Water weakening of chalk

A mechanistic study

Doctorial Thesis by

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Thesis submitted in fulfillment of
the requirements for the degree of
DOCTOR OF PHILOSOPHY
(Dr. Ing.)

University of
Stavanger

Faculty of Science and Technology
Department of Petroleum Engineering
2005

Dedicated to a very special person,
my supervisor
and friend, Rasmus.

Acknowledgements

We realised that we had to deeply listen to him whenever he was speaking about chalk (few words and deep ideas) because he knew a lot and we had a lot to learn from him.

Professor Pierre Delage
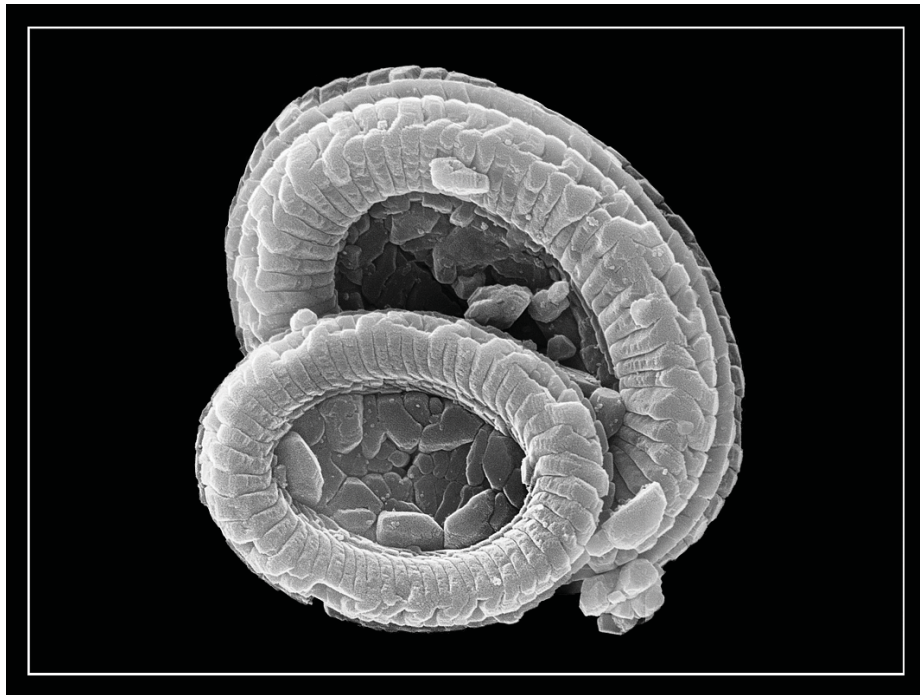
List of Papers

I   **Madland, M.V., Korsnes, R.I. & Risnes, R. (2002):** Temperature effects in Brazilian, uniaxial and triaxial compressive tests with high porosity chalk. SPE 77761, *SPE Annual Technical Conference and Exhibition,* San Antonio, Texas, 11 pp.

II   **Risnes, R., Madland, M.V., Hole, M. & Kwabiah, N.K., 2004:** Water weakening of chalk - Mechanical effects of water-glycol mixtures. *Journal of Petroleum Science and Engineering* **(in press)**, 26 pp.

III   **Heggheim, T., Madland, M.V., Risnes, R. & Austad, T. (2005):** A chemical induced enhanced weakening of chalk by seawater. *Journal of Petroleum Science and Engineering*, 46, 171-184.

IV   **Madland, M.V., Finsnes, A., Alkafadgi, A., Risnes, R. & Austad, T., 2005:** The influence of CO_2 gas and carbonate water on the mechanical stability of chalk. *Journal of Petroleum Science and Engineering* **(under referee),** 31 pp.

Contents

1.0 Introduction

Since the detection of the Ekofisk subsidence some 20 years ago, there has been a considerable research activity concerning chalk behaviour in general, and mechanical properties particularly. Due to the importance of water injection into chalk reservoirs to improve oil recovery, an extended experimental testing has been performed in order to further investigate the so-called *water weakening* effect. The mechanisms behind well instability, compaction, and subsidence experienced in the North Sea chalk reservoirs are, however, not completely understood.

1.1 Oil recovery from carbonates

Carbonate reservoirs are usually strongly fractured and the permeability varies considerably between matrix blocks and fractures. Spontaneous imbibition of water is an important improved oil recovery (IOR) technique, when considering oil recovery from highly fractured carbonates reservoirs with low-permeability matrix blocks (Chen et al. 2001). Due to the fact that approximately 90 % of carbonate reservoirs are neutral to oil-wet, and knowing that imbibition is described as a process, which sucks the wetting fluid into a porous medium by capillary attraction, no spontaneous imbibition of water will take place in these reservoirs (Rao et al. 1996). If, however, the rock wettability is altered from oil-wet to water-wet, a positive value of the capillary pressure is obtained, which causes a spontaneous imbibition of the injected water from the fractures into the matrix blocks, and the oil will be expelled. Several studies by Austad et al. (2005) have shown that the wettability of a chalk reservoir can be altered from preferential oil-wet to partly water-wet by using surfactants, or by simply using seawater as injection fluid.

1.1.1 Drive mechanisms

On the Norwegian sector in The North Sea, the Ekofisk field is an overpressured, naturally fractured high porosity chalk reservoir. The field produces a volatile oil from two chalk formations, the Ekofisk from the Danian age of the Palaeocene period, and the Tor from the Maastrichtian age of the Cretaceous period (Sylte et al. 1999). Production started in 1971, and the field produced with oil expansion, solution gas drive, reservoir compaction, and limited natural gas injection as the primary drive mechanisms until waterflooding started in 1987. Initially, the reservoir temperature was 130 $^{\circ}$C, and the initial pore pressure was approximately

7,000 psi (48.3 MPa). The overlying 9,500 ft (2900 m) of sediments and water exerted a load equivalent to 9,000 psi (62.1 MPa) on the reservoir. The chalk matrix was therefore initially exposed to net effective stress of 2,000 psi (13.8 MPa) (Sulak et al. 1989). During the period of primary depletion, the reservoir pressure declined below 3,500 psi (24.2 MPa) in large parts of the field, which did cause an increase in net effective stress (Gauer et al. 2002).

i. Compaction and pressure depletion

Significant pressure depletion may lead to compaction in weak formations. Subsidence may occur due to the transmission of compaction through the rock layers overlying the depleted formation (Nagel 1998). During the oil production by pressure depletion at the Ekofisk field, compaction of the reservoir took place. Seabed subsidence was not expected, but it was detected in 1984, and it was suggested that reservoir compaction was probably a more important mechanism for hydrocarbon production than previously assumed (Sulak et al. 1991). About 10 meters of seafloor subsidence has occurred at the Ekofisk Field since the start of production in 1971, and the rate of subsidence is reported to be almost 0.4 m per year (Nagel 1998; Gauer et al. 2002). This seafloor subsidence is due to compaction of the chalk reservoir, which is a result of both pore pressure depletion early in the field life, and water weakening induced by water injection at later stages (Gauer et al. 2002). Even after injection of large quantities of seawater, compaction and subsidence is still persisting in spite of an almost constant or slightly increasing average reservoir pressure (Maury et al. 1996; Teufel et al. 1991).

ii. EOR; Water injection and wettability alteration

Luckily, the highly fractured chalk reservoir at the Ekofisk field appeared to be preferentially water-wet towards seawater, and secondary oil recovery by injection of seawater was performed in order to improve the oil recovery and to reduce the compaction (Thomas et al. 1987). In general, injection of water into oil reservoirs is an important method to improve oil recovery for at least two reasons, i.e. the reservoir pressure is maintained above the bubble point pressure (undersaturated reservoir fluid), and the sweep efficiency is improved. In water-wet to mixed-wet fractured chalk reservoirs, with matrix blocks of low permeability, injected water will imbibe spontaneously into the matrix blocks and displace the oil (Torsæter 1984; Thomas et al. 1987). The fractures will then act as transport zones for both the injected water and the displaced oil. If, however, the matrix blocks are oil-wet, spontaneous imbibition of water will not take place due to the small or negative capillary pressure. The injected water will then follow the fractures

from the injector to the production well without displacing any significant amount of oil, and the result will be an early breakthrough and poor sweep efficiency.

The initial wetting state is mostly governed by the properties of the crude oil, where the acid number, AN (mgKOH/g), appeared to be a crucial parameter. The reservoir temperature, however, appeared to play a minor role as a wetting parameter (Zhang & Austad 2005). The relative high specific surface area of chalk, about 2-3 m^2/g, indicates that compositional properties of injected fluid could influence the wetting properties of the formation somewhat during the production phase. The exceptional good response of seawater injection into the Ekofisk Formation is an indication of a special rock-water interaction, which improves the spontaneous displacement of oil. The concentration of Ca^{2+} in the formation brine is usually high, which makes the water-rock interface positively charged. It is documented that Ca^{2+} is a strong potential determining ion towards chalk (Pierre et al. 1990). The oil-water interface is, however, negatively charged because of surface-active carboxylic material present in the crude oil. The waterfilm between the rock and the oil then becomes instable, and the rock will be in contact with the oil. The carboxylic compounds adsorb strongly onto the chalk surface, and the rock will act mixed-wet or even preferential oil-wet if the acid number (AN mgKOH/g) of the crude oil is high enough (Standnes & Austad 2000). An injection fluid contaning sulfate, SO_4^{2-}, like seawater, has the potential to reverse the wetting conditions, i. e. to make the rock preferential water-wet, and thereby improve the imbibition of water (Austad et al. 2005). The process is sensitive to the Ca^{2+} / SO_4^{2-} ratio and the temperature (Høgnesen et al. 2005; Zhang et al. 2005). Thus, even though sulfate is usually regarded as a problem due to scale formation ($BaSO_4$, $SrSO_4$, etc.) and souring (H_2S formation), it is a strong potential determining ion towards chalk, which can turn the surface negatively charged (Pierre et al. 1990). Desorption of negatively charged carboxylic matter is then facilitated, and positive capillary forces are created. The adsorption of sulfate onto chalk increases as the temperature increases (Strand et al. 2005).

iii. <u>Water weakening of chalk</u>

As water injection is one of the methods used for improved oil recovery, the question of the influence of water has received a lot of attention during the last decades. After compensating the decrease in pore pressure by injection of large amounts of water into the Ekofisk field, it is noticed that some compaction is still taking place (Maury et al. 1996; Teufel et al. 1991). The phenomenon has been termed "*water weakening of chalk*", and different mechanisms have been suggested. Chalk is, however, in many respects a very

complicated material, which has still not revealed all its secrets. The basic mechanisms behind this water weakening are still not completely understood.

1.2 Mechanical stability of chalk

Pure high porosity chalk is a reservoir rock for several oil and gas fields in the southern part of the North Sea. Ekofisk, Eldfisk, and Valhall in the Norwegian sector are maybe the most known examples, but important chalk reservoirs also exist on the Danish sector. Many of the chalk reservoirs have preserved high values of porosity, sometimes exceeding 40 %. Early invasion of hydrocarbons together with formation of overpressures, has prevented normal compaction, and limited the diagenetic processes (Machel 1999; Bell et al. 1999; Fabricius 2003).

1.2.1 Properties of chalk
i.   Geological
Apart from being an important reservoir rock, chalk is by itself a very fascinating granular material. Pure chalks are mainly built up of whole and fragmentary parts of the skeletons produced by planktonic algae known as coccoliths. The building blocks of these skeletons are calcite tablets or platelets with typical dimensions of 1 μm, while intact coccolith rings have diameters of the order of 10 μm. A typical picture of the structure of such chalks is presented in Fig. 1.1. This scanning electron microscope (SEM) picture illustrates the relatively open structure of the chalk material. The dimensions of the pores may be considerably greater than the dimensions of the individual grains, making such chalks highly susceptible to pore collapse.
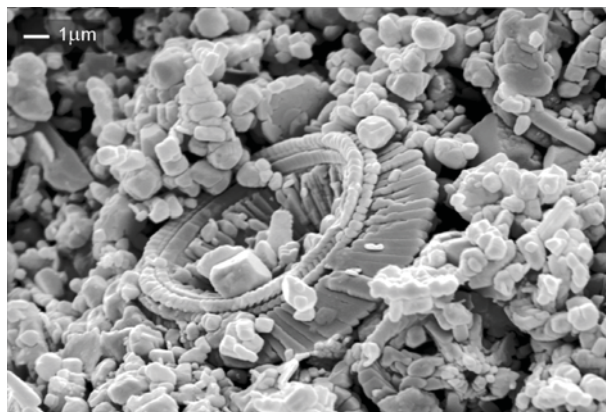
Figure 1.1. SEM photo of chalk from Aalborg (photo: M.L. Hjuler).

