GAS PRODUCTION FROM METHANE HYDRATE BEARING SEDIMENTS

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“The concept of an absolutely safe workplace is very likely to interfere with the progress of scientific research”

(Reg Garton)

“All starts on the foot of an overcast mountain. You start hiking and climbing, eagerly, driven, not without setbacks, but with an overall satisfying progress. Some years later you eventually emerge from the woods again, but finding yourself still at the foot of the same beautiful mountain. What went wrong? (∞ – 1, 2 steps, ...or even a few homeruns)\(^1\) is still ∞! Discouraging? No way!

The sun is up, fancy a walk?”

---

\(^1\) I have no doubts that one day a smart fellow will come up with a “novel infinite method” and put a fancy number to knowledge.
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I would like to dedicate this thesis to my siblings Maximilian, Hannah, Magdalena, Jakob and Benedikt, in the hope that they can find as much excitement and passion in their future undertakings.
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Abstract

Natural gas hydrates are solid clathrates of gas and water which are stable at high pressure and low temperature conditions. Estimates suggest that twice the amount of energy presently stored in conventional hydrocarbons is preserved in the form of natural gas hydrates. The vast amount of locally highly concentrated gas hydrate encountered in permafrost regions and deep sea sediments make them an attractive potential energy source for the near future. The required gas extraction method, however, differs from conventional gas reservoirs developments, as gas hydrates must first undergo an in-situ phase change (dissociation) before the freed gas can flow through the porous host sediment and be lifted through wells. This dissociation process is endothermic and thus absorbs energy in the form of heat from the sediment, pore fluid and adjacent non-dissociating regions. A reduction in temperature reduces the dissociation rate, or can even lead to hydrate reformation or pore water freezing. Controlling the temperature regime is therefore expected to be a key component in producing gas from hydrate deposits.

This study gives a brief background about the past- and ongoing experimental research on natural gas hydrates. It introduces the methane hydrate testing apparatus designed and built at NUS by describing the components’ working principles, stating the controlled and measured variables, as well as by giving some recommendations on the work procedures. Repeated small scale production tests show that the gas extraction rate can be increased by 3.6 times on average if the hydrate bearing sediment is dissociated by a combination of depressurised- and heated wellbore ($\Delta P + \Delta T$), as compared to depressurisation ($\Delta P$) only. It was further found that under
specific circumstances, $\Delta P + \Delta T$ is more efficient in terms of input- to recovered energy than a depressurisation to a lower wellbore pressure. Conductive heat transfer in stable hydrate- and water saturated sediments with a porosity of about 40% can be modeled with a bulk conductivity of 2.59 W/mK, which decreases only slightly under partially gas saturated conditions. The sensible heat of the formation is small compared to the required dissociation energy, and therefore the whole process is governed by the rate of heat supplied into the dissociating zone. A further finding of this study is a temperature increase during pressure reductions in stable gas hydrate conditions. This is caused by two consecutive exothermic reactions: the dissolution of gas from the pore water which subsequently forms hydrate together with the free water. The phenomena results in small increases in hydrate saturation and equilibrium pressure $P_{eq}$, which implies that hydrate dissociation commences at a higher wellbore pressure than initially assumed.
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1 Introduction

The objective of this chapter is to introduce the reader to natural gas hydrates, by explaining why they are of concern, describing their basic properties, showing where they are found and discussing how their research has evolved.

Gas hydrates are crystalline solids composed of water and gas. Under stable conditions of low temperatures and high pressures, gas molecules are trapped within cages of water molecules bonded by relatively strong hydrogen bonds and weaker van der Waals attraction forces between the host- and guest molecules. Depending on their host molecule, hydrates can be stable in three major different cage structures (type I, -II and -H), which differ in shape, guest- to host molecule ratio, and in turn in bonding energy. More on the chemical features of the different hydrates can be found in Sloan (2007) and Makogon (1997). A schematic molecular structure of a phase sharing type I methane hydrate is illustrated in Figure 1.

![Figure 1: Two phase sharing structure I methane hydrate molecules; the larger gas molecules are surrounded by bonded water molecules (Moon et al., 2003).](image)

In the engineering context, the main differentiation in the studies of hydrates is between the so called “artificial”- and naturally occurring gas hydrates. Artificial hydrates often form in petroleum transportation systems, where they are a substantial problem as they jeopardise its usage or limit the throughput. Natural gas hydrates
exist abundantly in nature, and are located in marine sediments and permafrost regions in almost all parts of the world (see Figure 2). This study focuses exclusively on natural gas hydrates.

Figure 2: Global discovered gas hydrate occurrences (modified from Makogon et al., 2007).

The largest hydrocarbon fraction of natural gas is methane, and as a result the vast majority of natural gas hydrates occurs as structure I hydrate. The phase boundary of methane hydrates is shown in Figure 3. The phase changing process (dissociation) back to gas and water is endothermic, and therefore requires energy to take place. The phase boundary is obtained by curve fitting dissociation points, and is described by the exponential equation (1.1) (Loh et al., 2011).

Figure 3: Methane hydrate phase diagram.
1. INTRODUCTION

\[ P_{eq} = 1 + 1.6 \exp(0.132 T_{eq}) \]  \hspace{1cm} (1.1)

Where \( P_{eq} \) and \( T_{eq} \) are the equilibrium pressure in MPa and temperature in °C respectively. A convenient set of reference values for methane hydrate stability is 4 MPa at 4°C.

1.1 Development of gas hydrates research

Gas hydrates were first discovered by Joseph Priestly in 1778, who created them by bubbling SO\(_2\) through 0°C water at atmospheric pressure, but he had missed out denoting the hydrates in his description (Makogon et al., 2007). In 1811, Humphrey Davy nucleated similar crystals of aqueous chlorine clathrate, which he then named hydrates of gas, and he became recognised as its official discoverer (Bennewitz, 1928).

For more than a century, gas hydrates remained of little interest. Only when Hammerschmidt (1934) was able to prove that flow limitations and blockages of gas pipelines were not caused by ice, as initially assumed, but rather by hydrates of the carrying gas itself, did the interest in gas hydrates gain a considerable boost throughout the petroleum industry, which was frightened of losing flowlines during winter time.

Naturally occurring gas hydrates were only discovered much later. A few years after production at the Messoyakha gas field in western Siberia began in 1968, the reservoir pressure diverged from its predicted path. The overlaying gas hydrate layer started to dissociate as the reservoir pressure fell below its stability zone, and as a consequence an increase in pressure was noted, which by coincidence confirmed the existence of naturally occurring hydrate bearing zones (Makogon et al., 1971, Collett, 1993).
Although at present no gas is being intentionally produced from hydrates, they are a subject of much research. The leading countries in natural gas hydrate research are Japan, the USA, Canada, South Korea, Germany and China. By far the most advanced research centre conducting laboratory tests on artificial gas hydrate sediments and core samples is the Japanese MH21 hydrate research consortium, with its impressive laboratories in Sapporo and Tsukuba. Natural gas hydrates are also actively experimentally researched at the Lawrence Berkeley Laboratory, the Colorado School of Mines, at the US Geological Survey, the US National Energy Technology Laboratory, the Georgia Institute of Technology, Natural Resources Canada, the University of Southampton, the Guangzhou gas hydrate research centre, the University of Petroleum in Beijing, Columbia University and the University of Calgary. The most active private companies researching hydrates are JOGMEC, Conoco-Phillips, Chevron, Schlumberger, Fugro and Geotek. The field’s standard reference books are Sloan and Koh (2007) and Makogon (2007).

1.2 Global hydrate reserves

Controversy arises in the global quantification of the potential methane preserved in form of hydrates. Initial estimations simply assumed the presence of hydrates in all gas hydrate stability zones (GHSZ). Trofimuk (1975) later differentiated the GHSZ further into gas hydrate occurrence zones (GHOZ), and estimated the gas volume trapped in hydrates worldwide to be $1135 \times 10^{15}$ m$^3$ under standard conditions (scm). Kvenvolden (1988, 1993) then came up with the illustrative quantification that more than twice as much organic carbon is being preserved in hydrates (53% or $\sim 21 \times 10^{15}$ scm) as it is in conventional fossil fuel reserves at present (27%). Milkov (2004) claims that all the existing models are misleading, and he estimated the global amount
of hydrate-bond methane to be $2.5 \times 10^{15}$ scm. However, in 2005 an approach using a fugacity-based model estimated the gas in hydrate reserves to be $1.2 \times 10^{18}$ scm (Klauda and Sandler). A comparison of these estimates to the global conventional natural gas reserves of $187 \times 10^{12}$ scm (BP, 2011), clearly highlights the potential of gas hydrates as a future energy source.

1.2.1 Gas concentration in hydrates

The in-situ hydrates energy concentration can be illustrated by the following example: the dissociation of 1 m$^3$ of methane hydrate releases about 164 scm of gas; if, on the other hand, 1 m$^3$ of conventional gas is produced from stable hydrate conditions at for example 4 MPa and 4°C, the gas only amounts to about 41 scm. It has to be mentioned, however, that gas from hydrates is in most cases more energy intensive to produce, as hydrate reservoirs lack any natural production drive and require energy for dissociation. To showcase the gas concentration in hydrates, pure methane hydrates were formed in the NUS laboratory and subsequently ignited (see Figure 4).

Figure 4: Burning pure methane hydrate formed at NUS, the first artificially formed in South East Asia.
1.3 Natural gas hydrate occurrence

The stability regions of natural gas hydrates are defined by the depth-associated pore pressure and the geothermal gradient, as it is schematically visualised in Figure 5 for a permafrost- and an offshore location. In moderate climate regions, where the seabed temperature reaches about 4°C, gas hydrates can be found in water depth equal or greater than 400 m. In arctic regions, where water temperatures can be as low as -1.7°C, hydrates can exist in water depth of about 260 m. In permafrost, the GHSZ’s upper bound is limited by pore pressure whereas its lower bound is determined by the geothermal gradient.

Figure 5: Methane hydrate occurrence zones in permafrost (above) and marine sediments (below) (Kvenvolden, 1988).
1. INTRODUCTION

Hydrates form either in the pore space of sand sediments or occur in non-uniform oriented nodules in tight silts and clays. In sand, hydrates are found as grains within the pore space (see Figure 6b), called pore-filling, but become load bearing as their saturation approaches 40% (Waite et al., 2009). Clayey and silty sediments are too fine grained and hence host random oriented hydrate nodules and veins (c). Matrix cementing hydrates as shown in (a) have only been artificially nucleated in the laboratory. The way hydrates exist in the sediments has obvious implications to the sediments response to dissociation and hence to the way gas can be produced from it.

Figure 6: Hydrate (black) occurring as cementing agent of the host sediment (grey) in (a), as pore filling in (b) and as non-uniform distributed lumps in (c) (modified from Waite et al., 2009).

1.3.1 Hydrate bearing sand properties

Gas hydrate bearing cores have been recovered in many parts of the world (see Figure 2), but at present, the most promising hydrate accumulations are in the Canadian Mackenzie river delta, offshore Japan in the Nankai Through, at the Alaskan North Slope and at the Alaminos Canyon in the Gulf of Mexico. The respective values of porosity and permeability of these accumulations can be found in Table 1.
Table 1: Sand characteristics of different hydrate deposits (Moridis, 2010, Lee and Waite, 2008, Soga et al., 2007, Winters et al., 2007).

<table>
<thead>
<tr>
<th>Hydrate Bearing Sand</th>
<th>Hydrate type</th>
<th>Porosity</th>
<th>Absolute permeability [mD]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mallik</td>
<td>Pore filling / load bearing</td>
<td>0.34 – 0.35</td>
<td>100 - 1,000</td>
</tr>
<tr>
<td>(Mackenzie Delta, Can)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nankai Trough</td>
<td>Pore filling / load bearing</td>
<td>0.40</td>
<td>800</td>
</tr>
<tr>
<td>(offshore Japan)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tigershark</td>
<td>Pore filling / load bearing</td>
<td>0.40 – 0.48</td>
<td>600 - 1,500</td>
</tr>
<tr>
<td>(GoM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eileen</td>
<td>Pore filling / load bearing</td>
<td>0.38 – 0.40</td>
<td>200</td>
</tr>
<tr>
<td>(Alaska North Slope)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All the above listed hydrates occur either as pore filling or load bearing, depending on the local strata saturation (Waite et al., 2009). Figure 7 shows hydrate saturation profiles of the reservoirs in Table 8, in which the dotted lines at 40% saturation mark the hydrate saturation used in this study for comparison purposes.
Figure 7: Methane hydrate saturation profiles at Mallik (top left), Tigershark (top centre), Milne Point, Eileen (top right), and Nankai Through, in meters below sea surface (mbss), meters below sea floor (mbsf), and meters below mean sea level (mMSL) (Lee and Waite, 2008, Fujii et al., 2008).

One notes that the hydrate bearing layer at Mallik and the Nankai Through are substantially thicker and more uniform saturated than the ones at Tigershark and Milne Point (Eileen field), but an average saturation of 40% is still representative for an averagely saturated strata. The grading curves of the Mallik- and Nankai deposits are again compared to the Toyoura sand used in this study and are shown in Figure 8. In some recent experiments small proportions of fines have been added to better represent the natural conditions in Mallik and the Nankai Trough.
1.4 Commercial aspects of hydrate

The commercial viability of gas production from hydrates depends on:

- Reservoir characteristics; class, permeability, saturation, size, $P-T$ conditions
- Location; onshore or offshore (water depth), accessibility
- Vicinity to gas transportation infrastructure and –markets
- Vicinity to potential conventional gas reservoirs
- Gas price
- Available production technology

The vast gas hydrate reserves in the Canadian Mackenzie Delta and the Alaskan North Slope will probably remain an asset for future decades. Gas pipelines will most likely be built to export the at present stranded conventional gas in these regions to Alberta and US markets further south; as these reservoirs start to deplete, hydrate reservoirs will increasingly be tapped to maintain the export capacity. Walsh et al. (2009) estimated that for a green field project in these arctic regions, the technical
price of class 1 and 3 onshore accumulations is 5.59 $/Mscf and 6.37 $/Mscf respectively (0% discount rate), which is compared to the actual gas price of around 4.8 $/Mscf not feasible, but it might be in future.

An estimated 265 tcf of methane in hydrates is preserved in the Nankai Trough offshore Japan, an amount equal to 100 years of their domestic gas consumption (Masuda et al., 2004). Due to the lack of conventional fossil reserves, Japan is particularly interested in gas hydrates, and first commercial production from the Nankai Trough is scheduled for 2016 (Kurihara et al., 2010).

### 1.5 Thesis structure

Chapter 1 introduces the subject of natural gas hydrates and provides some background information. The literature survey has been divided primarily between chapters 2 and 3, where the former presents the current state of the art in hydrate nucleation techniques and the physics of hydrate dissociation, and the latter addresses natural gas hydrates from an experimental testing- and gas production perspective. Chapter 4 covers the in-house designed testing apparatus by describing the working principles of each component. The bulk conductive heat transfer of hydrate bearing sand and its dissociation rate is covered in chapter 5. Chapter 6 compares different production schemes by varying the wellbore pressure- and temperature of small scale gas extraction tests. The effects of heat generation during depressurisation are described in chapter 7. Some concluding remarks and suggested future studies are put forward in chapter 8.
1.6 Objectives of this study

The first objective of this study was to design and build a methane hydrate testing apparatus, suitable for conducting a wide range of experiments to gain an understanding in the fundamental behaviour of hydrate bearing sediment during the dissociation process. Being the first study of this kind at NUS and in Singapore, this included a close collaboration with the regulatory authorities at the design stage to obtain several necessary permits for working at high pressure, working with flammable gas and a radio isotope.

Once the testing rig was set up and carefully calibrated, the aim was to carry out controlled dissociation tests which results are applicable to both production from a single wellbore as well as for a later development of a downhole testing probe. In terms of gas production from hydrates, the objective was to show that more gas can be extracted from the hydrate if the wellbore is heated in addition to being depressurised. After that could be shown, it was of interest to show how much further the wellbore pressure has to be reduced in order to extract a similar amount of gas over the same period.

It was quickly seen that heat transfer plays the dominant role in the endothermic hydrate dissociation process, as the required energy is large compared to the available sensible heat in the formation. This lead to the heat transfer studies. In a production scheme with a heated wellbore, conductive heat transfer will be the dominant method of energy supply to dissociating zones, thus it was aimed to quantify how quickly heat energy can be supplied, at which rate energy is consumed by the dissociation and how much heat can be conducted once the formation is left with a partial gas saturation. The determined bulk conductivity and heat consumption rate are essential parameters for heat transfer analysis of large scale production scenarios.
By chance it was observed that in depressurisation tests the temperature always increased with decreasing pressure. This lead to a study in that area, which eventually showed that this was due to dissolving gas from the water phase and subsequent hydrate reformation in the stable hydrate region.

