressure and the confining pressure was kept below 120 bar, except for an instance on 10th March 18:07 at the end of the pressure ramping. At this instance a failure in the pump controller caused the fluid pressure in the rock sample to drop approximately 100 bar without any reduction in the confining pressure. Therefore, the net overburden stress (NOB) was increased from the nominal 120 bar to approximately 220 bar. The increase in NOB took place within a few seconds and lasted for a few minutes. The NOB was normalized to below 120 bar within 9 minutes. Shortly before the incident, at 10th March 17:30, and again shortly after the incident at 10th March 18:26 the position of the core holder floating end piece was measured, cf. Fig. 5.4. These data show that sample FS-3 compacted 0.51 mm by the 100 bar NOB increase. Assuming isotropic compaction of the sample the length reduction of 0.51 mm is equivalent to a pore volume reduction of 1.64 ml or a porosity reduction of 1.15 %.

After pressurization, the reservoir rig was heated to 115 °C on 11^{th} to 12^{th} March, where the rig remained until 18^{th} March to attain equilibrium.

From 18th March to 19th March water was injected into the sample to determine the injectivity, which is necessary for selecting the flooding rate for the CO₂ flooding. A water volume of 22.4 ml was injected. Assuming one-phase flow of water, the injectivity indicated a





permeability to water of 0.074 mD. During the injectivity test most of the movable oil in the sample was flushed out.

5.4. CO₂-flooding

The CO₂-flooding took place in two parts separated by a period with repair of a leakage in one of the pressure cylinders. A log of the FS-3 CO₂-flooding is presented in Fig. 5.2.

The first part of the CO₂-flooding took place from 20th March 13:01 to 24th March 20:25 with injection of 99.3 ml of CO₂, equivalent to 0.734 pore volumes (PV). Before breakthrough the densitometer log shows that the produced fluid is mainly water with density 1.03 g/ml. Scattered occurrences of fluid density below 1.0 g/ml is interpreted as occasional production of oil. The measured density at these occasions is intermediate between the density of water and the density of oil, because the oil volume was too small to fill the measuring chamber of the densitometer. Breakthrough of a non-water phase occurred on 23rd March 18:36 after injection of 73.5 ml of CO₂, equivalent to 0.543 PV. Immediately after breakthrough, the non-water phase is interpreted to consist mainly of mobilized oil with the addition of a minor amount of CO₂, as indicated by the measured density of approximately 0.82 g/ml. After breakthrough the density of the non-water phase gradually decreases until 24th March 20:25 where it is approximately 0.78 g/ml. The gradual change indicates a gradual increase in the CO₂ contents of the produced fluid.



At 24th March 20:25 a leakage occurred that was stopped at 25th March 09:06 and repaired during the period until 27th March 20:36. The leakage caused 120 ml of CO₂-containing water to back-flow through the core sample from the outlet end to the inlet end. During the back-flow the differential pressure across the sample increased to a maximum of 91 bar and the NOB increased to a maximum of 209 bar, which is 89 bar above the nominal NOB of 120 bar.

After repairing the leakage, the CO₂-flooding was resumed at 27^{th} March 20:36. This second part of the CO₂-flooding lasted until 5th April 09:26. The volume of injected CO₂ in the second part of the CO₂-flooding was 283.2 ml equivalent to 2.094 PV. The combined volume of injected CO₂ in the first and second parts of the CO₂-flooding was 382.5 ml or 2.83 PV.

Breakthrough in the second part of the CO_2 -flooding took place 29th March 00:05 after injection of 35.1 ml of CO_2 equivalent to 0.259 PV. After breakthrough the fluid density log resumed the trend with decreasing fluid density from the first part of the CO_2 -flooding. At the end of the flooding the fluid density had dropped to 0.694 g/ml which indicates that the produced fluid was nearly pure CO_2 .

At the end of the CO_2 -flooding the permeability to CO_2 was 0.034 mD.