The nature of the bonding elements in such high porosity chalks is still not completely understood. By examining SEM pictures, like the one presented in Fig. 1.1, cement bonds between the grains is rarely, if ever, seen. But that does not imply that such bonds do not exist within the chalk material. If dry pieces of intact and deformed chalk are submerged in water, nothing happens to the intact chalk, while the deformed chalk disaggregates into a heap of chalk powder as water enters into the material (Risnes et al. 1994). In the work by Matà (2001), it has been shown that small recrystallized calcite crystals may act as bridges between the grains.

The picture in Fig. 1.1 is taken from an outcrop chalk from Roerdal near Aalborg, but the structures of high porosity reservoir chalks are rather similar. The presence of overpressured hydrocarbons at an early stage has prevented many reservoir chalks from being naturally compacted, and they have to a great extent preserved their high porosities, often 40 % or more.

ii.   **Mechanical**

Mechanically, high porosity chalks behave as frictional material, failing in a shear failure mode. The open structure of the rock matrix enhances another failure mechanism, often referred to as pore collapse (Blanton 1981). Chalk grains may be forced relatively easily into the pore space, resulting in a kind of internal implosion. This type of failure may take place even under hydrostatic loading where no macroscopic shear stresses are present. (Fjær et al. 1991). Microscopically, failure will be due to local excessive shear forces across grains and grain contacts, and pore collapse will thus largely be regarded as distributed shear failure within the material. The yield envelope for high porosity chalks may therefore be described by a Mohr-Coulomb criterion with an end-cap. Expressed with principal stresses, the Mohr-Coulomb criterion can be written:

$$\sigma_1' = 2S_o \tan \beta + \sigma_3' \cdot \tan^2 \beta \qquad (1.1)$$

where S_o = cohesion or inherent shear strength
β = failure angle, $\beta = 45^o + \varphi /2$
φ = internal friction angle
σ_1' and σ_3' = greatest and smallest effective principal stresses.
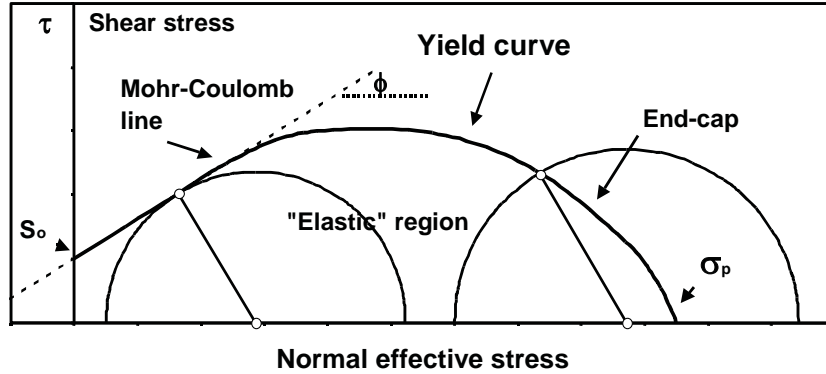
Figure 1.2. Mohr τ-σ' diagram.

The strength of the chalk is characterised by 3 parameters, the cohesion S_o, the friction angle φ, and the hydrostatic yield value or the pore collapse stress σ_p. According to in-house laboratory experience, there is a rather gradual transition from shear failure at low confining pressures to an increasing degree of pore collapse with higher confining pressures. But this is still a matter of dispute in chalk research. Other laboratories have reported sharper transitions between the shear failure and the end-cap regions (Schroeder & Shao 1996; Havmøller & Foged 1996).

The Mohr plot is not particularly suited for presentation of the end-cap part of the yield curve. When the pore collapse mechanism is activated, the interior of the Mohr circles cannot be assumed to belong entirely to the elastic region. It is therefore no longer true that the yield curve, in the sense of presenting the elastic limit, can be drawn as the envelope to the Mohr circles. In the end-cap region, the yield curve will plunge into the Mohr circles to approach the hydrostatic yield value. A consistent way to draw the yield curve is to assume the same failure angle as obtained in the shear failure region, as indicated in Fig. 1.2. This approach is supported by the fact that the failure angles observed on the samples after testing show no systematic change with increasing average stress level (Risnes 2001).

Yield and failure data are often presented in *q-p'* diagrams as shown in Fig. 1.3. Generalized shear stress *q* is defined by:

$$q = \frac{1}{\sqrt{2}} \sqrt{(\sigma_1' - \sigma_2')^2 + (\sigma_2' - \sigma_3')^2 + (\sigma_1' - \sigma_3')^2} \qquad (1.2)$$

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which reduces to the stress difference for tests on cylindrical samples where two of the principal stresses are equal. The prime denotes effective stress, but in the formula for q, only stress differences appear, and total stresses could be used as well. The average effective stress p' is given by

$$p' = \frac{1}{3}(\sigma_1' + \sigma_2' + \sigma_3')$$ (1.3)

These parameters are especially convenient in tracing out the yield envelope in the end-cap region, where the envelope to the Mohr circles no longer gives the yield curve. The q-p' parameters also permit to easily trace the stress path followed in the experiment.
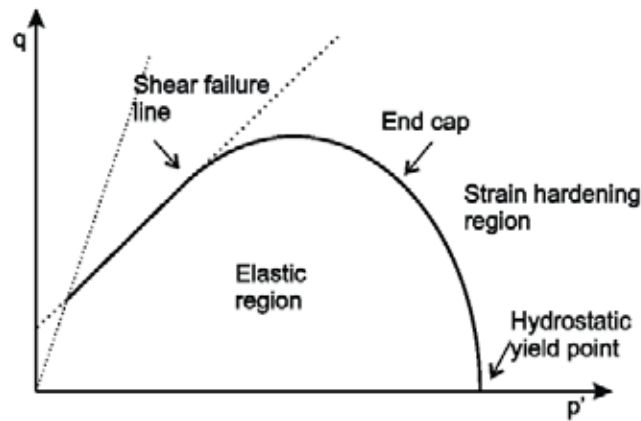
Figure 1.3. q-p' plot.

The chalk behaviour within the yield envelope is often referred to as elastic. Although the stress-strain response in this region is more or less linear, the material is far from being elastic. In performing stress cycles within the "elastic" area, the deformation modulus may increase by a factor of 2 to 3, and at constant load, creep deformation will occur (Risnes & Nygaard 1999). The irreversible part of the strain in the "elastic" domain may largely be due to frictional sliding between the grains, while yield then is associated with a transition to a deformational mode, where breaking of bonds is the dominating mechanism.

Shear failure between the grains seems to be the basic failure mechanism, not only in compression tests at low confining pressures where

shear bands are formed, but also in pore collapse, where distributed shear failure will occur in the material. Also tensile failure seems to be initiated by a shear failure mechanism, and as shown by Risnes et al. (2000), tensile strength can be predicted from the compressive Mohr-Coulomb yield criterion.

At an early stage, it was seen that the water weakening effect also affects the tensile strength as obtained in Brazilian tests (Risnes et al. 2000). The use of the Brazilian test raised the question of how this test correlates with the mechanical parameters obtained in compressive tests. In many rocks, tensile failure is associated with extensional cracks, resulting in a much lower tensile strength than predicted from compressional yield data. But this does not seem to be the case for high porosity chalks. As seen from Fig. 1.4, the compressive stress at the centre of the sample is 3 times the tensile stress perpendicular to the loading direction (Ripperger & Davids 1947). This relation makes it possible to draw the Mohr circle corresponding to failure.

The rather close relation between the Brazilian test and the Mohr-Coulomb failure criterion, probably valid only for high porosity chalks, can be exploited when cohesion and friction angle are to be determined. The cohesion value will be rather close to the intersection between the Brazilian circle and the shear stress axis.
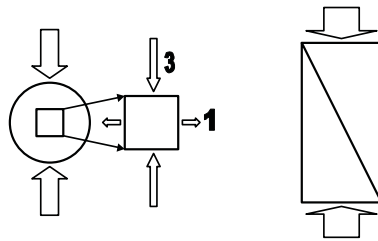
Figure 1.4. Brazilian and uniaxial compressive strength test.

The S_o value may thus be approximated by;

$$S_o \approx \sqrt{3} \cdot T_{oB} \tag{1.4}$$

Combined with uniaxial compressive tests, as seen from Fig. 1.5, estimates for the friction angle, φ, may also be obtained.
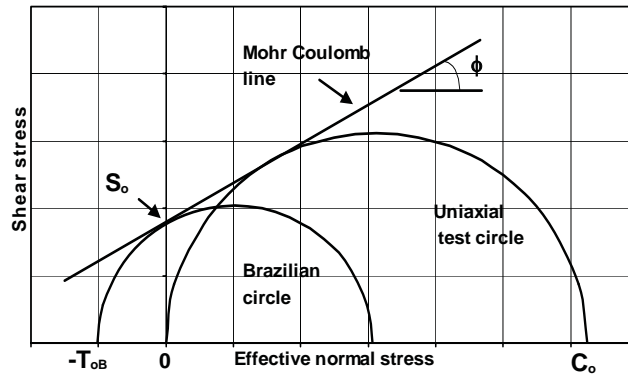
Figure 1.5. Mohr plot of Brazilian and uniaxial circles.

1.2.2 Chalk-fluid interactions

The strength of a chalk depends first of all on porosity and the silica content (DaSilva et al. 1985). The mechanical properties of high porosity chalk are also strongly dependent on the type of fluids in the pores. The generalized yield curves presented in Fig. 1.6, reflect in-house experience with outcrop chalk (Liège and Aalborg) and different fluids assembled through the years (Risnes 2001). Similar results have, however, been obtained in other laboratories, for instance by Monjoie & Schroeder (1989) and Delage et al. (1996). Dry, or air saturated, chalk is strongest. Saturated with oil or glycol, the strength is somewhat reduced, more or less to the same extent (Risnes et al. 2003). The most important strength reduction is obtained with water, while methanol is somewhere in between water and oil (or glycol). The weakening effect of the fluids seems to be a general one. All the strength parameters are affected; cohesion, friction angle, and hydrostatic yield stress. It is also seen that this fluid effect is not a small one. In going from dry to water saturated chalk, the hydrostatic yield value is reduced by almost a factor of 2. Also "elastic" properties are affected. It should be noted, that according to our experience, the region where a straight-line criterion is applicable, is limited to low confining pressures, typically less than 1-2 MPa.

Another important thing to notice is that "dry" chalk is not really dry. Heating to higher temperatures beyond standard drying temperature (approx. 110 ^{O}C) results in additional water loss and gain in strength, and this strenght increase seems to be reversible (Madland 1999). From previous studies, it is

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seen that very little water is needed to activate the water weakening mechanism (Schroeder et al. 1998; Lord et al. 1998; Madland et al. 1999).
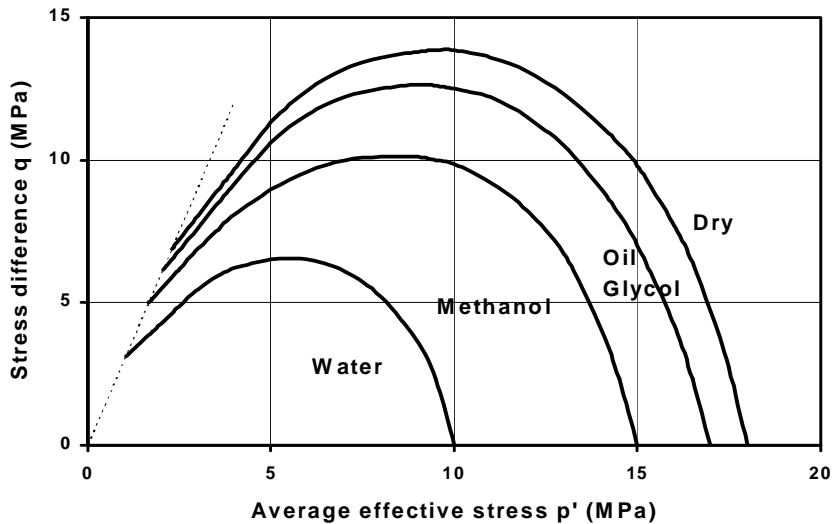
Figure 1.6. Typical yield curves for different fluids.