1.7 Data organisation

This section’s aim is to give subsequent researchers an overview of what data is available, where to find it, what was tested and where the data is presented. The first two tests were conducted to calibrate and check the system. In T1 the gas excess method was applied as explained later. The tests T3 to T5 were unsuccessful because during the data analysis it was noted that the volume put in for the hydrate formation was several time larger as the total gas extracted. After a thorough calibration of the electronic gas flow meter, it turned out that there must have been a small gas leak during the formation process. Those are not immediately noticeable, as the hydrate formation consumes gas continuously which implies pressure reductions. In the subsequent tests this was avoided by careful leak tests at every connection of the closed system. The heat transfer tests T8, T16 and T17 were all carried out under mass conservation conditions. In T6 to T14 the vertical effective stress was applied before the hydrate was formed, resulting in pore filling hydrates. In T15 and T17 the loading sequence was altered: hydrate was formed in the sediment under no load conditions and only before dissociation the load was applied. The aim was to see an increased strain development during dissociation in the load bearing sediment because of the redistribution of the effective stress, but to data the data scatters too widely so that some of the tests have to be repeated.
Table 2: Nomenclature of conducted tests.

<table>
<thead>
<tr>
<th>Test label</th>
<th>Dissociation:</th>
<th>Remarks:</th>
<th>Data in:</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>$\Delta P$ to 1 atm</td>
<td>Gas saturated sample</td>
<td>Figure 14</td>
</tr>
<tr>
<td>T2</td>
<td>$\Delta P$ to 1 atm</td>
<td>Water saturated sample</td>
<td></td>
</tr>
<tr>
<td>T3</td>
<td>$\Delta P_{\text{atm}}$</td>
<td>mass balance $\neq 0$</td>
<td>Figure 14</td>
</tr>
<tr>
<td>T4</td>
<td>$\Delta P_{\text{atm}} + \Delta T$</td>
<td>mass balance $\neq 0$</td>
<td></td>
</tr>
<tr>
<td>T5</td>
<td>$\Delta P_{1\text{MPa}} + \Delta T$</td>
<td>mass balance $\neq 0$</td>
<td></td>
</tr>
<tr>
<td>T6</td>
<td>$\Delta P_6 + \Delta T$</td>
<td></td>
<td>Chapter 6</td>
</tr>
<tr>
<td>T7</td>
<td>$\Delta P_6$</td>
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<td>6, 7</td>
</tr>
<tr>
<td>T8</td>
<td>Heat transfer</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>T9</td>
<td>$\Delta P_6$</td>
<td></td>
<td>6, 7</td>
</tr>
<tr>
<td>T10</td>
<td>$\Delta P_4$</td>
<td></td>
<td>6, 7</td>
</tr>
<tr>
<td>T11</td>
<td>$\Delta P_6 + \Delta T$</td>
<td>Malfunctioning gas flow meter</td>
<td></td>
</tr>
<tr>
<td>T12</td>
<td>$\Delta P$</td>
<td>failed pressure maintenance, rest ok</td>
<td></td>
</tr>
<tr>
<td>T13</td>
<td>$\Delta P_6 + \Delta T$</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>T14</td>
<td>$\Delta P_4$</td>
<td></td>
<td>6, 7</td>
</tr>
<tr>
<td>T15</td>
<td>$\Delta P_6 + \Delta T$</td>
<td>Load bearing hydrate</td>
<td></td>
</tr>
<tr>
<td>T16</td>
<td>Heat transfer</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>T17</td>
<td>Heat transfer</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>T18</td>
<td>$\Delta P_4$</td>
<td>Load bearing hydrate</td>
<td>7</td>
</tr>
</tbody>
</table>
2 Gas hydrate formation and dissociation

2.1 Introduction

In most gas hydrate deposits the contained gas is of biogenic origin, but in some regions like the Gulf of Mexico and the Caspian Sea, thermogenic originated gas hydrates are found (Kvenvolden, 1993, Dai et al., 2008). The gas in hydrate deposits on the Alaskan North Slope of both, biogenic and thermogenic origin (Lorenson et al., 2008, Dai et al., 2011). Although the geological history of gas in hydrates cannot be clearly defined, this has no effect on the gas – and for that matter on the gas hydrate properties.

2.2 Artificial hydrate formation methods

Artificial hydrates in sediments can be nucleated in different ways. The main differences regarding the end product are how-, where- and in which environment the hydrate forms. It can form at the grain contact of the hosting sediment, leading to a cemented hydrate sample, or in the pore space between the particles, which results in pore filling hydrates. Hydrate can be nucleated in a gassy environment, where all the remaining pore space is filled with gas, or as a water saturated sample. In nature, hydrates in sand layers like in the Nankai Trough or Mallik were found to be pore-filling in a water saturated sediment (Waite et al., 2009). All artificial formation techniques are based on the assumption of complete reaction in order to derive the hydrate saturation by a mass balance between the void volume and the known input of one reactant.
2.2.1 Gas saturated hydrate samples

A simple method to form artificial gas hydrates is to moisturise dry sand, pressurise the pore space with hydrate forming gas, and cool it well into the hydrate stability region. Since the water tends to accumulate at the grain contacts and hydrates start growing from the water gas interface inwards on the water side, the solid hydrate will eventually cement the sediment matrix, which results in a stiffness change that can be seen by resonant column testing (Priest et al., 2009). To keep the formation pressure at a reasonable value not exceeding 20 MPa, samples are generally formed in a cooled environment at temperatures just above 0°C. If the reaction is performed in a closed system where no additional gas is added during formation, the pressure will deplete with progressing hydrate formation until all the free water is used up and the pressure stabilises. Stern et al. (1996) introduced a methane hydrate formation method where fine ice seeds are mixed with sand of a comparable grain size at temperatures below 0°C. Cold gas is then injected at high pressure, and the temperature is risen to above the 0°C. The weakened but existing ice lattice in combination with the melting water facilitates hydrate formation. The dissociation behaviour of gas saturated hydrate bearing samples is heavily affected by the expansion cooling effects on the free flowing gas, and therefore do not represent the dissociation behaviour of water saturated natural gas hydrate deposits.

2.2.2 Water saturated hydrate samples

An efficient way of forming water saturated hydrates is the so called “water excess method”, in which dry sand is pre-pressurised with gas according to the desired hydrate saturation before raising the pressure with water. Nucleation with this method leads to pore-filling hydrates, and saturation uniformity has been achieved with
hydrate saturation of up to 40% (Priest et al., 2009). Since this method is used in the majority of the experiments of this study, its procedural steps and gas to water ratio calculations are described in more detail:

- Dry sand is filled into the pressure vessel at a dry density of 1.60 g/cm³
- Thermocouples are placed in a horizontal plane at half the sample’s height
- Vertical effective stress of 2.39 MPa is applied to the sample
- The sample is vacuumed for 30 sec to remove residual air from its pore space and supply piping
- Methane gas is filled into the sample and its pressure raised according to the desired hydrate saturation
- The pressure is increased further to 15 MPa by injecting water
- The sample is cooled to about +3°C
- The pressure during the hydrate formation process is maintained between 10 - 16 MPa by water injection

Figure 9: Sample formation steps on methane hydrate phase diagram (Falser et al., 2012b).
Figure 10: Pore pressure- (upper graph) and temperature histories (lower graphs) during sample formation process. The continuous pressure maintenance by water injection are shown by the sharp pressure increases during the formation process.

The formation steps are illustrated on the methane hydrate phase diagram in Figure 9, and its pore pressure- and temperature histories are given in Figure 10. Six water molecules are required to form one molecule of structure I methane hydrate out of a methane molecule. Based on this hydration number, the required methane molecules- and hence its pressure during formation can be calculated for the targeted hydrate saturation with equation (2.1). Despite the comparably low methane solubility in water, it is important to account for it in this setup due to the large excess water volume at the lower half of the pressure vessel (see Figure 17).

\[
n_{CH_4} = \frac{V_p S_h \rho_h}{M_h} + s_{CH_4-H_2O} \frac{\rho_w [V_p (1-S_h) + V_w]}{M_w}
\]  

(2.1)

where

- \( n_{CH_4} \) is the number of moles of methane [-]
- \( V_p \) is the pore volume [m³]
$S_h$ is the hydrate saturation [-]

$\rho_h$ is the density of methane hydrate (913 kg/m$^3$)

$M_h$ is the molar mass of methane hydrates (0.1196 kg/mol)

$s$ is the methane solubility in water (0.00355 mol CH$_4$/(mol H$_2$O) at 278 K and 15 MPa)

$\rho_w$ is the water density (1000 kg/m$^3$)

$V_w$ is the water volume at the lower part of the pressure vessel (5.6 litre)

$M_w$ is the molar mass of water (0.018 kg/mol)

The required pressure to inject the number of methane moles obtained from equation (2.2) can be calculated with the Peng-Robinson equation of state (1976):

$$P_{CH_4} = \frac{RT}{V_m-b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

$$a = \frac{0.45724RT_c^2}{P_c} \quad ; \quad b = \frac{0.07780RT_c}{P_c}$$

$$\alpha = \left(1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)(1 - T_r^{0.5})\right)^2$$

$$T_r = \frac{T}{T_c} \quad ; \quad V_m = \frac{V_p}{n_{CH_4}}$$

where (Setzmann and Wagner, 1991, Lin and Chao, 1984):

$R$ is the universal gas constant (8.314x 10$^6$ m$^3$MPa/(mol K))

$T$ is the actual temperature inside the sample [K]

$T_c$ is the critical temperature of methane (190.6 K)

$P_c$ is the critical pressure of methane (4.656 MPa)

$\omega$ is the accentric factor of methane (0.0108)

Increasing the pore-pressure by water compresses the gas into bubbles within the pore space. At the gas-water interface around those bubbles, hydrate nucleation initiates, resulting in exothermic temperature spikes as shown Figure 11.
Figure 11: Detail A in Figure 10: consecutive temperature spikes due to the exothermic hydrate formation reaction

Subsequent growth is governed by diffusion across the hydrate layer and therefore significantly slower (Makogon, 1997). The methane solubility in water is calculated after the hydrate has formed. The hydrate formation process is exothermic, which results in a release of heat energy as the hydrogen bonded cages form. This formation initiation is indicated by the pressure discontinuity at 284 K in Figure 9 and the temperature spikes in Figure 11. The completion of hydrate formation is indicated by no further decline in the gas pressure and by a constant temperature during the pressure increase by water, showing the absence of free gas, which is observed for dwell periods of about 70 hours at very stable conditions. The grading curve of the host sediment, a standard silica (Toyoura) sand, is given in Figure 8.

Another method to form a water saturated specimen is to fully saturate and pressurise the sand with water, and then insert a known quantity of gas prior to cooling (Winters et al., 2002). Unlike the water excess method, this technique forms cementing hydrate. Gas hydrates can also be formed by bringing dissolved gas in water into stable hydrate conditions while circulating it through the sediment (Tohidi et al., 2001). Due to the low solubility of methane in water, this method is mostly being used to form CO₂ hydrates. This is the most time intensive of all methods, but it leads
to highly saturated pore-filling hydrates. A comprehensive and detailed property analysis of hydrate bearing sediments is given by Soga et al. (2007) and Waite et al. (2009).

2.3 Hydrate dissociation

Dissociation is the process which describes the decomposition of hydrates back into gas and water. It is endothermic and therefore need energy in the form of heat to progress. Methane hydrate requires 410 kJ/kg (54.2 kJ/mol CH₄), which is compared to ice (334 kJ/kg) about 20% larger. Gas hydrates can generally be dissociated by three different means or combinations of them, depressurisation ($\Delta P$), heating ($\Delta T$), and inhibitor injection. Figure 12 illustrates the different dissociation methods schematically on a methane hydrate phase diagram.

![Figure 12: Schematic illustration of dissociation methods on a methane hydrate (MH) phase diagram.](image)

The endothermic effect during dissociation is best shown by depressurising a hydrate bearing sample (Figure 13); the moment the pressure reaches the equilibrium pressure for the initial temperature, the contained hydrate starts to dissociate. The only available heat energy is from the specific heat of the sediment and the pore water,
which in turn can only be released by a temperature reduction. Thus, the sample’s temperature decreases as the hydrate dissociation process progresses. Depending on the dissociation rate, the temperature regime will eventually reach steady state when the transferred heat flux from the surroundings equals the required dissociation energy. In this particular case, the temperature dropped by 12°C, from 284 to 272 K, causing the pore water to freeze.

\[ -\frac{dn_h}{dt} = K_d A_{h,d} \left( f_q - f \right) \]  \hspace{1cm} (2.3)

Figure 13: Endothermic cooling effect during depressurisation of a methane hydrate sample.

The hydrate dissociation model introduced by Bishnoi’s group at the University of Calgary (Kim et al., 1987) is still the basis of most studies and numerical codes. It describes the rate of dissociation as following:

- \( n_h \) is the number of gas moles present in the hydrate [mol]
- \( K_d \) is the decomposition rate constant [mol/(Pa s m^2)]
- \( A_{h,d} \) is the surface area of the decomposing hydrate particles [m^2]
The fugacity is the non-linear temperature dependent pressure of real gases, but for methane, equation (2.3) can be approximated by using a pressure difference. The Kim-Bishnoi model is on close scrutiny implicit, as the hydrate surface area $A_{h,d}$ decreases with progressing dissociation, which in turn makes it inversely proportional to the dissociation rate $dh/dt$.

The decomposition rate constant $K_d$ depends on the initial temperature $T_i$ and the activation energy $\Delta E$ required to initiate the breaking of the hydrogen bonds, which is equal or greater than the latent heat of the medium.

$$K_d = K_0 \exp \left( -\frac{\Delta E}{RT_i} \right)$$  \hspace{1cm} (2.4)

where

- $K_0$ is the intrinsic decomposition rate constant [mol/(Pa s m²)]
- $\Delta E$ is the activation energy [J/mol]
- $R$ is the universal gas constant [8.314 J/(mol K)]
- $T_i$ is the initial temperature [K]

The activation energy $\Delta H$ varies slightly between 78 kJ/mol, 81 kJ/mol and 89.7 kJ/mol in the literature (Kim et al., 1987, Clarke and Bishnoi, 2001, Moridis et al., 2005b). The intrinsic decomposition rate constant on the other hand, varies over several orders of magnitude, and the published values are listed in Table 3.

Moridis et al. (2005a) ran numerical dissociation tests using the TOUGH-Fx/HYDRATE reservoir simulation software, from which they calculated a rate constant two orders of magnitude higher than measured earlier. The in situ measurements at the Mallik well, however, lead to a intrinsic decomposition rate
constant comparable to the one obtained by Clarke and Bishnoi, and hence it can be concluded that $K_0$ is around $4 \times 10^4$ mol/(Pa s m$^2$).

Table 3: Range of intrinsic rate constant $K_0$ for methane hydrate decomposition.

<table>
<thead>
<tr>
<th>$K_0$ [mol/(Pa s m$^2$)]</th>
<th>reference:</th>
<th>remarks:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.24 \times 10^5$</td>
<td>(Kim et al., 1987)</td>
<td>pure hydrate, spherical grains 8 μm in diameter</td>
</tr>
<tr>
<td>$3.60 \times 10^4$</td>
<td>(Hong et al., 2003)</td>
<td>pure hydrate, spherical grains 16 μm in diameter</td>
</tr>
<tr>
<td>$1.78 \times 10^6$</td>
<td>(Clarke and Bishnoi, 2001)</td>
<td>numerical validation of hydrate in sediment</td>
</tr>
<tr>
<td>$4.21 \times 10^4$</td>
<td>(Moridis et al., 2005b)</td>
<td>history matching of in situ test data (Mallik)</td>
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</table>

Table 4: Hydrate surface area estimates.