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5.5. Water flush

After the CO₂-flooding, the core sample was flushed with water. A log of the water flush is given in Fig. 5.3. The flush started at 6^{th} April 08:59 and stopped at 11^{th} April 15:47 after injection of 193.1 ml of water equivalent to 1.427 PV. At the end of the brine flush the permeability to water was 0.123 mD.



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5.6. Compaction

During experiment FS-3 the position of the floating end piece of the core-holder was determined a number of times. The determinations were made manually with a caliper at convenient times, i.e. at times when the thermal disequilibrium created by the determination did not disturb other parts of the experiment. Fig. 5.4 presents a log of the caliper results.

During the initial pressurization of the sample from a NOB of 25 bar at 9th March 14:30 to a NOB of 120 bar at 10th March 17:30, the sample showed a length reduction of 1.02 mm.

Between 10^{th} March 17:30 and 18:26 where a technical failure caused the NOB to increase shortly from 120 bar to approximately 220 bar, the sample showed an additional length reduction of 0.51 mm to a cumulative length reduction of 1.53 mm.

During the heating of the rig and the first part of the ageing period the sample showed an additional length reduction of 0.52 mm to a cumulative length reduction of 2.05 mm.

During the last part of the ageing period and the CO_2 -flooding a further length reduction of 0.15 mm was took place to a cumulative length reduction of 2.20 mm. This period includes the failure on 24th March where the NOB increased to 209 bar.



During the depressurization and cooling of the rig the sample expanded 1.33 mm, leaving a

permanent length reduction of 0.87 mm.

5.7. Dissolution structures

After the CO_2 -flooding, the inlet end face of the composite sample FS-3, that is also the inlet end face of sub-sample 1A-142, did not show visible signs of dissolution, Fig. 5.5.

The outlet end face of composite sample FS-3, that is also the outlet end face of sub-sample ST-08A, did show clear signs of dissolution: A groove was etched at the centre of the end face, adjacent to the point where the outlet tube of the core holder is positioned. Some fractures present in the sample end face also appeared slightly etched, Fig. 5.6. The central



Fig. 5.5. Inlet end of composite sample FS-3, sub-sample 1A-142, after CO₂-flooding.

groove was not present before the CO_2 -flooding experiment, while the fractures were present before the CO_2 -flooding, cf. Fig. 5.6. The etchings are probably caused by the back-flowing water during the leakage that occurred on 24th March 20:25. The back-flowing water contained a significant amount of dissolved CO_2 that probably caused the etching. The end faces further back in the composite sample did not show any visible signs of etching.



Fig. 5.6. Left: Outlet end face of composite sample FS-3 before CO_2 -flooding, sub-sample ST-08A. Right: Outlet end of sample FS-3 after CO_2 -flooding, sub-sample ST-08A. The mesh pattern visible on the outlet end face after flooding is an impression of the inlet filter of the core holder. Diameter of sample is 37 mm.

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6. Documentation

The CD attached to this report contains the following documentation:

- 1. The present report in file FinalRep_ExpFS-3_v1.pdf
- 2. Measurements of the position of the core holder floating end piston in Excel file CoreHolderPiston_FS3_v5_export.xls
- 3. Log files of flooding experiment FS-3 covering the period 1st March 2010 10:24 to 11th March 2010 12:21 in Excel file FS3_01mr10_v2_export.xls.
- 4. Log files of flooding experiment FS-3 covering the period 11th Match 2010 12:20 to 14th April 2010 15:31 in Excel file FS3_11mr10_v7_export.xls.
- Images of samples taken on 3rd March 2010 before flooding experiment FS-3 in folder BeforeExp_3mr10.
- 6. Images of samples taken on 15th April 2010 after flooding experiment FS-3 in folder AfterExp_15ap10.

The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four themes: Water Resource Engineering, Urban Water Engineering, Residual Resource Engineering and Environmental Chemistry & Microbiology. Each theme hosts two to five research groups.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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