Chalk and fluids may interact through capillary forces and through surface physico-chemical reactions. Capillary forces will always be present when two immiscible fluids are present in the pore space. Capillary effects may, however, be removed by flooding with water or by saturation with a water-miscible fluid. One of the major results obtained by Risnes et al. (2003), was that the mechanical strength of glycol-saturated chalk appeared to be similar to that of oil-saturated chalk. As glycol is fully miscible with water, there should likewise be no capillary effects in glycol-saturated chalk. From this point of view, Risnes concluded that if water bridges between the grains were assumed to exist in "dry" and oil-saturated chalk, the effect of capillary forces must be rather small. In the same study, Risnes also showed that it is not only the amount of water that is of importance when discussing water weakening of chalk, but also the composition of the saturating fluid. He therefore suggested that the *activity of water* was a key parameter in the water-weakening mechanism.

Hellmann et al. (2002a) concluded that the chemical nature of the pore fluid plays a critical role in determining deformation rates. Their experimental results showed that the strain rate decreased in the following

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order: saline solution>water>propanol, and the strain rate was thus correlated with calcite solubility. Hellmann et al. (2002a) gave an explanation to the entire behaviour pattern as observed in the experiments performed with chalk saturated with different pore fluids (Fig. 1.6); *"......It is of interesting to note that the order of fluids with respect to increasing mechanical resistance of chalk (Delage et al., 1996 and Schroeder & Shao, 1996) follows qualitatively the solubility of chalk in these fluids, in decreasing order; in other words, the mechanical strength varies inversely with solubility"*.

1.2.3 Mechanisms of water weakening

For almost 20 years, the Ekofisk field has been water flooded with seawater in order to increase production and to mitigate subsidence. Extensive studies of water flooding of reservoir chalk have also been executed (Heugas & Charlez 1990; Rhett 1990 and 1998; Andersen et al. 1992; Piau & Maury 1994; Springer et al. 1996; Foged et al.1996; Sylte et al. 1999 among others). Hydrostatic, triaxial and oedometric tests have been conducted under conditions of stress and fluid saturations closely simulating the in-situ reservoir environment. Laboratory results indicate that the response to core flooding depends mainly on the initial water saturation of chalk. Core samples with initial brine saturation varying from 5 to 50 % (initial water saturation of the chalk varied from which part of the field the cores originated from) were waterflooded, and the weakening effect of the chalk was larger if chalk was already in a plastic state, but it does, however, also occur in the elastic state. With reference to Rhett (1990) and Foged (1996), the water-saturated chalk appeared to show a reduced pore collapse stress and higher creep rates compared to hydrocarbon-saturated chalk. From laboratory evidences in another study by Rhett (1998), possible organic coatings on the chalk surface seemed to protect portions of chalk from the weakening effect of formation brine. Rhett (1998) concluded, that water flooding of oil reservoirs would cause degradation of these protective coatings with the consequence of increased contact between water and calcite, which would lead to a weakening of the chalk and an enhanced compaction of the reservoir. Recently, it was confirmed by the studies of Austad et al. (2005) that seawater has the properties to increase the water wetness of chalk, especially at high reservoir temperatures.

Possible water weakening mechanisms have mostly been discussed in terms of pure physical interactions between grains. Mechanical stability of chalk has often been related to capillary forces, which is known to induce an apparent cohesion between chalk grains although several researchers have pointed out that other mechanisms need to be considered as well.

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Chemical effects have received a rather limited attention. In the paper of Gutierrez (2000), it is, however, reported as early as 1966 that an experimental study on the formation of aggregates of gypsum showed the effects of chemical compaction in terms of additional creep. Newman (1983) and Heugas & Charlez (1990) have also emphasized chemical effects and suggested dissolution as the main and secondary mechanism behind water weakening of chalk. In the monograph of M. Andersen (1995), which is based on investigations conducted largely over the time period between 1980 to 1992, it is, however, claimed that most authors believe the effect is of physical nature (Rhett 1990; Heugas & Charlez 1990; Loe et al. 1992; Andersen 1992) due to the fact that the amount of dissolved chalk is too small to explain the observed compaction (Rhett 1990). Andersen et al. (1992) reported an immediate compaction of the chalk when water is injected into an oil-saturated chalk. They conluded that this compaction front, which accompanied the water flood front through the chalk material could not be due to chemical effects, but rather a physical response of the weak chalk matrix.

Laboratory testing has so far quantitatively documented the process of chalk compaction, however, direct evidence for the actual mechanism(s) through which the process operates is not documented.

i.   **Physical effects**

After the subsidence of the seafloor above the Ekofisk reservoir was detected (1984), there has been a considerable research activity concerning chalk behaviour in general, and mechanical properties in particular. In an experimental study by Johnson & Rhett in 1986, it was concluded that the pore collapse deformation of high porosity chalk accounted for the majority of the reservoir compaction and subsidence, which had currently been observed until then. Schroeder & Shao (1996) also stated that pore collapse is the main mechanism for irreversible deformation in chalk. They also emphasized or highlighted the effect of capillary forces on the plastic behaviour of chalks.

It was Colback & Wiid (1965) who first identified the variation of rock mechanical properties with different degrees of saturation. In 1994 Brignoli et al. wrote; *"It is well known that capillary pressures are generated when a rock is partially saturated (this is what is called suction) or when chemical differences are induced between the fluids saturating the rock itself (osmosis); from these points of view, the effect of capillary pressures is an important aspect of the mechanical behaviour of soils".* Due to the fact that chalk is a reservoir rock with very small pores, they suggested that these capillary effects also could have important consequences on chalk behaviour.

Since the early 1990´s, weakening of chalks has been discussed in terms of capillary effects and/or wetting effects by several researchers

(Andersen et al. 1992; Piau & Maury 1994; Brignoli et al. 1994; Delage et al. 1996; Schroeder et al. 1996 and 1998; Papamichos 1997). By comparing experimental results from reservoir chalks and unsaturated soil, Delage & Cui (1996) showed that the mechanics of unsaturated soils provided a powerful framework for understanding the mechanical effects of water flooding in chalk reservoir rocks. They also concluded, that chalk compaction could be related to the collapse mechanism of unsaturated soils, and that the use of a well established constitutive model for unsaturated soils could describe the hydro-mechanical history of the chalk from its deposition to the oil exploitation. Mary & Piau (1994) proposed a refined model for short-term chalk-water interaction. Although they used capillary forces as the mechanism within this model, they suggested that a direct effect of capillary pressure probably should be discarded. They also mentioned the action of very local shear forces exerted by oil/water menisci on grains (Andersen et al. 1992) and suggested the existence of very localized and quasi-instantaneous chemical actions of brines on grain-to-grain contacts as possible weakening mechanisms.

Lord et al. (1998) produced a very strong argument against the theory of capillary suction. They used a thermal desorption method with a mass spectrometry technique to quantify the amount of adsorbed water that remains in "dry" chalk, and the obtained data indicated that the residual water content was 20 times too low to support capillary water menisci. In line with others (Heugas & Charlez 1990; Maury & Piau 1994), also Lord et al. (1998) pointed out that an alternative weakening mechanism, such as mineral dissolution at the grain-to-grain contacts, needed to be considered in order to explain the water weakening effect.

Gutierrez et al. (2000) performed an experimental study on the effect of fluids on the mechanical behaviour of natural fractures in chalk. They also considered other limited results available concerning the effects of water saturation on the frictional strength of intact chalk (Risnes & Kristensen 1996; Papamichos et al. 1997). Gutierrez et al. (2000) concluded that the best hyphotehsis for the mechanism of chalk-water interaction is; *"...a combination of capillary pressure, which accounts for the instantaneous volume change and reduction in apparent cohesion, and chemical dissolution/grain surface modification, which accounts for the reduction in frictional strength and some of the volumetric change."* As mentioned previously, the study with brines and glycol-saturated chalk performed by Risnes et al. (2003) led to the conclusion that capillary effects would play only a very minor role in chalk-fluid interactions.

ii.   **Physico-chemical effects**

Since the early 1990´s, "suction" was mainly considered to be generated by capillary effects. Based on experimental observations within the Pasachalk EC Project, the capillary force model was extended to a more general concept, which also includes various existing physico-chemical chalk-water interactions. In a study by De Gennaro et al. (2003), creep effects under controlled suction levels were investigated. An osmotic technique as well as an overpressured method (porous plate method), allowing for the independent control of both of the fluid pressures, was used to control suction. Increased suction levels caused stiffer response in the elastic regime, the mean total stress at yield was increased, and a more pronounced transition from elastic to elastoplastic regime when yield occured was observed. Evolution of creep seemed also to be affected by suction, i.e. a decrease in suction caused increasing volumetric strain rate and a progressive early dominance of creep.

In the study by Rhett et al. (1990), the increase in compaction rate, which was observed as the initial waterfree samples (i.e. with 100 % oil saturation) of reservoir chalk were exposed to injection of an aqueous solution (seawater or formation water), was suggested to be related to the adsorption of water on the chalk surface. Additionally, also stress corrosion was mentioned as a possible mechanism. The stress corrosion effect, which has been observed in sandstones (Hadizadeh & Law 1991; Ojala et al. 2003), is a well-known phenomenon within the field of hard rock mechanics. Highly stressed silicon-oxygen bonds at micro-crack tips may be hydrolysed and weakened, permitting the crack to propagate. This weakening process is time dependent through the diffusion rate of water molecules to the crack tip.

Risnes et al. (2003), proposed a new perspective for the physico-chemical explanation of the chalk-fluid interaction, and the most important conclusion drawn from this study was that the activity of the fluid seemed to be a key parameter in the water-weakening mechanism.

iii.   **Chemical effects**

Although several researchers have suggested that dissolution at grain-to-grain contacts should be considered (Mimran 1974 and 1977; Hancock & Scholle 1975; Newman 1983; Heugas & Charlez 1990; Maury & Piau 1994; Machel 1998; Lord et al. 1998; Gutierrez et al. 2000; Sylte et al. 1999; Hellman et al. 1996 and 2002a and 2002b; De Gennaro et al. 2003) rather few studies have been performed considering water weakening of chalks from a pure chemical point of view, probably due to the very low solubility of $CaCO_3(s)$ in pure water.

As early as 1983, i.e. four years before the waterflooding of the Ekofisk field started, Newman (1983) emphasized that compaction behaviour

of reservoir chalks depended on the water chemistry of the saturating fluid. He stated that: *"...Therefore, if water injection is considered for the chalk reservoirs and a suitable water is found to prevent dissolution, injection should be performed before pressure depletion and before a significant effective stress is developed within the reservoir."* Newman meant that seawater, as an injection fluid, could have an adverse effect on the rock properties, and therefore formation water or a chemical equivalent was proposed as a better choice. The main conclusion of Newman (1983) was that: *"Compaction is attributed to mechanical failure by dissolution of calcium carbonate at low stresses and to dissolution and pressure solution at high stresses."*

In the study by Gutierrez et al. (2000), it is reported that chemical chalk-fluid interaction or chalk-water interaction by chemical effects is likely to be associated with the migration of ions (Ca^{2+}, CO_3^{2-}), which accompanies dissolution. In the study by Sylte et al. (1999) it is concluded; *".....The sensitivity of the chalk to water most probably results from an intimate chemical interaction between the water and the calcite. This interaction changes the grain to grain relationships within the chalk resulting in easier rotation and translation of the grains. This is reflected as a reduction in the yield stress (though cohesion and internal friction angle are also affected) and an increase in compressibility."*

Increased stresses enhance the solubility of calcite in water, and pressure solution in chalk has also been demonstrated in the laboratory by Mimran (1974), Hellman et al. (2002a and 2002b) and Bjørlykke & Høeg (1997). Over long geological times, chemical compaction by pressure solution results in stylolitization. In a study by Fabricius (2003), it was concluded that in hydrocarbon-bearing chalk, porefilling cementation would be small, probably due to adsorption of polar hydrocarbons preventing pressure dissolution along stylolites. Further on, Fabricius (2003) pointed out that recrystallization may take place because chalk surfaces dissolve and/or grow in constant interchange with Ca^{2+} and CO_3^{2-} ions from the solution. The overall results of this recrystallization are that the crystals become larger, smoother and more regular, and smooth calcite particles may be fused by contact cementation (Fabricius 2003), but this recrystallization does not necessarily result in reduction of porosity (Maliva & Dickson 1992).