<table>
<thead>
<tr>
<th>$A_{h,d}$ [m$^2$/m$^3$]</th>
<th>reference:</th>
<th>remarks:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{h,d} = \frac{6 \rho_a G_c}{m_h D_{part}} n_0^{\frac{1}{2}} n_h^{\frac{3}{2}}$</td>
<td>(Kim et al., 1987)</td>
<td>$n_0$ is the initial gas mole content, $n_h$ is the remaining gas mole content at $t$</td>
</tr>
<tr>
<td>$A_{h,d} = \sqrt{\frac{n_1^3}{2K}}$</td>
<td>(Yousif et al., 1991)</td>
<td>$n_1$ is the porosity of the stable hydrate zone, $K$ is the absolute permeability</td>
</tr>
<tr>
<td>$A_{h,d} = 3.75 \times 10^5 n_1$</td>
<td>(Masuda et al., 2002)</td>
<td>assumed constant</td>
</tr>
<tr>
<td>$A_{h,d} = 3 \times 10^5 n_1 S_h$</td>
<td>(Ji et al., 2001)</td>
<td>based on a particle diameter of 20 μm $S_h$ is the hydrate saturation</td>
</tr>
<tr>
<td>$A_{h,d} = A_0 S_h^{\frac{3}{2}}$</td>
<td>(Moridis et al., 2005a)</td>
<td>$A_0$ is the initial hydrate surface area</td>
</tr>
<tr>
<td>$A_{h,d} = 3.85 \times 10^5 n_1 S_h$</td>
<td>(Klar and Soga, 2005)</td>
<td></td>
</tr>
<tr>
<td>$A_{h,d} = \sqrt{\frac{n_1^3}{2K}} S_h (1-S_h)$</td>
<td>(Sun and Mohanty, 2006)</td>
<td></td>
</tr>
</tbody>
</table>
The applicability of the model in equation (2.1) to methane hydrates in sediments is nonetheless not quite as clear. The largest uncertainties are in the modelling of the surface area, for which several approximations have been established (see Table 4). Some are however not accounting for the diminishing saturation during the dissociation process.

Most models are simplified based on the assumption of perfectly spherical hydrate grains, whose surface area is proportional to volume to the power of $2/3$. Hydrate dissociation in pore space must be more complex than that: hydrate particle may split into several pieces and their porosity increases its effective surface area too. It is believed here that this shrinking effect during dissociation can be expressed by a time dependent exponential decay, proportional to the dissociation drive. This is again addressed later in section 5.9.

It is not only the endothermic dissociation reaction which has an effect on the in-situ temperature, but the dissolving gas and the flow of free gas as well. The dissolving gas during depressurisation leads to a gentle temperature increase before the dissociation starts (see water saturated sample in Figure 14) for reasons described in chapter 7. The sudden expansion of the free gas during depressurisation, on the other hand, causes an almost immediate temperature drop (see gas saturated sample in Figure 14), a real gas phenomenon known as the Joule-Thomson effect. It is therefore of highest importance to carry out experiments on hydrate bearing samples which represent the investigated in-situ conditions in the most accurate way possible.
Figure 14: Comparison of temperature history at $r/r_0 = 4$ during depressurisation to atmospheric pressure of a gas- and water saturated hydrate bearing sand sample (Falser et al., 2010a).

2.4 Dissociation induced soil deformation

The expanding gas dissociated from the hydrate can lead to high excess pore pressure and substantial stress in the sediment.

Kwon et al. (2008) developed a model which quantifies the stress and strain in the sediment based on a volume and saturation balance of each phase (gas, water, hydrate, mineral) at a known degree of dissociation. They further derived a correlation between the degree of dissociation and the sediment’s failure stress. Their work concludes that higher hydrate saturation leads to higher excess pore pressure which subsequently increases the self preservation of the hydrates during thermal stimulation. Low skeletal stiffness reduces the pressure evolution but is limited by the sediment’s failure conditions. Capillary effects also reduce the excess pore pressure but vanish for pore sizes greater than 0.1 $\mu$m, and the gas solubility in water can conservatively be neglected for methane hydrates.
Klar and Soga (2005, Klar et al., 2011) elaborated a coupled deformation-flow model applicable for geotechnical hydrate modelling as well as production simulations. Their model is based on a mass balance and accounts for gas/water two phase flow, decomposition kinetics after Kim et al. (1987) and the soil deformation following the Terzaghi's effective stress principle. These were correlated by finite differences and implemented and solved with the commercial software FLAC. The authors conclude that the contribution of the hydrate to the soil’s strength is of cohesive nature rather than frictional, but which decreases due to plastic strain or breakage of the hydrates. The most widely used software for simulations of natural gas hydrate is the TOUGH+HYDRATE code, which implements a linear elastic soil deformation, but can be linked to FLAC3D for a more detailed geomechanic response (Moridis, 2008). In a recent study, it was shown that Toyoura sand samples cemented by hydrate can initially be stable at higher stress conditions than the failure envelope of standard Toyoura sand, but collapse when the hydrate is heat-dissociated because of the reduction in the sediment’s shear strength (Hyodo et al., 2011). The same phenomena was shown in depressurisation tests of similarly cemented samples, in which the initial pressure reduction was allowed to recover by the expanding dissociated gas, which lead to a sample collapse once the sediment’s (Toyoura sand) failure envelope was reached (Yoneda et al., 2011).
3 Gas hydrate dissociation tests

3.1 Introduction

The purpose of most current gas hydrate dissociation setups is to test gas production methods or associated behaviours. To date, the longest published large scale gas production tests from a hydrate deposit is over a period of seven days at the Canadian Mallik site. Unavoidable formation- and hydrate saturation heterogeneities make in-situ tests however less applicable for calibration purposes of numerical codes. It is therefore absolute essential that small scale dissociation experiments on samples with known properties are carried out. These measurements form the basis of more complex numerical analysis like simulating gas production from hydrate deposits in real scale and over long periods.

3.2 Potential production methods

The main technical difference between conventional gas production and the gas extraction from hydrates is the required in-situ phase change to free the gas and make it flowable through the porous host sediment. The second, perhaps the more severe difference, is that gas production from hydrate deposits has yet to reach commercial scale.

Hydrate has to be dissociated by artificially changing the in-situ pressure- and temperature conditions, either by pressure reduction through pumping, heating or by shifting the phase boundary by injecting inhibitors. Hydrate dissociation is an endothermic process with a latent heat of 54.2 kJ/(mol CH₄) (Handa, 1986). Whereas
class 1 and 2 hydrates deposits can be dissociated more uniformly by depressurising their underlying liquid layer, class 3 hydrate deposits can only be dissociated radially from the wellbore. The most attractive hydrate deposits are in class 3 sediments (Nankai Trough, Mallik, Alaskan North Slope), and therefore the focus of this study will be on their behaviour during dissociation.

Numerical simulations have shown that production by depressurising alone can reduce the temperatures to an extent that pore water freezes and hydrate reforms (Moridis and Reagan, 2007b), of which both significantly affect the formation’s permeability and in turn limit the overall recovery. Pore water freezing can be prevented by maintaining the bottom hole pressure above 3 MPa, but hydrate reformation can only be avoided by controlling the temperature. Hot water- and steam injection as well as in-situ combustion have all been investigated experimentally (Kawamura et al., 2008a, Castaldi et al., 2007, Schicks et al., 2011), but as this study will conclude, a significant lower heating temperature is sufficient to achieve a more efficient energy balance. A combination of inhibitors and steam injection, similar to that used in the for heavy oil recovery, has shown to be a potential stimulation method (Kawamura et al., 2008b). A detailed analysis of different production scenarios for class 2 and 3 accumulations can be found in Moridis and Reagan (2007a, 2007b).

Other novel hydrate dissociation methods like burial of nuclear waste, fire flooding or electromagnetic heating have been discussed (Li et al., 2008, Callarotti, 2010, Sloan and Koh, 2007). The use of electromagnetic waves would enable dissociation within the stable hydrate region, but significant uncertainties in wave channelling and ground penetration depth have to be worked on.

Unlike for conventional gas, the production of gas hydrates will require additional effort in compression, water handling and flow assurance. A higher inlet gas
compression is necessary when hydrate deposits are produced by depressurisation, as the wellbore pressure is significantly lower compared to conventional gas wells (Walsh et al., 2009). Due to the lack of existing production, individual recovery factors are still being estimated based on numerical simulation, which on the other hand are almost exclusively validated with the results of a few field tests, or with physical small scale tests on core samples.

### 3.2.1 Hydrate accumulation classes

Natural gas hydrate accumulations are divided into four categories. Class 1 accumulations consist of a hydrate occurring zone (GHOZ) overlaying a layer of free gas and water. A class 2 GHOZ overlays free water only, whereas a class 3 accumulation consists of a GHOZ lacking an underlying zone of mobile fluids. Class 4 accumulations are those in low saturated clay layers (Moridis and Reagan, 2007a).

### 3.2.2 Large scale production tests

The first production test from hydrates was conducted at the Mallik site in the Canadian North West Territories (refer to Figure 2). Hydrate was dissociated by injecting 70°C hot water, while the pore pressure in the well was maintained constant. The lack of a pressure gradient transporting the dissociated gas to the well combined with the thermal inertia of the entire formation has however been found to be too great for the method to be effective by itself. As a result, a combination of reduced pressure and heat has been thought to be the most promising option. In the second production tests at Mallik, the hydrate bearing layer was depressurised through a 12 m perforated casing, and gas was produced for 7 days without notable effects from endothermic cooling. This will be different in the production scheme in the Nankai
Trough, where in the proposed 100 m perforated sections the radial heat flow will govern the temperature evolution in the wellbore’s vicinity.

At the time of writing, Conoco Philips is carrying out the first long term production tests at the Mount Elbert well in the larger Prudhoe Bay area on the Alaskan North Slope. Their production scheme is partially based on the carbon dioxide replacement method, in which CO₂ is being pumped into the hydrate layer to replace the methane molecules from the hydrate cages without breaking the lattice. Few data about these tests have been published yet, but a related numerical simulation suggests that the well perforation length is about 11 m (similar to Mallik, see above). A temperature sensitivity analysis in the simulation has shown that the production can be increased eightfold only by raising the initial temperature by 1K (Moridis et al., 2010).

The Japanese MH21 research consortium in collaboration with JOGMEC has scheduled to carry out the first offshore production tests in the Nankai Trough in 2012, but recent events triggered by the Tsunami on March 11 could possibly alter this target.

### 3.3 Laboratory dissociation apparatus

Gas hydrate properties are being studied experimentally either by recovering hydrate bearing cores, or on artificially formed hydrates in the laboratory. Despite recent pressurised coring techniques, the handling and preservation of recovered hydrate cores leads to unavoidable disturbances of the sample (Kneafsey et al., 2011). Controlled dissociation experiments are therefore mostly conducted on artificial hydrate samples, whose formation procedures are described in section 2.2. Most hydrate test apparatus accommodate small diameter hydrate samples. The AIST laboratory in Sapporo conducts axial dissociation tests on two setups with 30x120 mm
and 50x150 mm diameter x length Toyoura samples (Oyama et al., 2009, Ebinuma et al., 2008), while at their laboratory in Tsukuba they perform linear dissociation tests on sectionalised 50x500 mm samples (Kawamura et al., 2010). The Lawrence Berkeley laboratory’s apparatus facilitate tests on 76x267 mm hydrate bearing samples, which are dissociated axially from an end-cap and radially from the outer surface (Seol and Kneafsey, 2009). The gas hydrate research centre in Guangzhou hosts apparatus with which they carry out axial dissociation experiments of 38x500 mm hydrate samples (Tang et al., 2005). Tests on comparably large hydrate samples with dimensions of 305x914 mm are being conducted at Columbia University (Zhou et al., 2009). All linear dissociation setups are listed in Table 5 for comparison purposes. It is noted that the majority of samples are remarkably small in diameter, which makes it difficult to represent a genuine dissociation behaviour as the temperature flux from the outer boundary distorts the heat regime within the sample.

Table 5: Linear dissociation apparatus

<table>
<thead>
<tr>
<th>Institution</th>
<th>Sample diameter x length [mm]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIST (Sapporo)</td>
<td>30 x 120 50 x 150</td>
<td>Two setups, one in X-ray CT scanner</td>
</tr>
<tr>
<td>AIST (Tsukuba)</td>
<td>50 x 500</td>
<td>External cooling temperature can be sectionalised</td>
</tr>
<tr>
<td>Berkeley Lab</td>
<td>76 x 267</td>
<td>In X-ray CT scanner</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>38 x 500</td>
<td>Hot water injection</td>
</tr>
<tr>
<td>Columbia University</td>
<td>305 x 914</td>
<td>CO₂ replacement</td>
</tr>
<tr>
<td>Hanyang University, Seoul</td>
<td>38.1 x 304</td>
<td>Can also host recovered cores</td>
</tr>
</tbody>
</table>

Only the following few hydrate apparatus are designed for radial dissociation from the cylinder axis of the hydrate sample (see Table 6): at the University of Petroleum in
Beijing dissociation experiments are carried out on 300x100 mm diameter x length samples (Yang et al., 2010). The University of Potsdam hosts the largest hydrate testing chamber to date, where production tests with in situ combustion in 460x1300 mm hydrate samples are planned (Schicks et al., 2011). Pressure vessels inside CT scanners are generally made of aluminium alloys to reduce X-ray diffraction, which in turn affects their maximum diameters for design pressures above 10 MPa.

Table 6: Radial dissociation apparatus

<table>
<thead>
<tr>
<th>Institution</th>
<th>Sample diameter x length [mm]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing University of Petroleum</td>
<td>300 x 100</td>
<td>Cyclic hot water injection</td>
</tr>
<tr>
<td>University of Potsdam</td>
<td>460 x 1300</td>
<td>In-situ combustion (planned)</td>
</tr>
<tr>
<td>NUS</td>
<td>180 x 225</td>
<td>Combination of line heating and depressurisation at the axis</td>
</tr>
</tbody>
</table>
4 NUS hydrate testing apparatuses

4.1 Introduction

Most natural gas consists of methane with only smaller fractions of other hydrocarbons. Gas hydrates in nature are therefore almost exclusively structure I methane hydrates, of which stability- and formation conditions were the main design criteria for the presented apparatus. This chapter’s purpose is to introduce new readers to the hydrate setup at NUS, and to serve as a reference for the apparatus’ details. This is the first methane hydrate testing apparatus worldwide which enables controlled cylindrical dissociation by depressurisation and electrical heating.

The controlled- and measured variables of the testing rig are listed in Table 7, together with the devices they directly depend on, which are described separately in subsequent paragraphs. Overviews of the hydrate rig at the National University of Singapore are shown in Figure 15 and Figure 16.

Figure 15: Overview of the NUS hydrate testing apparatus, with the pressure vessel at the centre.
Table 7: Controlled- and measured variables of hydrate testing apparatus.

<table>
<thead>
<tr>
<th>Controlled variables</th>
<th>symbol</th>
<th>Device(s) used:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environment temp.</td>
<td>$T_{env}$</td>
<td>Air-conditioning unit</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glycol circulation</td>
</tr>
<tr>
<td>Cell pressure</td>
<td>$P_0$</td>
<td>Gas pressure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hand pump</td>
</tr>
<tr>
<td>Vertical stress</td>
<td>$\sigma_v$</td>
<td>Weight loaded lever beam</td>
</tr>
<tr>
<td>Wellbore-pressure</td>
<td>$\Delta P(t)$</td>
<td>Backpressure regulator</td>
</tr>
<tr>
<td>Heating temp.</td>
<td>$T_{well}$</td>
<td>Electrical resistivity elements inside the wellbore</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measured variables</th>
<th>symbol</th>
<th>Device(s) used:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Local temperature</td>
<td>$T(r,t)$</td>
<td>Thermocouples</td>
</tr>
<tr>
<td>Extracted gas</td>
<td>$V_{gas}(t)$</td>
<td>Gas flow meter</td>
</tr>
<tr>
<td>Extracted water</td>
<td>$V_w(t)$</td>
<td>Weighing</td>
</tr>
<tr>
<td>Compaction</td>
<td>$\varepsilon_z(t)$</td>
<td>Displacement</td>
</tr>
<tr>
<td>Density changes</td>
<td>$\rho_z(r)$</td>
<td>Gamma ray transmissivity</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>$\rho_{el.}(t)$</td>
<td>Five horizontal copper electrodes</td>
</tr>
</tbody>
</table>

Figure 16: Schematics of NUS hydrate testing apparatus (Falser et al., 2012b).
4.2 Testing geometry

As highlighted in section 3.3, dissociation experiments can be carried out in different symmetries. Several testing techniques and the resulting apparatus design are considered here.

Most hydrate dissociation tests are conducted in one linear dimension on relatively slender cylindrical samples, with large length to diameter ratios. There, the boundary conditions on the wall, in particular with respect to temperature and permeability, are expected to have too great an influence on the process. A depressurised sample almost instantly cools to the pressure equivalent hydrate equilibrium temperature. But in a small diameter cell, where the outer surface is controlled by constant temperature fluid circulation, heat fluxes into the sample will immediately distort the natural process and artificially fuel dissociation. The prevention of higher permeability on the cylinder wall is possible with rubber sleeves, but insulating it to reduce temperature fluxes would be impractical.