Hellmann et al (2002a) concluded that *".....the overall effect of the chemistry of fluids on the deformation behaviour is similar between models based on capillary forces and pressure solution....., the main difference being that the former is based on physico-mechanical interactions between grains, whereas pressure solution is based on chemical dissolution reactions in stressed regions".* The ultimate goal of the study by Hellman et al. (2002a)

was to provide a better understanding of the mechanisms of pressure solution and enlarge the debate concerning the nature of chalk deformation mechanisms. Chalk samples were deformed in the presence of different fluids over long time periods, almost 700 days. The physico-chemical reactions that occur when chalk is exposed to different stress conditions and various fluids at temperatures within the range of 25 to 80 ^{o}C were studied in detail (Hellman et al. 2002a). Within the same study various types of pressure solution models were discussed. The models, based on grain-to-grain contacts, contain a trapped fluid, which cannot be squeezed out by the normal stresses imposed on the grains. The island-channel model, which appears to be a relevant model for porous chalk, posits an intergranular region consisting of solid-solid contacts at islands that support the imposed normal stress. These islands are then surrounded by a network of interconnected channels, which contain fluid. The rate determining step in the water weakening of chalk by such a model may be; (a) solubility of chalk in the actual fluid, (b) transport of dissolved common ions (Ca^{2+} and CO_3^{2-}) in the thin film close to the islands to a more open pore space. The pressure solution deformation of chalk was also investigated by SEM, porosimetry, synthetic permeability and X-ray computerized tomography (Hellman et al. 2002b). The overall conclusion from the study of Hellmann et al. (2002a) is that long-term creep behaviour of chalk points towards a pressure solution mechanism, but they also mentioned that this mechanism could probably be assisted by others when the chalk-fluid system is disturbed or abrupted as after a change in temperature, solution chemistry or effective stress.

Water may also modify the surface properties of the grains by absorbtion into the grain surface layers and this so-called Rehbinder effect (Rehbinder 1957), is also time dependent through diffusion. Surface modification is a mechanism that may be activated in chalks.

In the study by Rhett et al. (1990), and in contradiction to the results of Newman (1983), it was observed that waterfree reservoir chalks from the Tor Formation responded similarly to injections of heated seawater and formation water, despite substantial differences in the chemical composition of the brines. Based on this observation, it was concluded that the dominant mechanism by which seawater or formation brine weakened waterfree chalk, appeared not to be dissolution of calcium carbonate. Several years later Rhett (1998) performed additional seawater and brine injection tests. This time the tests were conducted on chalks from the Lower Ekofisk Formation, and now the results showed a greater response to water injection. From other laboratory observations, Rhett (1998) suggested that these differences in response to water injection possibly could be explained by the existence of so-called organic films (first reported by Baldwin et al. in 1985) or organic coating,

which would protect the chalk matrix from intimate chemical contact with connate brines. Comparing the results from these two studies of Rhett et al. (1990 and 1998), they concluded that the Upper Tor Formation chalk, which is relatively insensitive to water injection, may have a more extensive and/or durable organic coatings protecting the chalk matrix from water flooding compared to the Lower Ekofisk Formation.

1.2.4 Temperature effects

Although the temperature in chalk reservoirs is rather high, only few studies on temperature effects in chalks have been reported, and the results from these studies point in different directions.

In the study by Da Silva et al. (1985), the effect of the temperature on the mechanical properties of reservoir chalks from both the Ekofisk and Tor Formations were evaluated at ambient temperature and 130 $^{\circ}$C, which is the reservoir temperature of the Ekofisk field. Deformation modulus was reported to be unaffected by change in testing temperature for both dry and fluid saturated chalk (water in chemical equilibrium with North Sea Chalk; reconstituted North Sea water and reconstituted water of Upper Danian Formation). They observe a decrease in yield stress as temperature increased, but it was commented that the relative influence of porosity, content of silica as well as solvent extraction could not be evaluated due to the small number of samples. In another study, Brignoli et al. (1994) tested Italian outcrop chalk, and they found a slight decrease in static and dynamic Youngs moduli as temperature increased stepwise within the range of 20-100 $^{\circ}$C. No significant changes were observed for other mechanical parameters.

Risnes (1990) observed a rather strong temperature dependence in a series of chalk extrusion experiments performed with reservoir chalk from a Danish offshore gas field. Cylindrical water saturated samples were compressed axially in a rigid oedometer type cell. Tests were performed both at 20 and 90 $^{\circ}$C. At low stresses, the increase in temperature seemed to soften the chalk, but as the stress level increased, the high temperature chalk became stiffer, and a much higher extrusion pressure was needed. These experiments were carried out with deformation control, but the same temperature effect was later seen with a load control equipment (Bukkholm 1990).

A study by Charlez (1992), also on a Danish reservoir chalk, but from a different field, concluded in a strong temperature effect in pore collapse failure, however, no effect at shear failure conditions was observed nor did the thermoporoelastic parameters seem to be affected by temperature. Another study by Addis (1989) showed no significant temperature effects in uniaxial strain compaction experiments.

The chalk samples used within these previous studies were mainly reservoir chalk, and it should be emphasized that the porosity as well as silica content varied from sample to sample. Additionally, only a few numbers of samples were tested in each study, and it appeared impossible to draw any definitive conclusion from these works.

Laboratory testing has been reported on outcrop chalks in order to determine the thermal expansion coefficient of chalks (NGI 2003). Six chalks from six different locations in Belgium, Denmark and England were tested. The study documented only small variations in the dry linear thermal expansion (3.3-5.5E^{-6} ^{o}C^{-1}) between outcrop chalks with varying porosity (23-49 %) and calciumcarbonate content (79-96 %). The effects of introducing brine into the pores and the effect of stress on the coefficient of thermal expansion of chalk was not investigated in this study (NGI 2003).

Temperature was one of several parameters, which Hellmann et al. (2002a) investigated in their study. They reported that increasing temperature seemed to have two main consequences with respect to the rate of pressure solution and chalk weakening. As calcite solubility decreases, the rate of diffusion increases with temperature. From their experiment, where temperature was raised sequentially from 25 to 60 to 80 ^{o}C, they conclude that the dependence of the deformation rate on temperature seemed very weak. As far as the author knows, except for the work of Hellman et al. (2002a), no long-term creep tests on chalk saturated with different fluids and at various temperatures have been performed. Since rock-fluid interaction in thin films close to the inter-grain contacts is time dependent (Hellman et al. 2002a), a study considering long-term testing on companion samples at different temperatures levels should be further investigated. Testing temperature is of course an important parameter, especially if chemical effects are of significant relevance in water weakening of chalks. In the labortatory it is sometimes difficult to discriminate whether the process is determined by kinetics or thermodynamics.

2.0 Objectives

Compaction of chalk reservoirs are experienced by the Ekofisk field, and it is not only a result of an increase in effective stresses linked to oil recovery and pore pressure depletion. W*ater weakening* induced by water injection has been, and certainly still is, of viable concern. Laboratory studies have been performed worldwide, and different mechanisms have been proposed. Nevertheless, the main mechanism behind this *water weakening* is still not fully understood.

Although, compaction due to chemical dissolution of chalk at the grain-to-grain contacts has been indicated by several research groups to account for the pore collapse, serious experimental documentation is lacking. The main objective of the thesis is to gain further insight into the mechanisms behind *water weakening* of chalk, and to focus on the relationship between physico/mechanical and chemical effects. The experiments have been designed to obtain new information using different types of mechanical tests by focusing on the following aspects:

- *Water weakening* related to changes in temperature.
- Relationship between *water weakening* and water activity.
- Quantification of chemical induced *water weakening* by removing the common ions, Ca^{2+} and/or CO_3^{2-}, from the equilibrium solution.
- Discuss and extend the knowledge of the mechanism behind the *water weakening* of chalk.

3.0 Material and methods

3.1 Chalk material

Chalk formations appear on the surface many places in Europe. This offers the possibility of finding outcrop chalk with properties similar to that of the reservoir chalks. As core material from chalk wells usually is rather limited, outcrop chalks represent an interesting substitute and available in large quantities. Outcrop chalk from three different quarries has been used in this study.

The first one came from the quarry of Lixhe near Liège in Belgium, and is referred to as Liège chalk. This chalk is an ideal candidate for methodical studies, being reasonably homogeneous and isotropic, and having high porosity and low silica content. It has also been extensively used in chalk research, and the properties are reasonably well known (Monjoie & Schroeder 1989). Typical data for the Liège chalk are:

Age	Upper Campanian
Porosity approx.	42 %
Silica content	< 2 wt %
Permeability	1-2 mD (1-2 $\cdot$ 10^{-15} m^2)

The second chalk was taken from the quarry of Roerdal close to Aalborg in Denmark. This chalk has a higher porosity but also a higher silica content. Typical values are:

Age	Maastrichtian
Porosity approx.	45 %
Silica content approx.	4 wt %
Permeability	3-5 mD (3-5 $\cdot$ 10^{-15} m^2)

Most of the experiments were done on these two types of chalk, however, also a third outcrop chalk from the quarry of Stevns Klint nearby Copenhagen in Denmark, has been used:

Age	Maastrichtian
Porosity approx.	45 to 50 %
Silica content	< 2 wt %
Permeability	1-2 mD (1-2 $\cdot$ 10^{-15} m^2)

As already mentioned, generally the strength of a chalk decreases with increasing porosity and increases with increasing silica content (DaSilva et al. 1985). For the Aalborg chalk, the two effects compensate each other, and the Aalborg and Liège chalks are reasonably similar in many respects. Stevns Klint chalk is somewhat weaker due to the high porosity and a rather low silica content.

3.2 Mechanical testing

Within this work, several types of mechanical tests have been performed in order to quantify changes in the mechanical properties of chalk during the various types of experiments performed. The main purpose of the investigation in this work was to study the basic mechanisms behind water weakening of chalks.

3.2.1 Standard triaxial compression tests

A standard triaxial compression test consists of two phases; a hydrostatic phase and a deviatoric phase. In the hydrostatic phase, the axial and confining pressure is increased simultaneously to a chosen level. In the deviatoric phase, the confining pressure is kept constant, and the axial stress is increased until yield, failure or strain hardening then occurs. All tests within this study have been run under drained conditions, which means that the outlet is open to the atmosphere. The pore fluid pressure should be close to zero (although no measurements of water or glycol pore pressures have been performed), and the effective stresses are set equal to the total stresses for each sample. De Gennaro et al. (2003) have discussed the problem of possible pore pressure build-up in drained tests. As the pore pressures of the actual fluid are controlled by both permeability and compressibility of chalks as well as the loading rate the value of effective stresses may vary (De Gennaro et al. 2003). Within this present work, generally the loading rate was kept more or less constant.

A sketch of a standard triaxial compression test is shown in Fig. 3.1, where stresses are plotted as function of axial strain. The slope of the curve in the deviatoric phase gives directly the E-modulus, while the slope in the hydrostatic phase gives 3 times the bulk modulus K as the stresses are plotted against axial strain and not volumetric strain. If also the radial strain is recorded, Poissons ratio can be determined from the data in the deviatoric phase. If the radial strain is plotted versus axial strain, the slope is equal to the Poissons ratio (except for the sign). In addition to elastic properties, also failure or yield data are obtained from the stress-strain diagrams. The strength data obtained from a series of triaxial compression tests, which were performed at different confining pressures, will thus consist of pairs of

corresponding yield (or failure) data and confining stresses (Fjær et al. 1991). These sets of yield/failure data could then be plotted in different diagrams, i. e. Mohr τ-σ' diagrams (Fig. 1.2) and q-p' plots (Fig. 1.3).
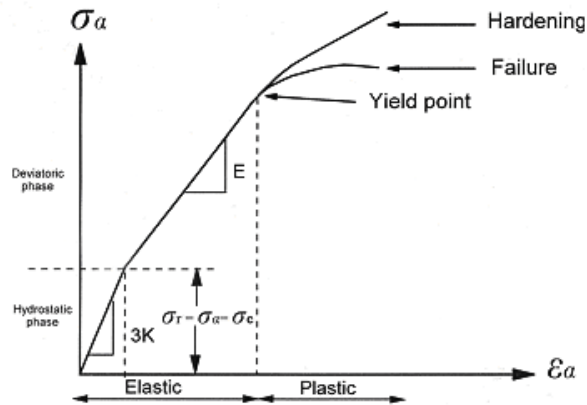
Figure 3.1. A sketch of a standard triaxial test where axial stress is plotted as function of axial strain.

3.2.2 Hydrostatic tests

In the hydrostatic tests, the hydrostatic yield point, σ_h, was determined and used as a measure for the mechanical strength. The yield point is determined from the point where the stress-strain curve starts to depart from the linear trend and is in general reasonably well defined. Based on the axial stress vs. volumetric strain plots, obtained from the hydrostatic tests, not only the yield point but also the bulk modulus (*K*-modulus) or framemodulus are determined for each of the chalk samples. The slope of the trend line in the elastic region determines the bulk modulus or the deformation modulus, which is a measure of the stiffness of the material.

By use of a Hoek cell, the hydrostatic tests were perfomed by pure hydrostatic loading. By use of a standard triaxial cell, stress path tests with the axial stress slightly higher than the confining stress (quasi-hydrostatic tests) were run as an alternative to pure hydrostatic tests.

The strain rates were approx. 1 %/hour and 0.3 to 0.4 %/hour for tests performed in the Hoek cell and the triaxial cell respectively.

3.2.3 Uniaxial tests

The uniaxial tests are unconfined compression tests, where the samples are placed into a load frame, and the axial load is increased with zero confining pressure. From this type of test, the uniaxial compressive strength, C_o, was calculated from the following formula;

$$C_o = \frac{4F}{\pi D^2}$$ (3.1)

where F (N) is the peak force at failure and D (mm) is the diameter of the sample. Due to sample heterogeneity and induced cracks by coring or other treatment procedures, experimental uncertainties may be expected when measuring uniaxial strength, unless the number of samples in each series is increased.

3.2.4 Brazilian tests

The simplest tensile test to perform is the "Brazilian" test. This type of test has been performed by use of a special designed cell, which also allows uniaxial compressive tests. This cell is made at the laboratory of Stavanger University and is further described in **Paper I**. The "Brazilian" test gives an indirect measure of chalks tensile strength, which is calculated from the formula;

$$T_{oB} = \frac{2F}{\pi D L}$$ (3.2)

where F (N) is the peak force, D (mm) and L (mm) the sample diameter and length, respectively. The "Brazilian" strength, T_{oB} (MPa) obtained this way, is equal to the horizontal tensile stress at failure conditions. Although the "Brazilian" test is very easy to perform, at least 10 tests are needed to establish a reasonable average value for the Brazilian strength.

3.2.5 Creep and rate dependency

Although most of the experimental work performed within this thesis has been standard triaxial compression tests, hydrostatic tests and "Brazilian" tests (**Paper I, II** and **III**), the main part of the experimental work reported in **Paper IV** was series of tests under creep conditions. Creep is a time-dependent deformation that may occur in materials under constant stress, and which is related to visco-elastic behaviour of the solid framework (Fjær et al. 1991). In designing tests with high porosity chalks, it has to be considered that

the mechanical properties of such chalks are time and loading rate dependent. Chalk exhibits creep behaviour even in the "elastic" region (Risnes & Nygaard 1999). This makes it important to record the strain or loading rates used in the various experiments. It should be mentioned that tests, which are to be compared within the work of each paper, have been performed at reasonably equal rates.

As partly mentioned, another strain - rate problem is the pore pressure build-up in drained tests. An estimate of the pore pressure can be obtained by applying Darcy's law to linear flow out of the sample (see **Paper II**). For the samples of tests with ethyleneglycol, the pore pressure may attain values in the 0.1 MPa range. With applied stresses of the order of 10 MPa, this was considered acceptable in the sense that such pore pressures should not invalidate the test data.

3.3 Chemical aspects

The specific surface area of the chalk used is about 2 m^2/g. Thus, the fluid inside the pores is exposed to a large surface area, which makes the fluid-rock interaction strong. Dissolved $CO_2(g)$ in water, $CO_2(aq)$, forms carbonic acid, H_2CO_3, which acts as a weak acid:

$$CO_2(aq) + H_2O = [H_2CO_3] = H^+ + HCO_3^- \qquad (3.3)$$
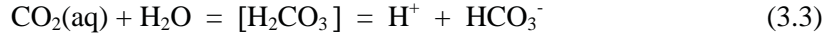
Under neutral and basic conditions, the solubility of chalk is very low, nearly negligible. The solubility product in distilled water is about $K_{sp} = 3.8 \times 10^{-9}$. Increased dissolution of chalk, $CaCO_3(s)$, takes place under acidic conditions because one of the common ions, carbonate CO_3^{2-}, is transformed to bicarbonate, HCO_3^-:

$$CO_3^{2-} + H^+ = HCO_3^- \qquad (3.4)$$

Thus, the overall reaction between $CO_2(aq)$ and $CaCO_3(s)$ is :

$$CaCO_3(s) + CO_2(aq) + H_2O = Ca^{2+} + 2HCO_3^- \qquad (3.5)$$

If the pressure of an aqueous solution in equilibrium with CaCO(s) and $CO_2(aq)$ decreases, CO_2-gas is liberated. The pH of the solution increases, and reprecipitation of $CaCO_3(s)$ may take place if the partial pressure of CO_2 is high enough. In the experiments, the CO_2 pressure in the initial fluid in most cases varied between 4 and 8 bars. The aqueous solution was flooded through

the cores without any back-pressure, causing a pressure gradient of 4 to 8 bars. Thus, precipitation of $CaCO_3(s)$ could be expected.

The solubility of $CO_2(g)$ in water is a function of the partial pressure of CO_2, P_{CO2}, temperature, and ionic strength of the water. Today there exists reliable and well-documented software to calculate complicated chemical equilibriums. The OLI-software was used to determine the solubility of $CO_2(g)$ in different waters at different partial pressures of $CO_2(g)$, 1-12 bars, and temperatures, 25 and 90 °C. At a given value of P_{CO2}, the solubility of $CO_2(aq)$ increases as the temperature and salinity decreases. The effect of salinity is low at high temperature.

As expected, the solubility of $CaCO_3(s)$ increases as P_{CO2} increases and decreases as the temperature increases, Fig.3.2
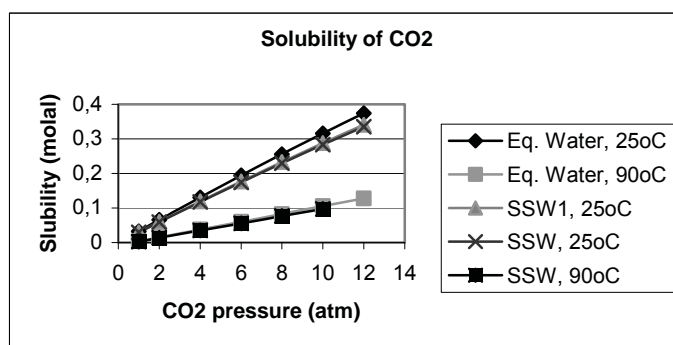
Figure 3.2. Solubility of $CO_2(g)$ at different partial pressures in different brines and temperatures

At low temperature, it is important to notice that the solubility of $CaCO_3(s)$ is very sensitive to the ionic strength and the composition of the water. In general, the solubility increases as the salinity of the water increases, **Paper IV**.

Because carbonic acid, H_2CO_3, acts as a weak acid in water, the decrease in the pH is much more pronounced at low pressure. Thus, an increase in P_{CO2} from 4 to 8 atm promotes a decrease in pH from 3.60 to 3.45. The dissolution rate of chalk is supposed to increase as the pH decreases, but the amount of chalk going into solution is related to the concentration of dissolved $CO_2(g)$.

Acid-base reactions, which involve proton transfer between molecules, are very fast and therefore usually described as diffusion-controlled reactions. Also solubility reactions are speeded up if an acid base reaction is involved. From a chemical point of view, it is therefore expected that carbonate water will respond fast with the chalk surface causing chalk

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dissolution and mechanical weakening during the flooding period. Other dissolution–precipitation reactions not involving acid–base reactions may be much slower, like formation of $CaSO_4(s)$ in chalk material.

If seawater or modified seawater is used in connection with CO_2 injection into chalk reservoirs, increased dissolution of chalk can cause precipitation of $CaSO_4(s)$ either as anhydrite at high temperature, or $CaSO_4.2H_2O$ at low temperature, $<43\ ^oC$, (Carlberg at al. 1973). In **Paper III**, it is demonstrated that increased weakening of chalk compared to seawater was obtained by spiking seawater with sulfate, keeping the salinity constant by adjusting the NaCl content. The cores were aged in the respective solutions for 4 weeks at 130 ^oC, and at that temperature, the modified seawater was close to the precipitation point of $CaSO_4(s)$. Thus, increased solubility of chalk was obtained because the dissolved common ion Ca^{2+} was removed from the equilibrium solution by the precipitation reaction:

$$Ca^{2+} + SO_4^{2-} = CaSO_4\ (s) \tag{3.6}$$

If both of the common ions are removed chemically, CO_3^{2-} by $CO_2(aq)$ and Ca^{2+} by SO_4^{2-}, an even more pronounced dissolution of chalk will take place promoting a stronger water weakening effect of chalk. This will be documented by experiments in **Paper IV**.

4.0 Main results and discussion

Based on the previously cited available literature dealing with water weakening of chalk, it is obvious that the mechanical effects on chalk are not easily explained by a single mechanism. Probably, several physico-chemical mechanisms are active depending on the actual experimental conditions. A search for a single mechanism to explain all the experimental evidences appears difficult. In order to obtain deeper insight into the problem, a possible way to go, is to design experimental methods or techniques, which promote a certain mechanism, i. e. a chemical induced mechanism on the cost of other physical mechanisms. In that way, the relative impact of the various mechanisms can be discussed. In the following sections, the most important results from the experimental work in the thesis will be presented, and the main purpose will be to show the connection between each of the papers and also the development of the dr. work.

4.1 Temperature effects

Originally, the main objective of the work presented in **Paper I**, was to study how the different mechanical parameters, like cohesion, friction angle, and hydrostatic yield were affected by the temperature. Temperature effects on the mechanical properties of chalks are important for translation of laboratory data to field conditions. The study of temperature effects may also be important in disclosing the basic mechanisms involved in chalk fluid interactions. As mentioned previously, most of the laboratory work has been carried out at ambient conditions, and rather few studies on temperature effects on chalks have been reported. Each of the previous studies on temperature effects seemed to include only a few experiments, and the chalk tested was mainly reservoir chalk with varying values of porosity and silica content. As Andersen (1995) pointed out, a careful study with controlled companion samples should be performed in order to evaluate temperature effects on yield and shear failure parameters.

In **Paper I**, four types of tests were performed: Standard triaxial compressive tests with different confining pressures, almost hydrostatic tests, "Brazilian" -and uniaxial compressive tests. The test series were performed by use of high porosity outcrop chalk from Aalborg and Liege at ambient and reservoir temperatures, 130 $^{\circ}$C, which is the Ekofisk temperature. Both water and glycol were used as the saturating fluids, and in addition, some tests series with dry samples were conducted.

Except for the tests with "dry" chalk, all types of tests have shown reduced yield or failure values with increasing temperature. With dry chalk a strengthening tendency with increasing temperature was observed, probably due to drying effects because the water content was not controlled during the heating of the samples. The ideal basis for discussion of temperature effects on mechanical properties of chalk would be to have completely water-free chalk available as a reference material. But this is difficult to achieve under normal experimental conditions, and therefore, temperature effects on the chalk matrix property can only be approached indirectly.

Comparing all the results obtained with water and glycol, the temperature effect is generally more pronounced with glycol as saturating fluid. The degree of weakening varied between the different test series. As a general result, it could be stated that typical strength reductions with water-saturated chalk are in the range 10-30 %, while the results with glycol indicate somewhat higher reductions, 20-40 %. Comparing the yield curves, which have been obtained with samples from the same block of chalk, the difference in temperature dependence between glycol and water is rather small, and the overall reduction in strength from 20 to 130 ^{o}C is about 15-20 %. As seen from Fig. 4.1, the strength reduction seems to be an overall-effect, and it affects cohesion on the shear failure side and the hydrostatic yield stress on the end-cap side. The values for friction angle, as obtained from the "Brazilian" and uniaxial compressive tests, were reduced with increasing temperature, but these values should only be regarded as rough estimates. The friction angle is, however, most directly determined by series of triaxial compression tests at different confining pressures, and the results from these tests indicate an increasing friction angle with increasing temperature.
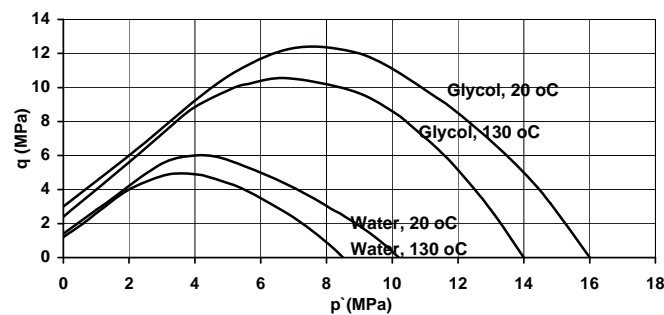

Figure 4.1. Complete yield curves from triaxial -and "Brazilian" tests, water and glycol saturated Liege chalk at 20 and 130 ^{o}C.