Another hydrate testing technique that has been evaluated during the design stage was a point dissociation by heating. Dissociation would be initiated from a heated cone-tip, either stable or penetrated into the hydrate bearing soil. The advantage of that variation would be to reduce the outer boundary effects as the dissociation takes place at the core of the sample. However, the analysis and interpretation of spherical dissociation is complex, as it is by definition a three-dimensional problem.

The third alternative was to build an apparatus with which hydrates are line-dissociated from the cylinder axis of the sample. This option was eventually chosen for several reasons: it allows the dissociation of pristine zones of the sample, where no sample/wall interfaces or instrumentation cables create temperature distortions or
artificial flow paths, while enabling the analysis of the process in one radial dimension due to the axial symmetry. The second advantage of line dissociation is that the results are relevant to two different field applications, to gas production from a single vertical wellbore, and to site investigation of hydrate sediments by a downhole probe.

4.3 Pressure vessel

The pressure vessel shown in Figure 17 is the central piece of equipment; it was designed to enable efficient hydrate formation under near in-situ conditions, which required a design pressure of 15 MPa and constant environment temperatures around 0°C. Its key design drivers were structural integrity and leak-tightness, to ensure safe operations and to avoid leaks of flammable gases at all cost. A balance between the sample’s diameter and the resulting required pressure vessel’s flange thickness had to be found in order to allow gamma ray transmissivity tests with the receiver mounted on top of the flange, operating at atmospheric pressure.

To simulate the in-situ overburden, vertical effective stress has to be applied to the sample. The mechanics for that are straightforward, as the plate on which the sample is placed is connected to a piston which in turn is loaded by weights (see section 4.7), pressing the sample against the top flange. Drained testing conditions are achieved by a clearance between the plate’s perimeter and the wall of the pressure vessel as well as a loop connection between port 1 and 3 shown in Figure 17. Technically trivial but important to the apparatus’ serviceability, was finding the right balance between the total internal height of the pressure vessel and the sample’s net height. The sample holder’s vertical position is defined by the flexible hose connecting the miniature wellbore, mounted at the centre of the sample holder, to the radially offset port 2, as
the connections have to be gas tight without restraining vertical movements (see Figure 18).

Sand is prevented from leaking out of the testing volume by an embedded porous stone in port 1 and a rubber ring around the piston plate. The flanges are connected to the main body by a reverse flange design (in contrast to a through-hole bolted connection), in order to facilitate the mounting of the cooling jacket for liquid circulation on the outside of the pressure vessel. The flanges are sealed with a single viton o-ring, which has to be lubricated before each test and placed in a spotlessly clean groove.

Figure 17: Cross section of the pressure vessel.
The wires for the thermocouples and electrical heating are led out of the pressure vessel by special wire connectors threaded into ½” and ¾” ports respectively. A list of the pressure vessel’s design specifications is given in Table 7, while its design and technical drawings can be found in Appendix A.

Table 8: Pressure vessel design specifications (Falser et al., 2010b).

<table>
<thead>
<tr>
<th>Material</th>
<th>SS316</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design code</td>
<td>ASME 2007-VIII</td>
</tr>
<tr>
<td>Design pressure</td>
<td>15 MPa</td>
</tr>
<tr>
<td>Design temperature</td>
<td>-5ºC to 60ºC</td>
</tr>
<tr>
<td>Total volume</td>
<td>0.01 m³</td>
</tr>
<tr>
<td>Sample volume (max)</td>
<td>0.0057 m³</td>
</tr>
<tr>
<td>Internal diameter</td>
<td>180 mm</td>
</tr>
<tr>
<td>Internal height (net)</td>
<td>225 mm</td>
</tr>
<tr>
<td>Vertical stress (max)</td>
<td>5.5 MPa</td>
</tr>
<tr>
<td>Piston stroke (max)</td>
<td>54 mm</td>
</tr>
<tr>
<td>Miniature wellbore outer diameter</td>
<td>10 mm</td>
</tr>
<tr>
<td>Wire feed-through Conax HD25 (40CU) PG4-312L comprising 32 wire</td>
<td>1/2” NPT</td>
</tr>
<tr>
<td>Wire feed-through Conax HD25 (40CU) MHC1-020-4-L comprising 2 heating wire (50 A max)</td>
<td>3/4” NPT</td>
</tr>
<tr>
<td>3 gas/water in- and outlet ports</td>
<td>3/8” NPT each</td>
</tr>
</tbody>
</table>
4.4 Cooling devices

The temperature during testing is controlled by a combination of fluid circulation around the pressure vessel and air-conditioning. Monopropylene glycol is circulated through a cooling jacket mounted onto the pressure vessel and an air-conditioning system cools the enclosed compartment in which the vessel is set up. The glycol temperature is controlled by the thermo-bath (Haake DC50-K41) with a minimum operating temperature of -40°C, a capacity of 15 l and a maximum fluid-circulation rate of 12.5 l/min. Its temperature accuracy and cooling power is 0.01°C and 750 W at 0°C respectively. The air-conditioning unit has a cooling capacity of 3.5 kW and consists of an open type compressor, a 500 kg evaporator, a 750 kg water condenser and a 1000 kg cooling tower.
4.5 Miniature wellbore

The miniature wellbore is located at the cylinder axis of the test sample. Its purpose is to dissociate the hydrate in a controlled manner, either by heat, pressure reduction or a combination of both. The advantages of and reasoning for line dissociation are discussed in section 4.2.

The dissociation pipe is 150 mm long and consists of a 10 mm outer diameter pipe-in-pipe system. Pore fluids are removed through the 1 mm diameter equally spaced perforations and the production annulus, and heat is supplied through the inner resistivity heating rod made of Nichrome 80/20. A fine copper mesh avoids sand clogging the pipe’s annulus. Figure 19 shows a cross section of the dissociation pipe.

![Cross section of the testing dissociation pipe](image)

Figure 19: Cross section of the testing dissociation pipe

The temperature is controlled by a thermocouple on the device’s outer surface and regulated through a solid state relay switching the current supply according to the set-and actual temperature reading. Temperatures of up to 60°C can be achieved by running 60V DC current through its 240 Ω resistivity rod, while the desired heat flux (W/m) is controlled by the voltage input.
4.5.1 Pressure regulation

For production simulations, it is important that the wellbore pressure can be set and kept constant over the testing period. This is achieved by a spring loaded backpressure regulator shown in Figure 20 where the pressure is slowly reduced by turning the handle, thus relaxing the spring between its casing and a short moving conical piston, until the desired pressure is reached.

![Figure 20: Backpressure regulator during testing (left), and disassembled after testing with visible sand traces (right).](image)

If the pressure on the upstream side exceeds the set pressure, the fluid is able to flow though the regulator until the pressure is equilibrated. Small pressure fluctuations arise from dynamic effects, in the sense that the initial activation pressure is slightly higher than is required for flow continuation (see Figure 53), an effect most likely attributed to friction.

The moving piston is sealed by a 50.8 mm diameter o-ring. If fine sand suspended in pore fluid flows into the backpressure regulator, it tends to accumulate around that o-ring making it prone to leak. In such an event the pore pressure can no longer be maintained and the production test at a specific wellbore pressure has to be repeated. To avoid sand from accumulating in the regulator, it is advisable to clean it after each test together with the further upstream installed filter element shown in Figure 21.
Figure 21: Sand filter installed on the 3/8” line between the miniature wellbore and the backpressure regulator

4.6 Thermocouples

The temperature within the hydrate bearing sample is measured by six k-type thermocouples. Their locations are given in Table 9. The thermocouples’ wires are led out of the pressure chamber through the ½” wire connector specified in Table 8. It must be ensured that artificial pathways through the wiring is minimised by leading them on the bottom of the sample to their location, attaching them to the pressure vessel’s wall at the desired height and putting them with a straight radial wire into position (see Figure 22). Accurate positioning of the thermocouples is essential; their bare wire end of 1 cm length is bent by 90° to measure the temperature at one radial point. It is further assumed that the effect of stress application and straining of the sample during testing on the thermocouple’s position is negligible. Their signal is processed by the NI 9213 module specified in Table 10. All six thermocouples were calibrated and unified by comparisons with a digital thermometer inside a water bath at different temperatures.
Table 9: Location of thermocouples within the sample

<table>
<thead>
<tr>
<th>Thermocouple</th>
<th>from centre [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>5 (at wellbore)</td>
</tr>
<tr>
<td>T2</td>
<td>20</td>
</tr>
<tr>
<td>T3</td>
<td>35</td>
</tr>
<tr>
<td>T4</td>
<td>50</td>
</tr>
<tr>
<td>T5</td>
<td>70</td>
</tr>
<tr>
<td>T6</td>
<td>90 (at wall)</td>
</tr>
</tbody>
</table>

Figure 22: Wiring at the interior of the pressure vessel: the cross wiring is limited to the bottom 10 mm of the specimen; the thermocouple wire is risen at the wall and radially brought into position.

4.7 Effective stress application

Effective vertical stress $\sigma_v$ is applied by compressing the soil sample vertically by a hydraulic piston. To achieve a constant effective stress in the sample despite compactions of the same during testing, the piston is loaded by dead weights. Since a direct loading would require an unpractical amount of weight, the weights are levered on a 5.2 m beam shown in Figure 23.
The piston’s design load pressure is 5.5 MPa, which enables simulations of about 550 m of a typical saturated soil overburden. Accounting for the lever beam’s dead load, the stress/weight relationship for this geometry is given in equation (4.1):

$$\sigma'_{v} = \frac{3.32 + 0.051w}{5.08}$$  \hspace{1cm} (4.1)$$

where

- $\sigma'_{v}$ is the vertical effective stress [MPa]
- $w$ is the load applied [kg]

The compaction during testing is measured by a linear transducer at the piston (see Figure 23, left), and its reading is processed by the analogue 0-10 V module listed in Table 10. To compensate for the differences in stroke volume of the loading piston and the one integrated into the pressure vessel (Figure 17), the strain measured at the lever beam’s end has to be factored by 1.8 to obtain the true sample strain.

It was observed that during testing a small volume of gas (a few bubbles) have most likely migrated from the pressure vessel into the hydraulic hose shown in Figure 23 (right). To ensure a load transfer through an incompressible medium, these gas
bubbles have to be removed occasionally by pressing the end ball-valves of the pressurised hose against a plain surface.

4.8 Gamma ray densitometer

The sample’s density is determined by calibrated gamma ray transmission measurements. Gamma rays are short electromagnetic waves, carrying no particles and are only dependent on the electron density of the material, which for most species is proportional to its mass density. Hence the density of wet sand and hydrate bearing samples can be derived from the transmissivity readings of reference samples with known density.

The NUS densitometer equipment consists of a gamma ray source sealed into a rod, a scintillation detector (Figure 24 (a)) and a decoder (c) to interpret the signal. The design and technical drawings of the thinner high strength cap, the detector and the dimensions of the source guide pipe can be found in Appendix A, page 161.

Figure 24: (a) detector mounted on top of the pressure vessel inside the air conditioned enclosure, (b) decoder (scaler) of signal from detector, (c) radial gamma ray source guide pipe and vertical miniature wellbore in dry sand.
The source is a cobalt-60 ($^{60}$Co) radioisotope with an intensity of 1.17 MeV. The intensity is comparable to 0.12 % of the kinetic energy of a flying mosquito (CERN, 2006), therefore very small indeed. It is sealed into the tip of a stainless steel pipe which is guided at atmospheric pressure inside the pipe shown in Figure 24 (c) along the sample’s radius.

Its gamma ray transmission through the 160 mm height of the sample (and the top pressure vessel flange) is counted by a scintillation detector mounted on top of the pressure vessel (see Figure 24 (a)). Its collimation window of 5 mm confines density measurements to approximately 10 mm in width. The measurements are statistical as the number of arriving gamma rays per second (cps) scatter within about ±6% of their average (see Figure 25), but after an exposure time of 60 seconds per location (and therefore obtaining 60 cps data), the reading’s mean-deviation from the long term average is reduced to about ±1%. Besides the profiling of samples at steady state, this also allows semi-dynamic measurements of transmissivity changes during dissociation, provided that the hydrate dissociation velocities are kept moderate.

To calibrate the wet sand density by the gamma ray transmissivity, samples with the same moisture ratio but different degree of compaction have been tested. Their respective densities were determined by mass balances of the known sample volume. As can be seen in Figure 25, the gamma rate of rays transmitted per time is inversely proportional to the soil’s density. Averaging the cps over a minute (counts per minute, cpm), their respective count rate ratio $R_c$ can be calculated with equations (4.2) and (4.3).
4. NUS HYDRATE TESTING APPARATUS

Figure 25: Detected counts per seconds for varying sand densities.

\[ R_c = \frac{N - B}{S} \]  
\[(4.2)\]

Where \( N \) and \( B \) are the measured- and background count rate respectively. The standard count rate \( S \) is defined as:

\[ S = 3.2 \times 10^4 \left( \frac{1}{2} \right)^{\frac{t}{T_{0.5}}} \]  
\[(4.3)\]

where:

\( t \) is the number of days between the measurement and the source’s base date on 15\(^{th}\) March 2011

\( T_{0.5} \) is the half life of Co\(^{60}\), 1925 days

The count rate ratio accounts for the measured transmissivity, the background radiation and the source’s natural decay. The correlation between \( R_c \) and their respective wet sand density is plotted in Figure 26. The bulk soil densities \( \rho_b \) in g/cm\(^3\) can subsequently be calculated from the linear regression line given in equation (4.4):
Figure 26: Correlations between the wet sand density and the count rate ratio.

\[ \rho_b = \frac{0.765 - R_c}{0.221} \quad \text{(4.4)} \]

4.9 Gas flow metering

The extracted gas during dissociation tests is being metered to quantify the amount of hydrate dissociated. This is achieved by two independent measurements, an in-line gas flow meter and by means of water displacement in a close container.

Figure 27: Gravity separator for recovered gas and water (left), and electronic in line gas flow meter for small gas flow rates (right).
Before the extracted gas is metered, it has to be separated from the recovered pore water. The gravity separator shown in Figure 27 (left) has a horizontal inlet of the two phase flow; the water accumulates in the container and its volume is recorded by weighing, while the gas flows through the vertical outlet towards the gas flow metering devices, driven by gravity and small pressure gradients.

The electronic in-line gas flow meter shown in Figure 27 (right) works by measuring the average flow velocity in a vertical tube, and is calibrated based on pure methane flow at 0.15 MPa and 8°C. Small adjustments to account for temperature differences have therefore to be made if production tests are carried out with a heated wellbore. The needle valve below the display enables the flow rate to be adjusted to suit the meter’s range between 8 and 50 litres at standard conditions per hour.\(^2\) The meter’s signal is gathered and processed with the NI9203 module in Table 10.

Figure 28 gives a schematic overview of the water displacement device: the tank is fully filled with water prior to the gas being inserted at the top. Any backflow of accumulated gas through the inlet is prevented by a check valve. The gas displaces the water, which flows through the outlet pipe at the tank’s bottom into an elevated container. Another check valve at the extreme end of the outlet prevents air from back-flowing after the gas stream from the pressure vessel ceases. The replaced water is continuously weighed on a data recordable balance.

The gas volume can then be derived from the water volume by accounting for the pressure on the gas \(P_{\text{gas}}\), which is a sum of the hydrostatic head \(P_{\text{stat}}\), the opening pressure of the check valve \(P_{\text{cv}}\), and the hydraulic pressure in the outflow \(P_{\text{hyd}}\).

\[^2\text{At the time of writing (Nov. 2011), the electronic gas flow meter is being serviced for malfunctioning. It is possible that it has to be replaced by a similar model.}\]
The hydrostatic head increases with increasing production as the water table inside the tank is lowered, and is calculated by:

\[ P_{\text{stat}} = \rho_w g (a + z) + P_{\text{atm}} \]  

where
\[ \rho_w \] is the fresh water density, 1000 kg/m\(^3\)
\[ a \] is the additional hydrostatic head of the outflow, 0.26 m

The check valve opening pressures in this setup are for both valves 6.9 kPa (1 psi). The gas extraction rate from hydrates is moderately slow in these experiments (~0.6 litres/min), and in turn the flow rate of the displaced water is of a comparable magnitude, limiting the hydraulic pressure given in equation (4.7) to only about 5% of the check valve opening pressure.
This justifies its calculation with an averaged velocity over the testing period. Based on the average velocity, the flow regime in the outlet pipe remains laminar with Reynold numbers well below $10^3$, which shows that even for small fluctuating flow the Fanning friction factor $f$ can be approximated by $16/Re$.