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If this is interpreted as an increase in frictional effects with increase in temperature at higher stress levels, then this hypothesis will agree with the observations made in the extrusion experiments previously mentioned in the introduction section, where the resistance at higher temperature increased with increasing stress or strain level (Risnes 1990).

The elastic properties, as measured by the *E*-modulus, show a great variation from sample to sample. Considering average values, there are indications in both directions, but mostly towards decreasing *E*-modulus with increasing temperature.

Mechanical stability of chalks has lately been discussed from a chemical point of view (**Paper III** and **Paper IV**). If weakening of chalk is caused by dissolution of chalk at the granular contacts or within the area of the capillary or thin film region, the results obtained in **Paper I** would be expected to be quite different. In general all chemical dissolution reactions speed up when increasing the temperature, but as seen from Fig. 4.2, the solubility of chalk decreases as temperature increases when chemical equilibrium is established.

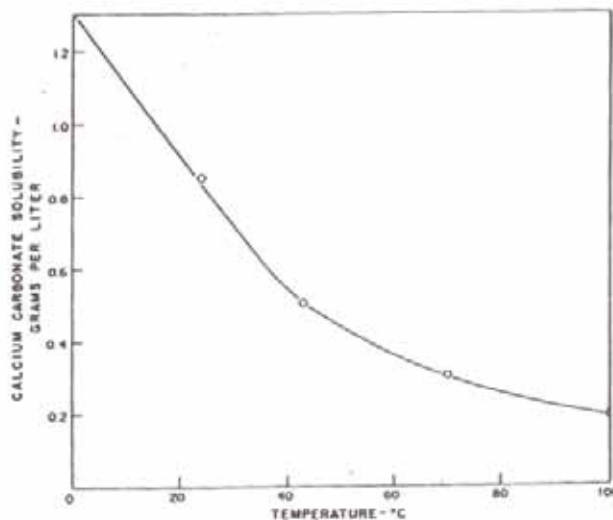*Figure 4.2. Effect of temperature on the solubility of CaCO$_3$ in pure water at 0.987 atm. CO$_2$ pressure. (From Miller 1952).*

A relevant question to ask is thus: "Is it established chemical equilibrium between the saturating fluid and the chalk surface both at room temperature and at 130 $^{\circ}$C during the experiments?" With reference to Hellmann (2002a), chemical equilibrium in thin water films present in rock

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materials involves both dissolution and transportation of ions by diffusion, which surely is very much affected by the temperature. Thus, from a chemical point of view, it is not unreasonable that a reverse effect of temperature regarding mechanical strength of chalk would be detected if the systems at room temperature were allowed to obtain thermodynamic equilibrium.

In the paper of Machel (1999), it is referred to the study of Robie et al. (1979), who report that for calcite, the decrease in solubility is about two orders of magnitude between 25 ^{o}C and 200 ^{o}C.

Although the overall picture from this early study on temperature effects shows a clear tendency towards decreasing chalk strength with increasing temperature, the results could perhaps be completely different if long-term tests under creep conditions had been performed at low and high temperatures. Due to the fact that chalk dissolution decreases with increasing temperature, and also having in mind that chalk behaviour is both time -and rate dependent, it turns out to be impossible to reveal or derive any definite conclusion on temperature effects from the series of uniaxial, the standard triaxial compression tests, or the "Brazilian" tests. The "Brazilian" -and uniaxial tests are quite rapid, which are performed within some minutes.

The triaxial compression and hydrostatic tests, which confirm the results obtained by the series of "Brazilian" -and uniaxial compressive tests, are all performed with a loading rate corresponding to a test time of only a couple of hours for each of the temperatures. A critical evaluation of these previous results on temperature effects therefore seems to lead to the following conclusion; namely that thermodynamic equilibrium is probably not reached considering the tests at ambient temperature, while those performed at an increased temperature will be much closer to equilibrium during the test period. Thus, it is very important to be aware of whether the system is in thermodynamic equilibrium or not.

From the series of triaxial tests in **Paper I** with low confining pressures, the increasing values of friction angle with increasing temperature and also from the extrusion tests performed by Risnes (1990) there are, however, indications of increased chalk strength with increasing temperature.

4.2 Chalk-fluid interactions

When two saturation phases are present, i.e. oil-water or gas-water, the mechanical stability of chalk has often been related to capillary forces, which is known to induce an apparent cohesion between chalk grains. In **Paper II**, the mechanical properties of high porosity outcrop chalk were studied with mixtures of water and glycol, which eliminate any capillary effects since glycol and water is fully miscible in any proportions. The main objective of this study was to test the hypothesis that the activity of water is a

key parameter in water weakening of chalk. This hypothesis was initially based on experiments with brine-saturated chalk of different salinities showing that the chalk strength increased with increasing salt content (Risnes et al. 2003). The solubility limits of the salts permitted, however, only a restricted variation of water activity. The fact that glycol-saturated chalk is about two times stronger than water-saturated chalk, and that water and glycol are fully miscible fluids, allowed variation of normalized water activity from 1 to 0 simply by varying the water-glycol ratio in the pore fluid.

4.2.1 Water activity and mechanical properties of chalk

In **Paper II**, mixtures of glycol and water were tested by performing four types of mechanical tests;

1. Triaxial tests at low confining pressure to assure shear failure conditions.
2. Triaxial tests at higher confining pressure to assure a stress path passing through the end-cap.
3. Hydrostatic tests to determine the hydrostatic yield stress.
4. "Brazilian" tests.

To make the different test types comparable, the mechanical strengths were normalized by taking the yield stress value obtained with pure water as the reference value. The interesting observation was that all the test series showed a similar trend of increasing chalk strength with decreasing water-activity. Compared with previous results from brines (Risnes et al. 2003), there was a good agreement, which confirmed the hypothesis of water activity being a basic parameter in chalk-water interaction (Fig. 4.3).

From the relative strength curves from Series I, as given in Fig.4.3, it was observed that there was a great similarity between the "Brazilian" and the hydrostatic curves. Further analysis of the results from the different types of tests indicated that chalk cohesion seems to be the parameter most strongly affected by the water weakening effect, and the resulting relative cohesion curves for all series are thus presented in Fig. 4.4.

From a previous study (Madland 1999), it was observed that "dry" chalk after drying at 120 $^\circ$C contained a residual water content of 0.2 wt % water, which corresponded to a water saturation of $S_w \approx 0.8$ % or 2.5 mole % with glycol filling the remaining pore space. In accordance to these observations, the curves in Fig. 4.4 are all corrected for this residual water content. The correction for the bonded water does not change the general shape of the curves, but the minimum water content to activate the water weakening mechanism increases to slightly more than 5 mole %.
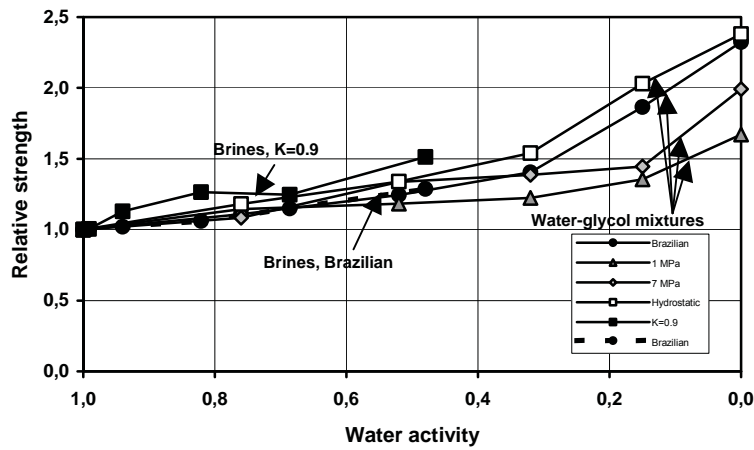
Figure 4.3. Comparison of brine results (Risnes et al. 2003) with water-glycol result, Series I.

Regarding the ensemble of curves in both Figs. 4.3 and 4.4, it seems that the water weakening effect follows a rather linear trend down to a water activity value of about 0.3. Translated to fluid composition, this corresponds to 35-40 mole % of water in glycol. When the water content is further reduced, the strength increases more rapidly until it reaches the terminal value at about 5 mole % of water (Fig. 4.4).

Figure 4.4. Relative cohesion versus water activity, all series.

4.2.2 Water weakening and possible mechanisms

Chalk-fluid interaction is a complex subject, and many different mechanisms may be involved. Depending on experimental -or field conditions, one or several mechanisms may dominate in the deformational processes, and specific properties of chalk grain surfaces may also be important. The conclusion reached in **Paper II**, that water activity is a key parameter in the water weakening effect, does not in itself provide an argumen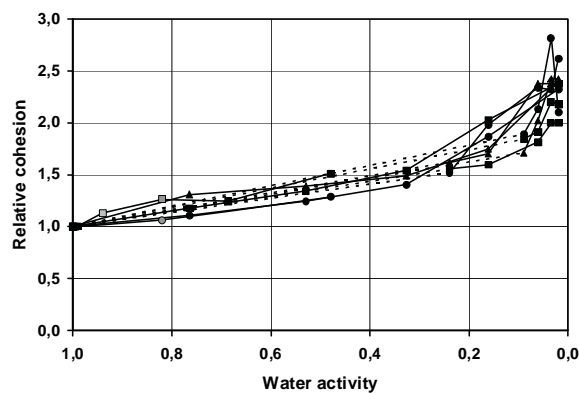t in favour of a specific process. Water activity will be important in almost any type of physico-chemical processes between water and chalk.

Capillary forces, van der Waals forces as well as electrical surface charge and oriented dipole layers have been mentioned and discussed briefly in **Paper II**. The forces are, however, at least one order of magnitude smaller than the changes in strength observed in chalk-fluid interaction, and it was suggested that none of these forces are strong enough to play a major role in the water weakening effect.

4.2.2.1 Adsorption pressure

Risnes et al. (2003) suggested that water weakening of chalk could be explained by growth of an adsorbed water layer, and if so, the water activity of the saturating fluid must be related to the extent of adsorption of water onto the chalk surface determined through the dynamic equilibrium:

$$H_2O \ (ads) = H_2O \ (sol) \tag{4.1}$$

As already mentioned, further analysis of the results from the different test series of brines and water-glycol mixtures indicated that chalk cohesion is the parameter most strongly affected by the water weakening effect. Knowing that cohesion between the chalk grains is strongly related to the water weakening effect, the basic mechanism behind the adsorption of water molecules was suggested to add extra pressure on the intergranular contacts, caused by attraction of water molecules to the chalk surface. This pressure may be referred to as an adsorption pressure, and it will act in addition to the pore pressure of the free fluid in the pores. Thus, the adsorption pressure is supposed to be active only on the inter-grain contacts and not in the pore bodies. A very simplified model calculation of the adsorption pressure of water is presented in **Paper II**.

Carles et al. (2004) believed that this adsorption pressure mechanism, could contribute strongly to chalk deformation, but they emphasize that this micro mechanism is difficult to demonstrate either by experiments or imaging techniques by saying: *"Only the mathematical transcription of the stress redistribution at the grain scale and a precise knowledge of the molecules*

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interactions at grain surface could validate or invalidate this hypothesis.", and later: "*If adsorption pressure is confirmed to be the preponderant mechanism, reservoir saturation state and all rock wettability will become critical in predicting carbonate mechanical behaviour.*"

The strength of the water layers at the chalk surface must be linked to the hydrogen bonding nature of water. At increased temperatures, especially above 100 $^{\circ}$C, the hydrogen bonding between water molecules is decreased, and consequently, the adsorption pressure should decrease, and the chalk should become stronger. This is, however, not in line with the observations from **Paper I**, where the experimental observations were opposite. This is also an indication, that the systems at room temperature studied in **Paper I**, were not at equilibrium, as discussed previously.

The adsorption pressure as described in **Paper II** is purely a mechanical phenomenon, and the question is whether chalk cohesion and water activity could only be explained in terms of a mechanical property. The results from **Paper III** and **Paper IV,** show that chemical effects also play an important role in chalk weakening. The relationship between water activity, grain cohesion and surface forces exerted by water is actually based on surface principles of physics and chemistry. The weakening of chalk discussed in **Paper II** could as well be discussed in terms of dissolution of chalk at grain-to-grain contacts. The dissolution rate of materials in aqueous solution is often expressed by a simple first order rate law:

$$R = k \, a_{H2O} \tag{4.2}$$

where the dissolution rate, R, is directly proportional to the water activity a_{H2O} and k is the first order rate constant.