The gas volume at standard conditions can be calculated from the displaced water volume by applying equation (2.2) or similar suitable equations of state. This simple gas flow metering device is most suitable for low fluctuating flow rates and its principle is widely scalable. Whereas the total recovered gas volume can be determined accurately, the gas flow rate during testing can only be approximated due to the variable hydraulic pressure heads, but the effect is nevertheless small. For the specific dimensions of the device at NUS, the gas volume can be calculated by equation (4.8).

$$V_{gas} = V_w (0.0134*V_w + 2.0218)$$  \hspace{1cm} (4.8)

After the experiments, the extracted methane gas is released to the atmosphere while its volume is again replaced with water. This is best carried out by connecting the gas vent to the vacuum pump, while diverting the inlet tubing through hoses into the water containers. Care has to be taken to immediately close the valve at the gas vent as soon as the all the gas has been replaced, to spare the vacuum pump being flooded with water (and hence spoiling it). One way of doing that is to insert a liquid trap between the gas vent and the vacuum pump, which increase in weight shows that the tank is filled and still gives the researcher enough time to close the valve.
4.10 Controlling and data acquisition

During testing, the data is acquired by a National Instruments data logger (NI-CR10-9074), in which a 400 MHz real-time controller comprises the modules listed in Table 10. The commercial software LabVIEW 9.1 is used for the signal processing and data extraction.

Table 10: Modules used for controlling and data collection

<table>
<thead>
<tr>
<th>Module</th>
<th>Operation</th>
<th>Model Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermocouples</td>
<td>± 10 V</td>
<td>NI 9213</td>
</tr>
<tr>
<td>Heating control</td>
<td>± 10 V (later amplified)</td>
<td>NI 9263</td>
</tr>
<tr>
<td>Pressure transducer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas flow meter</td>
<td>4 – 20 mA</td>
<td>NI 9203</td>
</tr>
</tbody>
</table>

4.11 Notes on the operational procedure

The standard operating procedures for the sample formation and hydrate dissociation tests can be found in the NUS structural laboratory, but this section gives some practical insights for new rig users.

For the sample formation with the excess water method (refer to section 2.2), it has to be ensured that both the lower part of the pressure vessel (the volume beneath the piston plate, see Figure 17) and the piping and hose connecting the miniature wellbore to the backpressure regulator, are fully filled with water before sand is placed into the dry pressure vessel. The sand is installed in layers of approximately 40 mm height, and each is to be compacted uniformly to avoid discrepancies in strain development for the same testing conditions. Sand is to be filled accurately until the top edge of the pressure vessel. An air gap leads to large initial compaction during stress application,
whereas excess sand, on the other hand, could possibly hinder the top cap from forming a gas tight seal with the o-ring.

After dissociation tests with applied vertical effective stress, it is advisable to release the compressive load before relaxing the flange nuts. For compacted samples, the sample holder has again to be brought down to the original sample height of about 206 mm. For this, a dummy PVC pipe with 206 mm height is placed inside the pressure vessel. Its lateral openings for the wires and the gamma ray guide pipe enable the formation of a rigid connection between the holder and the pressure vessel cap, which is then tightened and the sample holder pushed to its original position.

For the data recording during the sample formation a time step of not less than 10 seconds is desirable to avoid causing internal memory problems in the data acquisition unit. During testing, which takes only a fraction of the formation time, the time step has to be reduced to 1 second to ensure accurate recordings.

For the gamma ray measurements, the settings at the Multiservice Scaler are MCOM with a timer of 60 seconds to record counts per minute (cpm). PC-port problems caused by the RS-232 to USB conversion can usually be resolved by restarting the computer. Hence the programme should be started before testing is commenced.
5 Heat transfer in hydrate-bearing sediments

5.1 Introduction

Heat transfer within a dissociating hydrate-bearing soil must be extremely complicated. Starting on a microscale, Figure 29 sketches different possible arrangements of particles and other phases. (1) shows stable pore-filling hydrate and water in the sediment’s pore space: the water can move and convect heat, but the solid hydrate phase cannot, though it can dissociate if the temperature and pore pressure change. In (2), hydrate and water are still present, but there is a third fluid phase of free gas due to the dissociating hydrate: both the gas phase and the water phase can move, but not necessarily at the same rate, and both can convect heat. Once all the hydrate is dissociated only the two liquid phases gas and water are present in the pore space (3). Both can flow, but depending on their relative saturation the one or the other phase may not move at all, because of capillarity and the possibility that one relative permeability is zero. It is still possible that hydrate can reform.

Figure 29: Soil samples investigated for heat transfer: (1) hydrate and water saturated sand; (2) dissociating hydrate in water saturated sand; (3) partially saturated sediment without hydrate present; (4) gas saturated dry sand;
(4) shows a dry sand saturated with gas. This does not represent a natural physical state in terms of gas production from hydrates, because even in gas saturated hydrate bearing layers the dissociation results in residual pore water, but fully gas saturated conditions are used to quantify the effect of natural (free) convection.

That complexity persists in the macroscale of a production scenario. Figure 30 is a sketch of a production scheme, with a well where the temperature is increased and the pressure decreased. It shows the different heat transfer mechanisms that might be present, and a schematic radial distribution of temperature and pressure. At the moving dissociating zone, heat is being absorbed by the endothermic dissociation process. To the right of that zone, temperature changes induce conductive heat transfer towards the dissociating zone, and the pressure gradient creates a forced convection through the pore fluid flowing towards the well. To the left of the dissociating zone, heat is conducted through the soil, and gas and water moving towards the wellbore create forced convection. Superimposed on the forced convection, density differentials in the gas may induce local natural convection.

It has not been possible to carry out a complete analysis, in part because of limits of time and in part because of limitations of the apparatus, which was not primarily intended for heat transfer measurements. Some of the analysis will have to await a subsequent dissertation.
It seems likely that in the production scenarios of most interest, the mechanisms of conductive and forced convective heat transfer will have a dominant effect. An understanding of this point will be a centrally important to the design of a production scheme. The objective of this chapter is to first quantify the bulk conductivity in the stable- and the dissociated zone. The effects of natural convection are addressed by comparing measured temperature profiles to perfect conductive conditions. Finally, the energy consumption rate in the dissociating zone is quantified numerically based on the measured temperature histories. This is important to calibrate numerical heat transfer simulations, and in turn to gauge the efficiency of heated wellbores.
The heat transfer rate in sediments depends on the thermal properties of each component, the sediment’s grain characteristics, its porosity, its degree of grain cementation and its stress regime. For the assumption that natural convection occurs slow enough to allow the pore fluid and the host sediment to reach thermal equilibrium, the governing general equation for conductive- and natural convective heat transfer is:

\[
\left( \rho C_p \right)_b \frac{\partial T}{\partial t} + \left( \rho C_p \right)_f \mathbf{v} \nabla T = \nabla \left( k_b \nabla T \right) + s_b
\]  

(5.1)

where subscript \(b\) and \(f\) stands for bulk and fluid respectively.

The flow chart in Figure 31 shows the sequential approach in this study: four different heat transfer experiments were carried out, on a stable-, water filled-, and 40% methane hydrate saturated sample (1), on a partly moisturised and CH₄ saturated sample (3), on a methane saturated dry sand sample at nine different pressures (4), and on a dissociating methane hydrate bearing sample (2).

Figure 31: Flow chart of heat transfer analysis.
The assumption of pure conduction in experiment (1) is justified by comparing the measured temperature profile at steady state with the theoretical temperature profile due to pure heat conduction shown in Figure 32. The experiments 3 and 4 are carried out to understand the contribution of natural convection in gas within the same sediment. The convective term \((\rho C_p)_f \mathbf{v} \nabla T\) in equation (5.1) shows that the transferred heat is proportional to the fluid’s density and specific heat, which in turn is for gases a function of pressure. Another aspect which was therefore looked into was the correlation between methane pressure and the temperature divergence from a purely conductive profile, in order to better estimate heat transfer coefficients at a matured stage of hydrate dissociation. Existing mixing models to approximate the thermodynamic properties of the bulk sample are presented and validated with test results, by comparing the numerically obtained transient region with the measured temperature histories in the experiments.

The test geometry is idealised as a long hollow cylinder, where the inner surface is heated at a constant temperature maintained by an alternating- but on average constant heat flux. The outer surface of the sample is kept at a constant temperature by fluid circulating on the outside of the pressure vessel (refer to chapter 4).

### 5.2 Steady-state conduction

Steady state is reached when for the same boundary conditions, the temperature at any particular point within the sample does no longer change with time. Conductive heat transfer is described by Fourier’s law, here expressed in radial coordinates:

\[
q = k \frac{dT}{dr}
\]  

(5.2)
where
\[ q \] is the heat flux [W/m²]
\[ k \] is the thermal conductivity [W/(m K)]
\[ T \] is the Temperature [K]
\[ r \] is the radius [m]

For the hollow cylinder geometry in one radial dimension, the steady state temperature profile due to conductive heat transfer is described by:

\[
\frac{d}{dr} \left( r \frac{dT}{dr} \right) = 0
\]  
(5.3)

Integrating equation (5.3) twice leads to
\[ T(r) = C_1 \ln(r) + C_2 \]
which subjected to constant temperatures at both boundaries yields to the following temperature profile:

\[
\frac{T(r) - T_0}{T_\infty - T_0} = \frac{\ln \left( \frac{r}{r_0} \right)}{\ln \left( \frac{r_\infty}{r_0} \right)}
\]  
(5.4)

where subscript \( \theta \) and \( \infty \) stands for the wellbore- and outer boundary respectively.

Results for a wellbore temperature of 288.2 K at \( r/r_0 = 1 \) and a cooling temperature at the outer boundary (\( r/r_0 = 18 \)) of 282.2 K are shown in Figure 32. This shows a good agreement between the local measured temperatures and the simple model in equation (5.4). For the tested 180 mm diameter samples and temperature differences of 6 to 13°C, it took between 50 and 100 minutes for the temperature to reach steady state.
5.3 Transient conduction

Transient heat conduction with constant conductivity in cylindrical coordinates is described by the diffusion equation in the following form:

\[
\frac{1}{\alpha} \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right)
\]  

(5.5)

where \( \alpha \) is the thermal diffusivity, defined as:

\[
\alpha = \frac{k}{\rho C_p}
\]  

(5.6)

where

- \( C_p \) is the specific heat capacity \([\text{J/(kg K)}]\)
- \( k \) is the thermal conductivity \([\text{W/(m K)}]\)
- \( \rho \) is the density \([\text{kg/m}^3]\)

Solving transient problems is important to determine how quickly heat can be supplied into the formation. The numerical method described in section 5.6 is based on the above equations.
5.4 Sample properties and boundary conditions

The heat transfer rate is measured on the bulk sample consisting of different species and phases. Since the properties of each phase vary (see Table 11), it is necessary to model the heterogeneous sample by bulk property estimates, to allow solving equation (5.5) in a single form and hence enabling a comparison with the experimental results. This study is based on the species properties listed in Table 11 and the sample properties and test boundary condition in Table 12.

Table 11: Species properties used in this study (Revil, 2000, Sloan and Koh, 2007).

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Water</th>
<th>Hydrate</th>
<th>CH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, $\rho$ [kg/m$^3$]</td>
<td>2620</td>
<td>1000</td>
<td>913</td>
<td>16 g/mol</td>
</tr>
<tr>
<td>Thermal conductivity, $k$ [W/(mK)]</td>
<td>7.7</td>
<td>0.58</td>
<td>0.62</td>
<td>Figure 33</td>
</tr>
<tr>
<td>Specific heat capacity, $C_p$ [J/(kgK)]</td>
<td>800</td>
<td>4190</td>
<td>2010</td>
<td>Figure 34</td>
</tr>
</tbody>
</table>

Table 12: Sample properties and test boundary conditions.

<table>
<thead>
<tr>
<th></th>
<th>Stable MH 1</th>
<th>Stable MH 2</th>
<th>Stable MH 3</th>
<th>65 % CH4</th>
<th>100 % CH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity, $n$ [-]</td>
<td>0.40</td>
<td>0.40</td>
<td>0.38</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>Hydrate saturation, $S_h$ [-]</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Initial- and boundary temp., $T_0$, $T_\infty$ [K]</td>
<td>275.5</td>
<td>275.4</td>
<td>281.0</td>
<td>275.5</td>
<td>275.2</td>
</tr>
<tr>
<td>Heating temp., $T_{wb}$ [K]</td>
<td>288</td>
<td>288</td>
<td>288</td>
<td>288</td>
<td>288</td>
</tr>
<tr>
<td>Vertical effective stress $\sigma$ [MPa]</td>
<td>2.37</td>
<td>2.37</td>
<td>2.37</td>
<td>2.37</td>
<td>0</td>
</tr>
<tr>
<td>Pressure, $P$ [MPa]</td>
<td>15.3</td>
<td>15.2</td>
<td>14.6</td>
<td>5.6</td>
<td>3.5</td>
</tr>
<tr>
<td>Heating rate $Q'$ at steady state [W/m]</td>
<td>70</td>
<td>70</td>
<td>35</td>
<td>70</td>
<td>70</td>
</tr>
</tbody>
</table>

The thermophysical properties of all species in Table 11 have a small temperature dependency, but are here assumed to be constant for near isothermal conditions. The
conductivity and specific heat of methane, are however, substantially pressure dependent. Figure 33 and Figure 34 give values for $k_{CH4}$ and $C_{p,CH4}$ for the pressures between 0 – 16 MPa and temperatures between 270 – 310 K. The graphs’ vertical scales have a suppressed zero to obtain a higher resolution. For the given pressure range, methane’s thermal conductivity and specific heat can vary by factors of 1.9 and 1.7 respectively for isothermal conditions.

Figure 33: thermal conductivity of methane $k_{CH4}$ for different pressure- and temperature conditions (data from Friend et al., 1989, and Roder, 1985).
The dynamic viscosity of methane $\mu_g$ has an almost linear pressure dependency while it is not very sensitive to temperature. Diller’s data (1984) leads to the following linear correlation between $\mu_g$ [Pa s] and the pressure $P$ [MPa], at 300 K and for pressures of up to 27.5 MPa:

$$\mu_g = \left(4.7P + 97.15\right) \times 10^{-6}$$  \hspace{1cm} (5.7)

Between 270 and 300 K, the methane viscosity is only increased by about 10 % (Reda, 1986).

Numerous studies were carried out to determine the thermal conductivity of pure gas hydrate and gas hydrate saturated with water or gas (Gupta et al., 2006, Waite et al., 2007, Li et al., 2012), showing the small pressure- and temperature dependencies of the pure hydrate’s conductivity. The bulk conductivity of hydrates in gas saturated sediments has been studied by Waite et al. (2002). Other studies were carried out with the hydrate proxy Tetrahydrofuran (THF) (Huang and Fang, 2005, Cortes et al.,...
A comprehensive study on recovered hydrate bearing cores from the Mallik site was conducted by Wright et al. (2005).

All cited studies were carried out with a needle probe, which comprises of a resistivity heater rod and an implanted thermocouple. It measures how quickly the temperature at the needle’s surface rises for a known power input, from which the material’s conductivity can be derived in the transient state. The needle probe is widely used for conductivity measurements, as it can be applied from the material’s surface, and is therefore also applicable for in-situ testing. A limitation is the often imperfect heat transfer across its interface, especially in irregular granular materials.

An alternative is to measure the thermal conductivity at steady state. This study applies that method and evaluates the bulk thermal conductivity of methane hydrates synthesised in the laboratory. Tests were carried out to determine conductivities in stable- and dissociated hydrate zones and no flow conditions.

The thermal conductivities of methane hydrate and water are relatively close and about 15 times greater than that of methane gas. For the assumption of an immobile and uniform host sediment, this indicates that the heat transfer in hydrate bearing soil will depend less on the hydrate saturation, but mostly on the saturation of free gas as well as on the dissociation energy for destabilised hydrate layers.

### 5.5 Mixing models for bulk thermal properties of granular materials

The bulk thermal diffusivity is determined by the bulk density $\rho_b$, the bulk specific heat capacity $C_{p,b}$, and the bulk thermal conductivity $k_b$ (see equation (5.6)). The bulk density is obtained by a volume weighted average:

$$\rho_b = \rho_s (1-n) + n \left[ \rho_w S_w + \rho_h S_h + \rho_g S_g \right]$$

(5.8)
where the subscripts $b$, $s$, $w$, $h$ and $g$ stand for bulk, sand, water, hydrate and gas, and $n$ is the porosity and $S$ the pore volume saturation. The bulk’s specific heat capacity is modelled by a mass weighted average:

$$C_{p,b} = \frac{1}{\rho_b} \left[ C_{p,b} \rho_s (1-n) + C_{p,w} \rho_w n S_w + C_{p,h} \rho_h n S_h + C_{p,g} \rho_g n S_g \right]$$ (5.9)

The bulk thermal conductivity can be modelled by the geometric mean (Jaupart and Mareschal, 2010, Nield, 1991):

$$k_b = k_s^{(1-n)} k_w^n k_h^n k_g^n$$ (5.10)

or by the square root mean (Beardsmore and Cull, 2001):

$$k_b = \left[ \sqrt{k_s (1-n)} + \sqrt{k_w S_w n} + \sqrt{k_h S_h n} + \sqrt{k_g S_g n} \right]^2$$ (5.11)

The Hashin and Shtrikman (1962) upper- and lower bound for thermal conductivity provide a range of where the conductivities must lie, but are too general for engineering purposes. Thus, their average is in some cases used to determine the bulk thermal conductivity (Hartmann et al., 2005):

$$k_p = \left( S_h k_h + S_w k_w + S_g k_g \right)$$

$$k_{b,=} = k_p + \frac{1-n}{\left( \frac{1}{k_s} - \frac{1}{k_p} \right) + \frac{n}{3k_p}}$$ (5.13)

$$k_{b,=} = k_s + \frac{n}{\left( \frac{1}{k_p} - \frac{1}{k_s} \right) + \frac{n}{3k_s}}$$ (5.14)

Johansen’s (1975) bulk conductivity model is often used for natural soil; it interpolates between the dry- and saturated conductivity:
For hydrate bearing soil, the Kersten number $K_e$ is approximated by

$$K_e = \log \left( S_h + S_w \right) + 1,$$

which for fully saturated conditions reduces equation (5.15) to

$$k_b = k_{sat} = 0.57^n k_e (1-n)^2.$$  

The dry conductivity for crushed sands is given as $k_{dry} = 0.039 n^{-2.2}$. The most widely applied heat transfer models are given here, but several more for partially saturated natural soils can be found in Farouki (1981) and Revil (2000, Jougnot and Revil, 2010).

Some bulk thermal conductivities obtained by the different mixing models obtained above are tabulated for different saturations in Table 13. Despite the claim that most mixing models work accurately in saturated sediments but less so in partially saturated conditions (Hartmann et al., 2005, Nield, 1991), the thermal conductivities for stable methane hydrate conditions vary by more than 20% between the different models. By volume, however, a dissociated hydrate results in 93% water and only 7% of free gas. That means that by the dissociation of a 40% hydrate saturated sample, only 2.8% of the pore space will eventually be occupied by free gas under isochoric conditions.
Table 13: Thermal conductivities for different saturation cases obtained by the models described above.

<table>
<thead>
<tr>
<th>Pore saturation:</th>
<th>Bulk conductivity $k_b$ based on:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>geometric mean</td>
</tr>
<tr>
<td>Water</td>
<td>0.6 0.4 0</td>
</tr>
<tr>
<td>Hydrate</td>
<td>0.6 0.3 0.1</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.6 0.2 0.2</td>
</tr>
<tr>
<td></td>
<td>0.6 0.1 0.3</td>
</tr>
<tr>
<td></td>
<td>0.6 0 0.4</td>
</tr>
</tbody>
</table>

5.6 Numerical heat transfer modelling

The conducted heat transfer experiments presented in sections 5.7 are replicated by numerical methods to validate the bulk properties discussed in section 5.5, and subsequently to estimate the volumetric heat sink during the hydrate dissociation process (see section 5.9). The commercial software MATLAB is used to approximate solutions of the governing diffusion equation in (5.5). The heat transfer problem is solved for conduction alone, as natural convection effects are expected to be negligible in fully saturated conditions, and assumed to be minor during the early stage of dissociation due to the small content of free gas. The MATLAB routine `pdepe` solves equation (5.5) by the finite difference method in a forward time and centred space form (explicit method). Equations (5.16) and (5.17) show the routine’s time- and space discretisation.
\[
\frac{\partial u}{\partial t} = \lim_{\Delta t \to 0} \frac{u(x, t + \Delta t) - u(x, t)}{\Delta t} \tag{5.16}
\]
\[
\frac{\partial^2 u}{\partial x^2} = \lim_{\Delta x \to 0} \frac{u(x - 1, t) - 2u(x, t) + u(x + 1, t)}{\Delta x^2} \tag{5.17}
\]
MATLAB expresses the diffusion equation in the following form:
\[
c \left( x, t, u, \frac{\partial u}{\partial x} \right) \frac{\partial u}{\partial t} = x^m \frac{\partial}{\partial x} \left( x^m f \left( x, t, u, \frac{\partial u}{\partial x} \right) \right) + s \left( x, t, u, \frac{\partial u}{\partial x} \right) \tag{5.18}
\]
Where \( m \) is equal to 0, 1, 2 for linear, cylindrical and spherical problems respectively.
For specific heat transfer problems in cylindrical coordinates, equation (5.18) becomes:
\[
\rho_b C_{p,b} \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( k_b r \frac{\partial T}{\partial r} \right) + s \tag{5.19}
\]
where \( s \) is the heat sink- (energy consumption rate) or source term per time step. It is important to note that in most textbooks this heat diffusion equation is expressed with the inverse thermal diffusivity on the left hand side as illustrated in equation (5.5) (Rolle, 2000, Poulikakos, 1994), but the \textit{pdepe} routine requires the separation of thermal conductivity and specific heat as shown in equation (5.19) in order to satisfy their definition of boundary conditions. Those are described in the general form of:
\[
p \left( x, t, u \right) + q \left( x, t \right) f \left( x, t, u, \frac{\partial u}{\partial x} \right) = 0 \tag{5.20}
\]
In which \( p \) and \( q \) are defined on the left- and right spatial boundary. The flux term in equation (5.20) is \( f = k_b \partial T/\partial r \).
Although a self-written algorithm to discretise the time- and space differentials in a foolproof way would have been preferable, the experimental boundary conditions at the wellbore did not allow that. The heater temperature in the wellbore is controlled
through a solid state relay, alternating the power supply in accordance to the set temperature. As such, the left boundary condition describing the heat flux had to be expressed with a conditional `if` command, alternating the heat flux in the numerical simulation depending on the calculated actual temperature. The left boundary conditions at the heated wellbore therefore equals the input heat flux $Q'$ per unit length $L$ with the system’s heat flux $f$ time the wellbore’s surface area per unit length:

$$
\frac{\dot{Q}}{L} + 2\pi r_{wb} k_b \frac{\partial T}{\partial r} = 0
$$

(5.21)

The right boundary condition is stated as constant and equal the initial temperature. For more details about the input file the reader may refer to Appendix B.

### 5.6.1 Numerical stability

In the explicit finite difference method, the accumulating truncation error can lead to instabilities if the following condition is not met (Holzbecher, 2007, Elsherbeni and Demir, 2009):

$$
\frac{\alpha \Delta t}{\Delta x^2} = \lambda \leq \frac{1}{2}
$$

(5.22)

Where $\alpha$, $\Delta t$, and $\Delta x$ are the defined diffusivity, time- and space steps respectively. The `pdepe` routine has an implemented dynamic time discretisation algorithm to avoid matrix singularities by temporarily reducing the time step (Skeel and Berzins, 1990). Minor fluctuations in results could however still be observed despite a $\lambda < 0.25$, but that was most likely due to iterations to meet the conditional left boundary condition. Hozbecher (2007) recommends to keep $\lambda < 1/6$ to minimise accumulated errors.
5.7 Thermal conductivity measurements

A material’s thermal conductivity can be measured by two principles: in the transient heating phase by measuring temperature changes at the same location at specified times (equation (5.23)), or at steady state by measuring the temperature at specified locations (equation (5.24)). The IEEE Standard 442 (1991) for measuring thermal resistivities of soil proposes the transient approach, inverse but similar to the transient conductivity equation in (5.23). Care has to be taken to account for the imperfect heat transfer at the heater – sample interface due to layers acting as insulators. A comprehensive review of conductivity measurement techniques is given by Presley and Christensen (1982).

\[ k_b = \frac{\dot{Q}}{4\pi L} \frac{\ln(t_2/t_1)}{T(r_2,t_2) - T(r_1,t_1)} \]  

(5.23)

\[ k_b = \frac{\dot{Q}}{2\pi L} \frac{\ln(r_2/r_1)}{T(r_2) - T(r_1)} \]  

(5.24)

where

- \( k_b \) is the bulk thermal conductivity [W/(mK)]
- \( \dot{Q} \) is the heating rate at \( r_1 \) [W]
- \( L \) is the heated length [m]
- \( t_i \) time [sec]
- \( r_i \) distance from the heater [m]
- \( T \) is the measured [K]

The power input into the heater is 15 W over a net heated height of 15 cm. The heating rate per unit length is therefore 100 W/m in the transient phase until the set wellbore temperature is reached. At steady state, the heating rate averaged over the time intervals is 5.8 W/(m\( \Delta T \)), where \( \Delta T \) is the difference between the wellbore temperature and the constant outer boundary temperature.
Figure 32 shows that the heat transfer in water saturated hydrate bearing sediment is purely conductive. As such, the thermal bulk conductivity $k_b$ is calculated in accordance to the steady state temperature at different distances from the heated wellbore. Typical temperature histories of a heat transfer test in stable (non-dissociating) hydrate is shown in Figure 35.

Figure 35: Temperature histories at different radii from the heater wellbore of a methane hydrate (40%) and water (60%) saturated sediment with a porosity of 0.4.

The temperature fluctuations at the wellbore $r/r_0 = 1$ (reference point $r_f$ in equation (5.24)) were numerically filtered with the MATLAB `sgolayfilt` command. The $k_b$ was calculated for each thermocouple in three different test samples, and are compared to the theoretical conductivities in Figure 36. Their average values are given in Table 14, in which the standard deviation for the individual tests reflects the variation of the measured conductivities between the different thermocouples, whereas $\sigma$ of the mixing model approximations shows their deviation from the measured average bulk conductivity of 2.59 W/mK. The obtained bulk thermal conductivity are in good agreement with the measurements on recovered hydrate bearing cores from the Mallik site reported by Wright et al. (2005), which $k_b$ range from about 2.4 to 2.9 W/(mK).
It can be concluded that both the geometric mean as well as the model by Johansen (1975) lead to accurate estimates of the bulk thermal conductivity $k_b$ in these conditions, but the former is preferred over the latter for its simplicity and reduced empiricism.

Figure 36: Thermal bulk conductivities at different radii measured at steady state in comparison to the models of $k_b$ (Falser et al., 2012a).

Table 14: Measured bulk thermal conductivities of water saturated hydrate bearing sediments compared with mixing model approximations (*italics*).

<table>
<thead>
<tr>
<th></th>
<th>$k_b$ [W/(mK)]</th>
<th>$\sigma$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable MH 1</td>
<td>2.59</td>
<td>13.7%</td>
</tr>
<tr>
<td>Stable MH 2</td>
<td>2.57</td>
<td>11.5%</td>
</tr>
<tr>
<td>Stable MH 3</td>
<td>2.61</td>
<td>9.2%</td>
</tr>
<tr>
<td>Geometric mean</td>
<td>2.74</td>
<td>11%</td>
</tr>
<tr>
<td>Square-root mean</td>
<td>3.88</td>
<td>92%</td>
</tr>
<tr>
<td>HS average</td>
<td>3.33</td>
<td>53%</td>
</tr>
<tr>
<td>Johansen (1975)</td>
<td>2.72</td>
<td>9%</td>
</tr>
</tbody>
</table>
To check how sensitive the bulk conductivity measurements are to partial- and full gas saturation, and how far that can be assessed with the presented models, the theoretical values are benchmarked with two experiments. Figure 37 plots the conductivity values for each model for different gas saturations, where the remaining pore space is assumed to be water filled in the absence of methane hydrate. This is relevant during production, when heat is to be transmitted from the heated wellbore, through the dissociated zone into the dissociating zone. The dissociated layer is partially saturated with residual trapped gas and water bound by the host sediment. This case reflects no flow conditions with an immobile fluid layer. This is applicable for heat transfers during well shut-in times or in zones with very low fluid velocities far from the well.

Figure 37: Bulk thermal conductivity based on different mixing models for varying theoretical methane and water saturations at 1.8 MPa and 290 K in absence of methane hydrate.

Comparing the measured conductivities with the conductivity for fully saturated conditions \( k_b = 2.59 \text{ W/(mK)} \) and the test results for 65% and 100% gas saturation, it can generally be seen that the actual measured values decrease less with increasing
gas saturation as compared to those obtained by the theoretical models. The measured bulk conductivities now agree closest to the HS average model (see Table 15). This discrepancy between the models and measurements, might in this case be attributed to the fact that the mixing models overestimate the effect of a low conductivity phase like free gas, while the actual heat flux is diverted more towards the relative high conductivity phases. In partially saturated conditions, capillary effects make the pore water accumulate at the pore throats, and thus increasing the thermal conductivity at the grain contact points. The standard deviation between the individual measurements was also in the presence of free gas in the range of 10%, which indicates that for the stated gas pressures, no effects of natural convection could be observed.

Table 15: Measured bulk thermal conductivities of partially (65%) and fully (100%) gas saturated bearing sediments compared with mixing model approximations.

<table>
<thead>
<tr>
<th>$k_b$ [W/(mK)]</th>
<th>65% gas saturated</th>
<th>$\sigma$ [%]</th>
<th>100% gas saturated</th>
<th>$\sigma$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>2.33</td>
<td>11.2%</td>
<td>2.29</td>
<td>10.2%</td>
</tr>
<tr>
<td>Geometric mean</td>
<td>1.23</td>
<td>78%</td>
<td>0.88</td>
<td>100%</td>
</tr>
<tr>
<td>Square-root mean</td>
<td>3.26</td>
<td>66%</td>
<td>3.02</td>
<td>52%</td>
</tr>
<tr>
<td>HS average</td>
<td>2.58</td>
<td>18%</td>
<td>2.17</td>
<td>9%</td>
</tr>
<tr>
<td>Johansen (1975)</td>
<td>1.45</td>
<td>63%</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
5.8 Conductive heat transfer in stable methane hydrate

In this section, the thermal conductivities derived from the experiments in section 5.7 are applied to numerical heat transfer simulations in MATLAB as described in section 5.6. The aim is to validate their accuracy based on comparisons with the experimental results.

Whether the heat transfer is governed by the flux $Q'$ on the sample’s surface, at the heated wellbore in this case, or the heat flux through the sample can be seen from the ratio of both, known as the Biot number $Bi$.

$$Bi = \frac{\dot{Q}_b}{\dot{Q}_c} = \frac{\dot{Q}_b}{Ak_b(T_{wb} - T_\infty)}$$ (5.25)

where the subscripts $b$ and $c$ stand for boundary and conductivity respectively. $A$ is the wellbore’s surface area, $k_b$ the thermal bulk conductivity and $T_{wb} - T_\infty$ the difference between the heated wellbore and the constant outer boundary temperature.

For $Bi < 10^{-1}$, the heat transfer is dominated by the interface heat flux and hence uniform temperature profiles throughout the sample can be assumed. In this study, with $\Delta T \sim 10^1 \text{ K}$, $A \sim 10^{-2} \text{ m}^2/\text{m}$, $k_b \sim 1 \text{ W/mK}$ and $Q_b \sim 100 \text{ W/m}$, the Biot number remains for any possible variations to the sample in the order of $10^2$. As expected, this confirms that in this study the sample’s internal heat transfer processes are governing.

Heat transfer tests in stable methane hydrate bearing sediment were carried out at high pressure low temperature conditions in order to avoid hydrate from dissociating. In this set of experiments, the initial sample temperature of 275 K was raised at the miniature wellbore to 288.2 K by at a constant pressure 15 MPa. The temperature at the outer sample’s surface was kept constant by continuous fluid circulation. The temperature within the sample progressively moved from the heated centre outwards.
for a duration approximately 70 minutes, until it reaches steady where the temperature at any specific location remains unchanged with time. Temperature profiles of the experiments are shown together with their corresponding numerical simulation in Figure 38. The numerical simulation is based on the same sample properties with 40 % methane hydrate and 60 % water saturated sediment with the experimentally derived bulk thermal conductivity $k_b$ of 2.59 W/mK. The experimental- and numerical temperature profiles agree closely, and comparing their profiles to the one of pure conduction (equation (5.4)), it is again confirmed that the effect of natural convection in the above described conditions is negligible. Interestingly, also for the partially saturated sample (35% water, 65% CH₄) the temperature profile shown in Figure 38 indicates that the heat transfer is purely by conduction. This is most likely due to the fact that the residual water accumulates at the grain contact points, at the so called pore throat, reducing the relative permeability of air significantly and thus preventing convective heat transfer to take place. In fully gas saturated conditions, it was noted that the heat transfer by free convection is dependent on the gas pressure, as can be seen from the temperature profile at 9 MPa. It was observed that the convection did not gradually increase with pressure, but rather started occurring once a critical pressure of about 5.5 MPa was reached.
5.8.1 $k_b$ sensitivity

To validate the accuracy of the thermal conductivities derived from the experiments at steady state conditions, a heat transfer analysis with the measured bulk conductivity $k_b$ was carried out in MATLAB to check their accuracy and hence applicability in the transient heat transfer phase.