Based on the conclusion that water activity seemed to be a key parameter in the water weakening mechanism, Risnes et al. (2003) suggested that water weakening would mainly be a chemical type phenomenon, which could be; chemical dissolution, adsorption of water at the chalk surfaces or both. Due to the fact that the process of water weakening is largely reversible as water is added and removed/evaporated from the chalk (Madland 1999), Risnes et al. (2003) concluded that the adsorption of water to the chalk surface probably was the most important mechanism. This observation can, however, as well be explained as a dissolution and precipitation/cementing process, i. e. a chemical explanation. As the chalk is oven-dried dissolved ions in the menisci may precipitate at higher temperatures (250 $^{\circ}$C) due to the decrease in the volume of water. The strength is then increased due to cementation, and when saturated and dried at the standard drying temperature of 120 $^{\circ}$C, once

again the menisci is increased, and the cemented or the precipitated $CaCO_3$ is dissolved until equilibrium is established in a reversible process.

4.3 Chemically induced weakening

Even though the stability of chalk is very often related to capillary forces or "suction", the results from **Paper II** using mixtures of completely miscible fluids, water and glycol, have shown that the mechanical strength cannot be explained by only capillary forces, and the activity of water is important as well. The question is: "Is the activity of water related only to a physical parameter, i. e. the adsorption pressure as discussed in **Paper II**, or is it related to a chemical dissolution of chalk?"

In **Paper III**, experiments have been designed to promote the chemical dissolution effect by removing one of the common ions, in this case Ca^{2+}, as the dissolution process is going on. This is done by increasing the amount of sulfate, SO_4^{2-}, in artificial seawater 4 times. At 130 ^{o}C, this solution is very close to the saturation point regarding precipitation of $CaSO_4(s)$. Thus, when one or both of the common ions, Ca^{2+} or CO_3^{2-}, are chemically removed from the equilibrium solution, enhanced dissolution of the sparely soluble $CaCO_3(s)$ takes place, which will have a considerable impact on the mechanical strength of chalk.

4.3.1 Weakening of chalk by modified seawater

In **Paper III**, three different saturating fluids were used; artificial Ekofisk Formation brine (EF-brine), artificial seawater (SSW), and modified seawater containing 4 times the sulfate concentration with respect to artificial seawater (SSW1), Table 4.1.

Table 4.1. Molar concentrations of components in the saturating brines.

Molar concentration of components in the brine used

Compound	EF-water (mol/l)	SSW (mol/l)	SSW1 (mol/l)
Na^+	0.6849	0.450	0.419
K^+	0	0.010	0.010
Mg^{2+}	0.0246	0.045	0.045
Ca^{2+}	0.2317	0.013	0.013
Cl^-	1.1975	0.528	0.343
HCO_3^-	0	0.002	0.002
SO_4^{2-}	0	0.024	0.096

It is important to note that the salinity of SSW and SSW1 is kept constant by adjusting the concentration of NaCl, and the salinity of EF-brine is about twice the salinity of SSW and SSW1.

In order to be as close as possible to the chemical equilibrium of the brine-rock systems, three series of chalk cores from Stevns Klint were saturated and aged in the respective fluids for 6 weeks at 130 ^{o}C, which is the reservoir temperature of the Ekofisk field. At this temperature, SSW1 is about to precipitate $CaSO_4(s)$, for SSW, the concentration of Ca^{2+} must increase to 0.0235 mole/l by chalk dissolution in order to precipitate $CaSO_4(s)$. No sulfate is present in the EF-brine, and no removal of dissolved Ca^{2+} by precipitation can take place.

"Brazilian" tests as well as hydrostatic tests were performed in order to investigate the impact of the different brines on the strength of the chalk. From the series of "Brazilian" and hydrostatic tests, it is observed that the cores aged in EF-brine is significantly stronger compared to the cores aged in SSW1-brine, Fig. 4.5. This decrease in strength is observed in tensile strength, hydrostatic yield, and bulk-modulus. The decrease in strength is in the order of 20 to 25 %. It is also interesting to note that the "Brazilian" tests gave no significant difference in the mechanical strength of the chalk cores saturated with EF-water and SSW. Thus, the dissolution of chalk using SSW is not high enough to exceed the solubility limit of $CaSO_4(s)$, and no enhanced dissolution of chalk will take place due to removal of common ions.

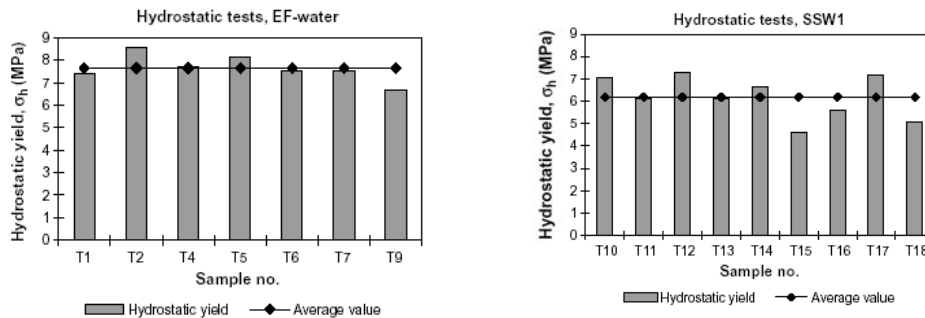*Figure 4.5. Yield points from hydrostatic tests for cores aged in EF-water and SSW1 at 130 ^{o}C for 6 weeks.*

From the present study, it is quite obvious that the difference in the water weakening effect of SSW1 compared to EF-water and SSW cannot be explained by the capillary force theory because the cores are completely saturated with water and no capillary forces are present. It is also hard to see

any correlation between the water activity and chalk weakening due to adsorption of water molecules onto the calcite surface, as suggested by Risnes et al. (2003). If the strength of chalk is governed by the water activity, which is different for EF-water and SSW/SSW1, the mechanical strength should be greater for the EF-water saturated cores and quite similar for the cores saturated with SSW and SSW1. This is not in agreement with the experimental results, which must be discussed from a chemical point of view. The general water weakening of chalk by increasing the water saturation may, however, be explained by capillary effect or water activity or adsorption pressure, but the <u>difference</u> in the mechanical strength of the cores in the present tests is most reasonably described by pure chemical effects. Possibly, the water activity and also the so-called adsorption pressure, which is restricted to the thin water films at the intergranular contacts (**Paper III**) should still be considered as important elements in water weakening of chalks (**Paper III**).

As stated previously, the intergranular pressure solution theory has been discussed by Hellman et al. (2002) as a possible mechanism for water-weakening. In **Paper III**, the mechanical strength of the cores is believed to be affected by the rock-fluid interaction during the aging period. Thus, the cores were subjected to the same external pressure, which should be close to the pore pressure. Therefore, also pressure solution can then be excluded as a mechanism to explain the differences in mechanical strength. The experimental results have therefore been discussed and interpreted by pure chemical dissolution/precipitation and the chemistry of thin water film between two charged solid surfaces.

Taking into account that chalk has a very low solubility, the strength of chalk is governed by the intergranular contacts, and also due to the fact that the specific surface area of chalk is relatively high, about 2 g/cm^3, it is hard to believe that dissolution of chalk evenly from the total surface should affect its mechanical strength. The area close to the grain-to-grain contacts constitutes probably only a very minor fraction of the total area. The calcium ion is the only ion present in the brines, which is part of the solid structure, and in that sense, it is a very strong potential determining ion (Pierre et al. 1990). The solid surface is therefore positively charged. Thus, when discussing the chemistry of thin aqua films, the initial charge of the solid materials must be included. As schematically illustrated in Fig. 4.6, the chemical potential of Ca^{2+} in the equilibrium solution within this region must be different and smaller than the chemical potential of Ca^{2+} in the equilibrium solution in the more open pore body, taking into account the total charge balance at the rock surface and in the thin film. The total chemical effect is that relatively more chalk is dissolved from the surface of the narrow capillaries than from the

surface related to the more open pore space. It is not unreasonable to believe that enhanced dissolution of chalk at the intergranular contacts would take place if the cores were exposed to external load, i.e. impact of pressure solution.
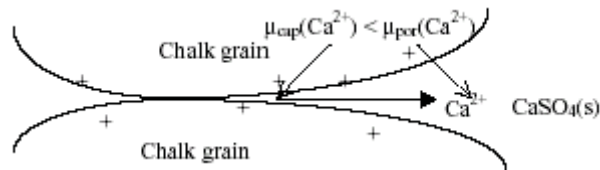

Figure 4.6. Schematic illustration of enhanced solubility of chalk from the intergranular contacts by a dissolution/precipitation process and chemistry related to thin films.

4.3.2 Chalk mechanical stability in the presence of CO_2-gas and carbonate water

In **Paper III**, chemical induced enhanced weakening of chalk was promoted by adding sufficient SO_4^{2-} to the injected water to cause precipitation of $CaSO_4(s)$ at elevated temperature. A similar chemical effect will be obtained if CO_3^{2-} is removed from the equilibrium solution. Dissolved $CO_2(g)$ in water, $CO_2(aq)$, forms carbonic acid, H_2CO_3, which acts as a weak acid, and the overall reaction between $CO_2(aq)$ and $CaCO_3(s)$ is given by;

$$CaCO_3(s) + CO_2(aq) + H_2O = Ca^{2+} + 2HCO_3^- \qquad (4.3)$$
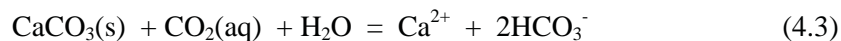
Acid-base reactions, involving proton transfer between molecules, are very fast and therefore usually described as diffusion-controlled reactions. Also solubility reactions are speeded up if an acid base reaction is involved. From a chemical point of view, it is therefore expected that carbonate water will respond fast with the chalk surface causing chalk dissolution and mechanical weakening during the flooding period. Other dissolution–precipitation reactions not involving acid–base reactions may be much slower, like the formation of $CaSO_4(s)$ in chalk material (**Paper III**).

The main objective of the work in **Paper IV** was to study deformation of chalk during alternating creep and flooding phases using carbonate water. All samples experienced a hydrostatic loading up to yield point. Further on,

the confining pressure was in all cases increased to a level of 10-13 MPa. Then subsequent or alternating creep and flooding phases were performed, and additional strain was detected. In the experiments, the CO_2 pressure in the initial fluid varied between 4 and 8 bars. It is important to note that the aqueous solution was flooded through the cores without any back-pressure, causing a pressure gradient of 4 to 8 bars. Thus, precipitation of $CaCO_3(s)$ could be expected due to increase in pH by evaporation of some $CO_2(g)$.

Different series of tests under creep conditions were performed.

1. Pure CO_2-gas was injected into water saturated chalk cores.
2. Two series of samples were exposed to subsequent creep and flooding by CO_2-enriched equilibrium water at ambient temperature and 90 ^{o}C.
3. In another series, the samples were exposed to varying flooding phases of pure equilibrium water and carbonate water.
4. In one case, injection of modified seawater, with and without $CO_2(g)$, containing 4 times the sulfate concentration was injected.
5. Finally, a series of preferential oil-wet samples at residual oil saturation was flooded with CO_2 saturated equilibrium water.

Only marginal weakening of the chalk material was detected when pure CO_2 gas was injected into the water-saturated chalk, which confirmed the results obtained by Schroeder et al. (2001).

Large mechanical deformation is, however observed during the flooding phase using carbonate water, Fig. 4.7. It is observed that while pre-flooding or within the initial flooding at 1 MPa confining pressure, the corresponding strain was less than 1 mS. As the stress level was increased to 10 MPa, the strain increased by a factor of 5, even for a much shorter flooding period. In general, an increase in confining pressure by a factor of 10 resulted in strain values of about 10 times higher or even more when cores were flooded with carbonate equilibrium water. This clearly illustrates the effect of stress level on the deformation process of chalk, which may indicate impact also of pressure solution (Newman 1983; Hellmann et al. 2002a).

It was also noticed that the mechanical deformation appeared to decrease as the number of flooding phases with carbonate water increased. During the creep phases without flooding of carbonate water, the mechanical deformation was surprisingly low, which indicates that supply of fresh carbonate water is needed to maintain a strong deformation. It should also be noted that at stress levels beyond the yield point, the chalk exposed to carbonate water became considerably weaker than chalk flooded with pure equilibrium water.

For the samples flooded with carbonate water at 90 ^{o}C, the axial strain was reduced by a factor of almost 2, compared to the corresponding tests performed at ambient temperature. At a given pressure of CO_2 gas, the solubility of CO_2 in equilibrium water will decrease as the temperature is increased, which will surely lower solubility of $CaCO_3(s)$, and a less weakening of chalk is then observed. It should also be noticed that the solubility of chalk, in general, decreases as the temperature increases.
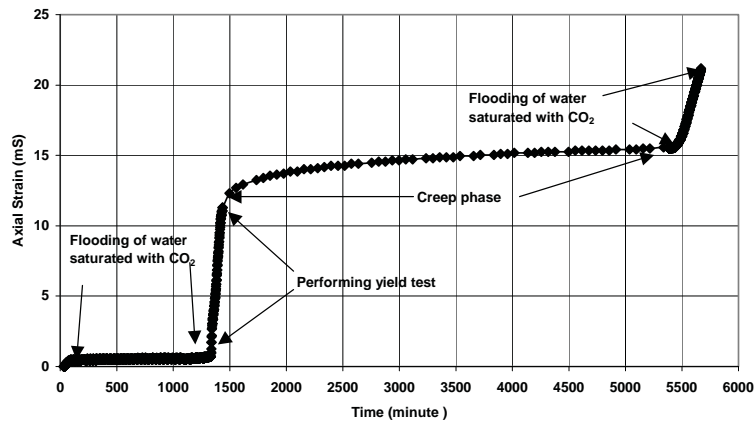

Figure 4.7. Axial strain vs. time. Sample B12; initial flooding at σ_c=1 MPa, creep and final flooding with carbonate water at σ_c=10 MPa and 8 bars flooding pressure.

When flooded with carbonate equilibrium water, the preferential oil-wet cores at S_{or} =0.62 experienced an increased strain of 20 % compared to the complete water-wet cores. A possible explanation may be that the core dried at 120 ^{o}C always will contain some water, $S_{wi} \approx 0.8\%$, (Madland 1999; **Paper II**). This small amount of water will be present at the capillaries close to the contact between the chalk grains. Thus, during the aging process, the chalk will remain water-wet at these intergranular contacts, which will be contacted by the injected carbonate water. Because about 60% of the pore volume was occupied by oil, these intergranular contacts will be exposed to a larger volume of carbonate water compared to a completely water saturated core, provided that the same volume of carbonate water was injected. The

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weakening of the chalk by carbonate water is surely related to the dissolution of chalk at the intergranular contacts.

While creep behaviour of chalk in the "elastic" region may be truly transient, creep at higher stress levels seems to follow a logarithmic time dependence (Andersen et al. 1992). Based on the first creep phase from each test, a logarithmic creep curve was determined, and correlations between the creep model and the experimental data were made for most of the samples. The additional strain during the injection periods was subtracted, and a general observation was that subsequent creep phases seemed to follow the predicted creep curve rather closely. A different behaviour was, however, observed for the sample B17, which was flooded with the modified seawater, SSW1, in combination with CO_2. This SSW1 brine was also used as a saturating fluid in **Paper III**, and compared to normal seawater; the sulfate content is increased by a factor of 4 (salinity is kept constant by adjusting the amount of NaCl).
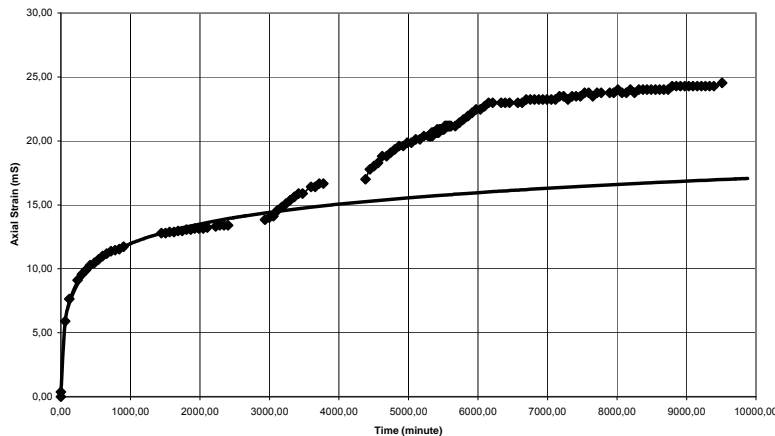
Figure 4.8. Creep behaviour, Sample B17.

As seen from Fig. 4.8, the first injection of seawater did not cause any noticeable additional strain, and the following creep phase followed the predicted creep curve rather closely. In the second flooding phase, the modified seawater was charged with CO_2, and in the final flooding, carbonate equilibrium water was used. The creep phases following these two last flooding phases show very clearly an additional deformation process that increases more or less linearly with time. This process seems to terminate at

about 6000 min, and then the sample seems to follow the regular creep trend, although at a higher strain level. This is of course a strong documentation that an additional weakening process of the chalk is taking place, namely precipitation of $CaSO_4.2H_2O.$, which is the form with the lowest solubility at room temperature (Carlberg & Matthews 1973). This dissolution-precipitation process is slower than the dissolution of chalk in the presence of acidic CO_2 gas. After about 6000 min, no precipitation of $CaSO_4(s)$ no longer takes place, and the dissolution of chalk has thus stopped. From this experiment, it is concluded that significant enhanced chemical induced weakening of chalk will take place if both of the common ions, Ca^{2+} and CO_3^{2-}, are removed from the equilibrium solution. It was also observed a misfit between the bulk strain measured on the plug, and the strain measured at the end of the first creep phase during the test. These results seemed to show a clear indication that the plug has expanded after the test was finished and removed from the cell. A possible explanation is that due to the presence of SO_4^{2-} ions, gypsum $CaSO_4.2H_2O$ has been formed within the chalk sample and caused an expansion.

Intact and damaged zones have been studied by using the Scanning Electron Microscope. In Fig. 4.9 SEM pictures of about 3000 times magnification from an intact and damaged zone, i.e. chalk exposed to carbonate water. The intact sample of chalk has not been exposed to any flooding while the photo of the damaged zone has been taken from a sample of chalk that has been flooded with carbonate water. Here the grains have been rounded and compacted due to dissolution.

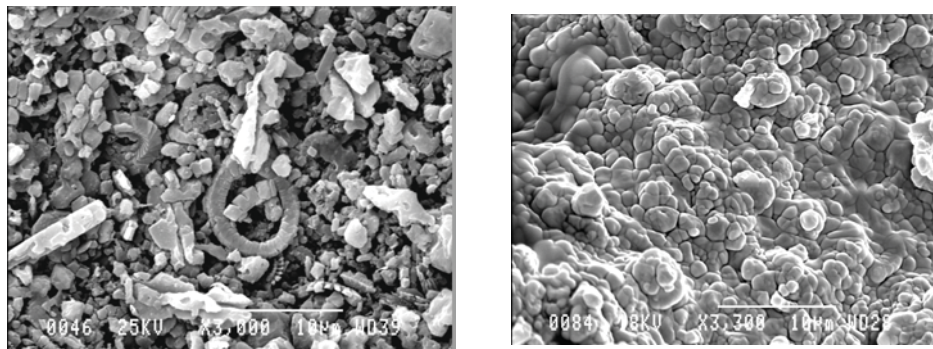*Figure 4.9. SEM pictures from an intact sample of chalk (left) and from a damaged zone after flooding with carbonate water (right).*

Further investigation of localization of damage in general showed that short-term flooding only caused localized damage and compression of the sample close to the fluid inlet, while long-term flooding of CO_2-saturated water affected the whole bulk volume of the cores.

5.0 Concluding remarks and future work

Seawater has been injected into the Ekofisk chalk formation for almost 20 years with a tremendous success regarding oil recovery. Even though increase in pore pressure is noticed, compaction of the reservoir is still going on. In the near future, also the Valhall and Eldfisk fields will be flooded with seawater. The oil companies need to update their reservoir models to be able to handle the physico-chemical rock-water interaction regarding compaction etc. It is therefore urgent to increase our knowledge about *water-weakening* of chalk, especially when seawater is used as the injection fluid. During several international research programs, (Joint Research Program (JCR), Pasachalk projects), a lot of results have been produced, and various mechanisms behind the *water-weakening* effect have been proposed. Several researchers have briefly discussed compaction due to chemical reactions (dissolution-precipitation), but from these previous studies it has been hard to detect or verify exactly the impact of chemistry on the corresponding changes in mechanical properties.

The main conclusions from this dr. thesis and possible future work are shortly presented in the following sections.

5.1 Concluding remarks

The main conclusions, which are based on the results from each of the papers and comments made in this review article, are listed.

Paper 1:

The overall picture from the early study on temperature effects shows a clear tendency towards decreasing chalk strength with increasing temperature. The results may, however, be opposite if long-term testing under creep conditions had been performed at low and high temperatures. A critical re-evaluation of the results from Paper I, seems to lead to the conclusion that *thermodynamic equilibrium* was not obtained at both temperatures during the timeframe of the mechanical tests. Ongoing tests, for the time being performed at our laboratory, appear to confirm this statement.

Paper II:

The main conclusion from Paper II is that *water-weakening* of chalk observed in glycol-water mixtures does not need to be linked to the capillary pressure, or suction statement. The hypothesis of *water activity* being a key parameter in chalk-water interaction was confirmed. It was observed that

water weakening of chalk increases as the *water activity* increases. Two mechanisms were discussed/suggested:

- A physico-chemical mechanism where the water molecules create an *adsorption pressure* at the grain surface, which acts at the inter-grain contacts in the same way as the pore pressure.
- A chemical related process based on enhanced *dissolution* and *precipitation* process close to the intergranular contacts. The *water activity* could then be related to a first order dissolution rate equation.

Paper III:

In this paper, it was documented that enhanced *water weakening* of chalk took place if one of the common ions, in this case Ca^{2+}, was removed from the equilibrium solution. Even though, the solubility of $CaCO_3(s)$ is very low in water, and it also decreases as the temperature increases, it was experimentally verified that *chemical dissolution/precipitation* has an impact on the strength of the chalk.

Paper IV:

In this paper, the *chemical weakening* of chalk was further documented by performing creep studies with carbonate water. *Enhanced dissolution* of chalk took place due to the reaction between the common ion CO_3^{2-} and the acidic CO_2 gas dissolved in the water. It was also verified by changes in the creep rates, that the mechanical strength of the chalk was more strongly affected if both of the common ions, Ca^{2+} and CO_3^{2-}, were removed from the equilibrium solution.

As an overall conclusion from this dr. work it could be stated that:

- Chemical aspects regarding *water weakening* of chalk cannot be overruled when designing/upgrading reservoir models for injection of seawater into weak chalk oil formations.

5.2 Future work

Chalk behaviour is strongly time and loading-rate dependent. De Gennaro et al. (2003) have pointed out that chemistry could play an important role in characterising time-dependent behaviour of chalk. Long-term creep tests should therefore be performed in order to gain improved insight into the mechanisms behind this time dependent behaviour of chalks. The experimental tests should be designed with an ultimate goal, namely to determine the relative importance of the different mechanisms, like chalk dissolution, pressure solution and precipitation processes. As observed from

the results obtained from the present thesis; temperature, pressure and also the composition of the actual fluid are important parameters, which should be studied during an extended test period.

It is also very important to focus on whether an actual process is of kinetic nature or if thermodynamic equilibrium is established. In that sense, the results from **Paper I** should be re-evaluated during long-term creep conditions at different temperatures. One could also study temperature effects by aging series of cores with different temperatures and ionic composition of water. The time needed to obtain chemical equilibrium should also be evaluated.

If the model of the adsorption pressure (**Paper II**) is correct, the mechanical strength of chalks may be affected by the wetting conditions of the material. It has been reported that some reservoir chalks had preserved a coating of organic material (Baldwin et al. 1985). Such films will greatly reduce the water weakening effect as long as they remain in place. The conclusion from these background experiences is that; chemical effects within the chalk and especially effects that will change the wettability of the chalk surface, should be investigated with respect to changes in mechanical properties.

In an ongoing Ph.D. work at the University of Stavanger the chalk properties at the grain size level is studied. This is be done by using electron microscopes, both scanning electron microscope (SEM) to study surface morphology, and transmission electron microscope (TEM) to study crystal structure. In combination with rock mechanical tests it may for future studies be possible to include both undeformed and deformed material. If so, this would give an opportunity to get a better insight in bonding properties and deformational processes in chalk, and maybe also a more in-depth understanding of chalk fluid interactions could be achieved.

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