The numerical simulations are based on the same sample properties, with 40% methane hydrate and 60% water saturated sediments with a porosity of 40%. Figure 39 shows the measured temperature evolutions at the six measurement locations in comparison with the numerical simulations. Three repetitive simulations with thermal conductivities of 0.5, 2.6, and 10 W/(mK) were performed to check the mechanism’s sensitivity to it in the transient period.
Figure 39: Comparison between the experimentally measured- and numerically simulated temperature histories in the transient phase for varying bulk thermal conductivity $k_b$ [W/mK].

The measured and simulated temperature histories agree closely for the previously determined thermal conductivity of 2.6 W/(mK), except at the two extreme boundaries $r/r_0 = 1$, where the measured temperature is affected by interface between the heater and attached thermocouple, and at $r/r_0 = 18$, where the temperature in the experiments could not be precisely kept at 275.4 K, but increased by about 0.6 K over 60 min. This confirms that the boundary conditions in the experiments were accurately assessed and subsequently implemented in the numerical study. The repetitive simulations show that the heating rate is substantially affected for
conductivities varying by an order of magnitude. It can be concluded that the bulk thermal conductivity determined by the steady state method is precise as it represents the heating rate at each location accurately.

5.9 **Hydrate dissociation rate**

In this section the energy consumption rate of the dissociation process is quantified. The total energy required to dissociate the methane hydrate present is known by its formation- and dissociation enthalpy $\Delta H$ of 54.2 kJ/(mol CH$_4$) or 410 kJ/kg (Handa, 1986), but the rate at which it dissociates in the pore space is not yet clearly defined. Most dissociation studies of hydrate bearing sediments still apply Kim-Bishnoi’s model (1987) described in section 2.3, but which was formulated for pure hydrates in a stirred tank to eliminate the effect of temperature gradients. Hydrate in sediment, however, is by definition immobile, and therefore its dissociation rate is expected to depend on the heat transferred into the dissolving zone. The material and sample properties used in this study are given in Table 16:

Table 16: Material and sample properties of this study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.4</td>
</tr>
<tr>
<td>Methane hydrate saturation</td>
<td>0.4</td>
</tr>
<tr>
<td>Enthalpy change</td>
<td>410</td>
</tr>
<tr>
<td>Hydrate density</td>
<td>913</td>
</tr>
<tr>
<td>Bulk density</td>
<td>1946</td>
</tr>
<tr>
<td>Bulk specific heat capacity</td>
<td>1.31</td>
</tr>
<tr>
<td>Total energy sink</td>
<td>5.99 x 10$^3$</td>
</tr>
<tr>
<td>Energy input</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 40: temperature evolutions at different radial locations and the methane hydrate equilibrium temperature $T_{eq}$ for the 3.65 MPa pore pressure.

Figure 40 shows temperature histories during ongoing hydrate dissociation at different distances from the heated wellbore. The pore pressure was set to 3.65 MPa so that a progressive dissociation away from the miniature wellbore could be observed. The discontinuities in the individual temperature evolutions are in line with the pressure equivalent equilibrium temperature $T_{eq}$. They mark the moment when the supplied energy flux from the wellbore exceeds the required dissociation enthalpy, either because all the hydrate in that zone is dissociated or because the remaining requires less energy to progress, and therefore the temperature at that location rises above the equilibrium temperature.

In addition to dissociation, the energy required to heat the sediment must also be accounted for. The analysis is conducted in cylindrical coordinates per unit length, as axial heat fluxes are assumed to be negligible compared to the radial heat flow. The zones’ volume and required energies are given in Table 17.
Table 17: Dimensions and energy requirements of each zone shown in Figure 40.

<table>
<thead>
<tr>
<th></th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner radius [m]</td>
<td>0.005</td>
<td>0.02</td>
<td>0.035</td>
</tr>
<tr>
<td>Outer radius [m]</td>
<td>0.02</td>
<td>0.035</td>
<td>0.05</td>
</tr>
<tr>
<td>Zone’s bulk volume [m³/m]</td>
<td>1.18</td>
<td>2.59</td>
<td>4.01</td>
</tr>
<tr>
<td>Accumulated bulk volume [m³/m]</td>
<td>1.18</td>
<td>3.77</td>
<td>7.78</td>
</tr>
<tr>
<td>Required dissociation energy [kJ/m]</td>
<td>70.6</td>
<td>155</td>
<td>240</td>
</tr>
<tr>
<td>Required heating energy [kJ/mK]</td>
<td>3.00</td>
<td>6.60</td>
<td>10.2</td>
</tr>
<tr>
<td>Total required energy per zone [kJ/mK]</td>
<td>90.2</td>
<td>165</td>
<td>243</td>
</tr>
<tr>
<td>time until $T_{eq}$ is reached [min]</td>
<td>9.45</td>
<td>28.3</td>
<td>41.3</td>
</tr>
<tr>
<td>temperature increase in zone [K]</td>
<td>6.55</td>
<td>1.55</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The dissociation rate can be determined by two approaches: in one it is assumed that the zone two highlighted in Figure 40 only starts dissociating when the temperature at the interface with zone one exceeds the equilibrium temperature. In the second approach it is assumed that all three zones start dissociating simultaneously at $t = 0$, just at a different pace. By comparing the dissociation rate of both approaches (see Figure 41 left), it can be seen that for both assumptions the consumed energy for dissociation and heating remains about constant over time. The inconsistency in the dissociated volume over time (Figure 41 right) is because near the wellbore, where the temperature is higher, more energy is initially lost for heating of the sample. In zone 1 where the temperature change is the largest (6.55 K), the heating energy still only accounts for 20% of the total dissociation energy.
Figure 41: Required energy for dissociation and heating over time for the zone- and total volume $V_{tot}$ approach (left); dissociated volume $V_{diss}$ over time (right).

The two approaches have their own legitimacies. The zone model is legitimate because the temperature at the interface to the adjacent zone remains suppressed below $T_{eq}$ and therefore no dissociation should theoretically take place. The gentle increase in temperature during dissociation, however, (refer to $r/r = 7$ to $14$ between $0$ and $10$ min), shows that a small amount of heat is flowing through the dissociating layer. If the energy consumption is constant over time, it contradicts Kim-Bishnoi’s model in equation (2.3), which defines the rate $dn/dt$ proportional to the shrinking hydrate surface area $A_h$ during dissociation. A quantification of the hydrate surface area in the pore space and its development during dissociation leaves too much room for speculations: the assumption of perfectly spherical hydrate particles in the pore space is only partly justifiable because gas bubbles of different sizes will during the formation process (70 hours) eventually conglomerate to unsymmetrical hydrate particles. But a more fundamental reason why equation (2.3) is not applicable to hydrate dissociation in a porous media is because the heat fluxes are not uniform on a macro scale. The thermal conductivity of the sediment is one order of magnitude larger than the pore fluid’s, and two orders of magnitude larger than that of free gas. That results in greater heat fluxes through the sediment skeleton in the case of a
present temperature gradient, and therefore during the dissociation process, the hydrate at the grain particles will dissociate more rapidly. Therefore the original shape will not be preserved and a splitting of the particles is likely. That in turn would increase the surface to volume ratio and accelerating the dissociation rate if the pressure- and temperature conditions are kept constant.

The average rate of energy consumption \( \frac{dE_{\text{req}}}{dt} \) varies in both approaches between 161 and 170 W/m, both exceeding the set heating input of 100 W. Unlike in depressurisation dissociation (see chapter 6) in this case there is no energy supplied from the outer boundary, because the environment temperature remains below the sample temperature at all times of testing. Thus, the discontinuities in temperature in Figure 40 are marking the points where the supplied 100 W exceed the energy consumed by the dissociation of the remaining hydrate in that zone, and as a result the temperature rises above the dissociation equilibrium temperature. Based on the available energy, it can be determined how much the hydrate pore volume saturation is reduced before the bulk sample becomes heat conductive despite ongoing dissociation. The theoretical remaining methane hydrate saturations in each zone at which the temperature rises above \( T_{eq} \) are given in Table 18.

Table 18: Remaining hydrate saturation \( S_{h,T_{eq}} \) at the equilibrium temperature \( T_{eq} \) and the correspondent relative change in saturation \( \Delta S_h \) for both the zone model and the total volume approach.

<table>
<thead>
<tr>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>( S_{h,T_{eq}} )</td>
<td>( \text{rel. } \Delta S_h )</td>
</tr>
<tr>
<td>Zone ( V_{tot} )</td>
<td>0.10</td>
<td>76%</td>
</tr>
<tr>
<td>Zone 0.10</td>
<td>0.10</td>
<td>76%</td>
</tr>
</tbody>
</table>
For the zone model the saturations were estimated with the assumption that at the time one zone reaches $T_{eq}$, only a negligible amount of heat is absorbed by the hydrate and its temperature has become steady, so that all input heat is transmitted to the adjacent zone. For the total volume approach the saturations at $T_{eq}$ can be determined more accurately by factoring in the remaining energy due to the partial dissociation of the previous zone. The results in both cases suggest, however, that the degree of dissociation when the sediment starts conducting heat energy is highest in the zones near the wellbore, and then decreases with increasing distance from it.

This effect is beneficial from a gas production perspective. It does not imply that the remaining hydrate is not being dissociated, but rather that an energy input can be chosen to eventually overcome the heat insulating effect of dissociating hydrate and to extend the influence zone of a heated wellbore. How the dissociation energy can be modelled numerically by an energy consumption rate is addressed in the following section.

### 5.9.1 Constant energy consumption rate

In this section the temperature evolutions measured in the experiments are compared with heat transfer simulations with a constant heat energy consumption rate $s$ uniformly distributed throughout the sample. The aim for this is to scale the order of magnitude, as well as to see where this simplified approach deviates from the measurements in time and space. The numerical analysis is carried out with the MATLAB *pdepe* solver described earlier, in which the heat sink is defined as energy loss per unit volume per defined time step [J/(Δt m$^3$)]. An input file can for this simulation be found in Appendix B.
Figure 42: Comparison between experimental temperature profiles during the hydrate dissociation process at different times and numerical simulations without-, and with a uniform heat energy consumption rate of 10, 40 and 100 kW/m³.

The required energies given in Table 17 for dissociating the zones shown in Figure 40 are stated for their respective volume per meter length. Their average per unit volume varies between 40 and 46 kW/m³ for the total volume- and the zone approach respectively. Sequential temperature profiles of the experiment and numerical simulations are shown in Figure 42. The simulations were carried out without a heat sink (short-dashed line), and with a uniformly distributed energy consumption rate of 10 kW/m³ (solid line), 40 kW/m³ (dashed line) and 100 kW/m³ (dashed-dotted line). As can be seen, the uniform heat energy consumption rate of 40 W/m³ gives only a fair agreement with the measurements over time, being too small as the dissociation process commences and being too large as it ceases. At 5 minutes, the measured
temperature profile is closer to an energy consumption of 100 kW/m$^3$, but then approaches the 10 kW/m$^3$ simulation after 25 min, which it matches closely until about 45 min where all the hydrate is dissociated. To increase the temperature of a bulk volume hydrate bearing sediment by 1K requires 4% of the energy required to dissociate the contained hydrate (assuming the hydrate saturation is 40%). It can therefore be concluded that the initial higher energy consumption rate is primarily due to an increased hydrate dissociation rate and not due to the heating of the sediment. For the bulk sample properties in Table 16 and a line dissociation with 100 W/m energy input, the dissociation energy in the sediment can be approximated with constant heat energy consumption rate in the order of $10^4$ W/m$^3$ during the dissociation process.

The decrease in heat sink can be attributed to the fact that the hydrate bearing sediments become conductive before all the hydrate is dissociated. This simulation confirms that the dissociation rate depends on the heat energy supplied to it. That means that the dissociation kinetics as described by Kim-Bishnoi are only of secondary importance in dissociating hydrates in sediment, because the process is governed by the energy supply rate. Hence the energy consumption in Figure 41 (left), which reflects essentially the supplied heating energy, can for these conditions justifiable be treated as linear.

5.10 Conclusion

The heat transfer mechanisms during gas production from hydrates are complex but of crucial importance. In a production scheme with a heated and depressurised wellbore (termed $\Delta P + \Delta T$ later), the right assessments of heat conduction and forced convection through the mobile layer allow a quantification of the dissociation rate and in turn the
gas production rate. The measured average bulk thermal conductivity of 2.59 W/mK in hydrate and water saturated sediment matches the transient heat transfer region accurately, and is therefore widely applicable to numerical studies. It was further noted that the same only slightly decreases for partially saturated conditions such as dissociated zones with residual free gas. The theoretical mixing models for the bulk thermal conductivity (geometric mean and Johansen’s) lead to accurate estimates for the stable hydrate zones, but then deviate significantly in partial saturated conditions. No effects of natural (free) conduction were observed in partially saturated sediment, and for fully gas saturated conditions only at pressures greater than about 5.5 MPa. The dissociation rate of hydrates in sediment is governed by the supplied heat, independent of how the dissociation volume and its respective time is assessed, and hence the Kim-Bishnoi (1987) model becomes of secondary importance (perhaps more relevant for unusual events in sediment hydrates, like a heat explosion or instant large pressure drop). Gas hydrate bearing layers become heat conductive during the dissociation process if the saturation is sufficiently reduced, thus extending the influence zone of a heated wellbore after the initial insulative behaviour. The dissociation energy for this study’s sample and boundary conditions could be approximated with a constant volumetric heat consumption rate of $10^4$ W/m$^3$. 
6 Gas production tests from hydrate bearing sediments

6.1 Introduction

To exploit the energy potential of natural gas hydrates, their contained gas has to be extracted, collected and brought to the surface. The processes involved are similar to those of conventional natural gas production, except for the required in-situ phase change to free the gas from the solid hydrate, allowing it to penetrate the porous host media and to flow towards the wellbore. As described in section 2.3, the endothermic dissociation process cools the formation and in turn reduces the dissociation drive (see Figure 13), which can be interpreted as the distance between the actual- and the equilibrium pressure- and temperature conditions. This makes hydrate dissociation a process governed by heat transfer.

The various researched production methods are described in chapter 3. The general conclusion drawn from the two full-scale tests at the Mallik site was that the most efficient method to extract gas from hydrates is depressurisation. This might be true for that particular well design with a perforation length of 12 meters. But in a commercial production scheme, where perforation lengths of 100 m are proposed (Kurihara et al., 2008), the heat transfer into the dissociating region will be different; it will no longer be dominated by the axial heat fluxes from the over- and underburden, but by radial ones from the stable hydrate reservoir itself. This will in most cases lead to comparably smaller and decreasing heat fluxes as dissociation progresses, as heat energy has to be withdrawn from increasingly farther zones from the dissociating region. The importance of heat transfer is also confirmed by the fact...
that many numerical simulations on gas production from hydrates are performed with soil strata of 30 meters above- and below the usually 5 – 12 meter thick dissociating hydrate layer to supply the necessary heat for dissociation. Thus, the aim of this chapter is to investigate two different methods to extract gas from hydrate bearing soil in axisymmetric conditions with radial heat transfer.

This chapter presents the first small-scale gas production tests from hydrates with a combination of depressurisation and a heated wellbore. It examines what effect a moderately heated wellbore during depressurisation has compared to a depressurisation scheme alone with the same wellbore- or Bottom Hole Pressure (BHP). It further investigates to which level the BHP has to be reduced to extract a similar amount of gas without heating compared to the higher BHP and heating scheme. Based on the results, an energy balance is carried out to determine which method is more effective for certain conditions. All the experimental tests were replicated numerically with the hydrate simulation code of the Cambridge University. The initial pressure and temperature conditions are typical values encountered in offshore gas hydrate reservoirs in deep water as illustrated in Figure 43.
6.2 Sample properties and testing conditions

Tests were conducted on artificial methane hydrate samples using the rigid wall pressure vessel shown in Figure 17. The cylindrical soil samples had a diameter of 180 mm and an initial height of around 195 mm. The excess-water hydrate formation technique was used to obtain pore-filling hydrates with saturations of approximately 40% in a water saturated environment, which represent Class 3 hydrate deposits in nature. The detailed formation steps are described in section 2.2.2.

The required gas pressure to inject methane gas into the soil model was calculated with equation (2.2) accounting for the sample’s reduced porosity after stress application, the methane solubility in water, and the hydration number of 6 for structure I hydrates. The assumption of full cage occupancy was thought to be
legitimate for dwell periods of about 70 hours at very stable conditions. The completion of hydrate formation was indicated by no further decline in the gas pressure and by a constant temperature during the pressure increase by water. If gas were present, a pressure increase would cause the gas temperature to rise as its volume is constraint (ideal gas law, \( PV=RnT \)).

The radial density profiles in Figure 44 were obtained by calibrated \( \gamma \)-ray transmissivity measurements in the axial direction. They show the sample’s uniformity during hydrate formation, in which the density was raised from the original dry density of 1.60 g/cm\(^3\) with increasing hydrate cage filling and hence the diminution of free methane.

Figure 44: Radial density profiles of samples at different hydrate formation stages.

Upon complete formation, the hydrate samples were dissociated from a miniature wellbore with a diameter of 10 mm located on the cylinder axis (see schematic overview in Figure 16). Dissociation was carried out by a pressure reduction, or a combination of depressurisation and resistivity heating. The wellbore pressure was controlled by a spring loaded regulator valve. The heating temperature was achieved by running 60 V direct current (DC) through the 240 \( \Omega \) heater, and was controlled by a solid state relay regulating the current supply. Thermocouples were placed at radial distances of 1, 4, 7, 10, 14, 18 wellbore radii from the axis as shown in Table 9. The extracted gas and water were separated by gravity before the gas was metered and the
water production recorded by weighing. The vertical effective stress was applied through a weight loaded hydraulic piston, which maintained the stress level independent of the vertical straining. The sample’s environment temperature was controlled by glycol circulation around the pressure vessel and an air conditioned enclosure, and was maintained constant throughout the testing.

The three different dissociation tests were:

- \( \Delta P_6 \)  depressurisation to 6 MPa BHP without heating
- \( \Delta P_6 + \Delta T \)  depressurisation to 6 MPa BHP and heating from 9°C to 15°C
- \( \Delta P_4 \)  depressurisation to 4 MPa BHP without heating

Each experimental test was duplicated to check repeatability. The wellbore temperature- and pressure conditions before and during testing are shown in the methane hydrate phase diagram (Figure 45). In \( \Delta P_6 + \Delta T \), the miniature well was first heated until the set temperature was reached before the pressure was reduced at about 2 MPa/min. The slight increase in temperature during pressure reduction in \( \Delta P_6 \) and \( \Delta P_4 \) is most likely a combination of two related exothermic reactions: (i) the dissolution enthalpy of methane dissolving out of the water (17.56 kJ/mol, Naghibi et al. (1986)) and (ii) the hydrate formation initiation on the interface of the separated gas bubbles. These phenomena are covered in more detail in chapter 7. The change from the initial temperature and the wellbore temperature during testing in \( \Delta P_4 \) and \( \Delta P_6 + \Delta T \) was of comparable magnitude but opposed direction, as in the former the change was caused by the endothermic dissociation while in the latter test the wellbore was heated. The significance of deviations from the initial temperature for hydrate dissociation is discussed later.
Figure 45: Wellbore pressure- and temperature conditions during the production tests.

A total of six experimental tests and six numerical simulations (subscript $n$) were conducted. The samples’ properties, initial- and boundary conditions are given in Table 19 and are similar to those found in the $\alpha$ – field of the Nankai Trough (Kurihara et al., 2008). The final sample porosity depended on its compaction during stress application and varied slightly between the different test runs.
Table 19: Properties of hydrate bearing test samples.

<table>
<thead>
<tr>
<th>TEST</th>
<th>$\Delta P_6$</th>
<th>$\Delta P_6'$</th>
<th>$\Delta P_{6,n}$</th>
<th>$\Delta P_4$</th>
<th>$\Delta P_{4,n}$</th>
<th>$\Delta P_{6,+}$</th>
<th>$\Delta P_{6,+T}$</th>
<th>$\Delta P_{6,+T,n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity $\phi$</td>
<td>0.375</td>
<td>0.383</td>
<td>0.38</td>
<td>0.397</td>
<td>0.385</td>
<td>0.38</td>
<td>0.378</td>
<td>0.395</td>
</tr>
<tr>
<td>Hydrate saturation $S_h$</td>
<td>0.40</td>
<td>0.38</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
<td>0.42</td>
<td>0.41</td>
</tr>
<tr>
<td>Initial temperature $T_0$ [K]</td>
<td>282.0</td>
<td>282.0</td>
<td>282.0</td>
<td>282.0</td>
<td>282.1</td>
<td>282.0</td>
<td>282.2</td>
<td>282.3</td>
</tr>
<tr>
<td>Bottom hole pressure BHP [MPa]</td>
<td>5.97</td>
<td>5.86</td>
<td>6.0</td>
<td>4.24</td>
<td>3.88</td>
<td>4.0</td>
<td>5.95</td>
<td>5.87</td>
</tr>
<tr>
<td>Heating temperature $T_{well}$ [K]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>288.1</td>
<td>288.1</td>
</tr>
<tr>
<td>Depress. rate $dP/dt$ [MPa/min]</td>
<td>-1.22</td>
<td>-2.38</td>
<td>-1.73</td>
<td>-1.93</td>
<td>-1.35</td>
<td>-2.07</td>
<td>-2.5</td>
<td>-1.56</td>
</tr>
<tr>
<td>Vertical effective stress $\sigma_z$ [MPa]</td>
<td>2.37</td>
<td>2.37</td>
<td>2.37</td>
<td>2.37</td>
<td>2.37</td>
<td>2.37</td>
<td>2.37</td>
<td>2.37</td>
</tr>
<tr>
<td>Initial sample height [mm]</td>
<td>202</td>
<td>198</td>
<td>200</td>
<td>198</td>
<td>206</td>
<td>200</td>
<td>206</td>
<td>207</td>
</tr>
</tbody>
</table>

6.3 Numerical simulation

The numerical simulations of the experiments were carried out in 1 radial dimension, using a fully-coupled thermo-hydro-mechanical code for hydrate bearing sediments by Klar et al. (2011). The boundary conditions at the wellbore varied between the different tests: for depressurisation ($\Delta P$), the temperature was defined as the equivalent hydrate equilibrium temperature for the set wellbore pressure (as observed
in the experiments, see Figure 45), and is termed insulated boundary condition. For tests with wellbore heating ($\Delta P + \Delta T$), the wellbore temperature was set as equal the heating temperature. The outer boundary was modelled with a steel element representing the pressure vessel’s wall, at whose outer side the environment temperature was controlled in two different ways: in the first simulations the temperature was kept constant to simulate the laboratory experiments (subscript $n, \ exp$). Since a constant temperature boundary is a limitation imposed by the experiments compared to in-situ conditions, additional numerical simulations with the methane hydrate equilibrium temperature as the outer boundary condition were performed (subscript $n, \ ins$) to show this boundary-effect on the gas production. The parameters used in the simulation are listed in Table 20.

<table>
<thead>
<tr>
<th>Table 20: Species properties used in the numerical simulation.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Specific heat capacity, $C_p$ [J/(kg K)]</strong></td>
</tr>
<tr>
<td>Sand</td>
</tr>
<tr>
<td>800</td>
</tr>
<tr>
<td><strong>Thermal conductivity, $k$ [W/(m K)]</strong></td>
</tr>
<tr>
<td>3.92</td>
</tr>
<tr>
<td><strong>Viscosity, $\mu$ [Pa s]</strong></td>
</tr>
<tr>
<td>-</td>
</tr>
<tr>
<td><strong>Density, $\rho$ [g/cm$^3$]</strong></td>
</tr>
<tr>
<td>2.60</td>
</tr>
</tbody>
</table>

The absolute permeability $k_0$ was chosen as 350 mD (Oyama et al., 2009). Changes during dissociation were modelled by the following semi-empirical power law in equation (6.1) (Minagawa et al., 2005). The relative permeability for two-phase flow and the capillary pressure relationship was modelled by the van Genuchten (1980) relations. Further details of the models implemented in the numerical code can be found in Klar et al. (2011).
6.4 Produced gas and dissociation driving mechanism

The production period for each test was 90 minutes after the methane hydrate phase boundary conditions were reached. The wellbore pressure was kept constant during that period, despite some small fluctuation due to intermittent production rates. Figure 46 shows the wellbore pressure (top) and the accumulated gas volume (bottom) for each experimental test (solid lines) and the corresponding numerical simulation (dashed lines). By comparing $\Delta P_6$ with $\Delta P_6 + \Delta T$, an increase in gas production by several times can be observed if the wellbore is simultaneously heated during depressurisation. This substantial difference is caused by the difference in dissociation drive; the endothermic hydrate dissociation in sediments is clearly a heat transfer limited process. The larger the difference between the initial in-situ temperature and the equilibrium temperature for the corresponding wellbore pressure, the faster dissociation takes place, leading to a higher production rate.

The mechanism of this dissociation drive can be understood from the temperature histories shown for each test in Figure 47. The equilibrium temperatures $T_{eq}$ in Figure 47 are calculated from the measured pore pressure histories shown in the upper graph in Figure 46, which are constant within the sample as there is no flow condition. In $\Delta P_6$ the difference between the initial- and equilibrium temperature is just 1 K. That means that little heat energy can be obtained from the sediment, and that the temperature gradient is small between the well and the outer-boundary temperature, which is kept constant at 282 K at 18 wellbore radii. As a result the conditions are at
equilibrium throughout the testing period of 90 minutes, leading to an intermittent gas production rate as shown in Figure 53 and discussed in section 6.6.

Figure 46: Top: pore pressure development during production tests with 4 MPa bottom hole pressure (BHP) ($\Delta P_4$), 6 MPa BHP ($\Delta P_6$) and 6 MPa BHP combined with wellbore heating to 288 K ($\Delta P_6 + \Delta T$) tests; Bottom: cumulative gas production of the same tests. Experimental results are shown by solid lines and numerical simulation by dashed lines (Falser et al., 2012c).

In $\Delta P_4$, where a larger pressure reduction was applied than the $\Delta P_6$ case, the temperature difference is 5 K. Hence the immediate dissociation drive is larger as more heat energy is available from the formation and the constant temperature container. At the outer boundary ($18 r/r_{wb}$), where the temperature outside the pressure vessel is maintained constant at 282 K by fluid circulation, the sample’s temperature does not drop to the equilibrium temperature, but remains below the
initial temperature throughout the testing period, suggesting that the dissociation process was not fully completed after 90 minutes. The comparatively enhanced heat flux from the environment leads to a progressive deviation from equilibrium, resulting in a more sustained production rate.

In $\Delta P_6 + \Delta T$ the same small natural heat energy as in $\Delta P_6$ is available, but the flux from the heated wellbore leads to a constant disequilibrium zone in its vicinity. Because of this, a similar sustained production rate as in $\Delta P_4$ is achieved. The initial temperature spike at around -5 min is due to the test procedure: the miniature wellbore was first heated and only once the set 288 K had been reached, the pressure was decreased to 6 MPa. The initially high pore-water flux towards the well equilibrated the temperature just before dissociation commenced at time zero.
Figure 47: Temperature evolutions of $\Delta P_6$ (top), $\Delta P_4$ (centre), and $\Delta P_6 + \Delta T$ (bottom) at different wellbore radii $r/r_{wb}$. The dashed lines represent the methane hydrate phase equilibrium temperature $T_{eq}$. 
Figure 48: Temperature- and methane hydrate saturation profiles for constant outer boundary temperature conditions after 10, 50 and 90 minutes of dissociation. Experimental data and numerical simulations are shown as bullets and dashed lines respectively; the colour for $\Delta P_6$ is blue, for $\Delta P_6 + \Delta T$ red, and for $\Delta P_4$ green.

As shown in Figure 46, the numerical simulations (subscript $n$, exp) confirm the production trends in each test, and the produced volumes agree within 25%. The differences arise from discrepancies in temperature evolution at the boundaries. The left column in Figure 48 shows the temperature profile in the radial direction at different times (10, 50 and 90 minutes). The experimentally measured heat flux from the well in $\Delta P_6 + \Delta T$ is initially larger than in the simulation, resulting in a higher measured production volume than that obtained numerically. The heating of the well affected a zone extending to about 8-10 wellbore radii from the centre after 90 min, which is in good agreement with the simulation. In $\Delta P_4$, on the other hand, where the radial temperature gradient is largest at the outer boundary, the measured heat flux from the outer boundary was smaller than in the numerical simulation. Hence the
produced gas volumes in the experiments are smaller than those calculated from the simulations.

Figure 49: Produced gas after 90 min controlled methane hydrate dissociation, and total produced gas with the three dissociation schemes (subscript \( n, \infty \)) in litres at standard conditions [SL], which took 600 min in \( \Delta P_{6, n, \infty} \), 228 min in \( \Delta P_{6} + \Delta T_{n, \infty} \), and 202 min in \( \Delta P_{4, n, \infty} \) for completion.

This is illustrated in Figure 49, which gives the produced volumes and recovery factors of the experimental tests and its numerical simulations (subscript \( n, \text{exp} \)), as well as the total gas recovery (subscript \( n, \infty \)). The total producible gas volume for the three different recovery methods has been determined by simulations. Production stops when the available heat from the environment and the specific heat from the formation have been exhausted or are no longer sufficient for the endothermic hydrate dissociation process. Two experimental tests were carried out for each production scheme, and the good agreement between their results confirms their repeatability. By comparing the production volumes after 90 min with the total recovered gas, one notes the following: In \( \Delta P_{6} \) the production continues over 10 hours, and the recovery is increased by three times to about 50%. In \( \Delta P_{4} \) the production ceases much earlier, after about 3.4 hours, and the recovery is only increased by about 20% to 80% total
recovery, which shows that a large proportion of the hydrate was dissociated and recovered within the first 90 min of testing. In $\Delta P_6 + \Delta T$ the gas volume recovered after 90 min is doubled within 4 hours, giving a gas recovery of 62%. This confirms the heat transfer dependency on the dissociation process; the production rate is proportional to the dissociation drive, which is the difference between the initial temperature and the equilibrium temperature during dissociation. In production schemes with a larger thermal dissociation drive (approximately $\Delta T = 5^\circ C$ for $\Delta P_4$ and $\Delta T = 6^\circ C$ at the wellbore for $\Delta P_6 + \Delta T$) a larger proportion of gas can be recovered from hydrates in a shorter time than in those with a comparably smaller thermal dissociation drive (approximately $\Delta T = 1^\circ C$ for $\Delta P_6$).

The hydrate saturation profiles after 10, 50 and 90 minutes gas production are given in the right column of Figure 48. The numerically obtained saturation profiles confirm that in the depressurisation cases $\Delta P_6$ and $\Delta P_4$ the dissociation front moves from the outer boundary towards the centre, as all the required heat energy is supplied from the environment held constantly at 282 K. In $\Delta P_6 + \Delta T$ the hydrate is simultaneously dissociated from the wellbore and the outer boundary, but at a higher rate from the wellbore as a result of the higher dissociation drive.

### 6.5 Comparison to production with insulated outer boundary conditions

In the same way as in the tests presented here, in a full scale production scheme from a uniform class 3 hydrate reservoir, the radial heat transfer will govern the dissociation rate and hence the recovery. One of the unavoidable differences lies in the radial outer boundary condition; whereas in the laboratory tests the temperature was kept constant at the fixed boundary at 18 wellbore radii, in a reservoir the
temperature at the dissociation front will always be at the hydrate equilibrium temperature. Accordingly a numerical simulation has been conducted, in which the outer boundary of the same geometry was kept at the hydrate equilibrium temperature for the respective wellbore pressure. This limits the heat flux from the environment and hence most of the required heat for dissociation has to be absorbed from the formation and pore fluid (for depressurisation) or obtained through conduction from the heated wellbore. The production curves in Figure 50 confirm this hypothesis: if the available sensible heat is approximated with the specific heat of the sand only (800 J/(kg K)), which is reasonable as a large proportion of the water was very rapidly drained in the experiments, it amounts to about 37.4 kJ in $\Delta P_{4,n,\text{ins}}$. Assuming that all the energy is used for dissociation, it frees 16 litres of CH$_4$ from hydrates, which is in good agreement with the recovered 11.4 litres if the residual gas in the pore space is accounted for. It further shows that this sensible heat from the formation is used up by the hydrate dissociation very rapidly, whereas a heated wellbore ($\Delta P_{6} + \Delta T_{n,\text{ins}}$) leads to a slower but more sustained production rate.
Figure 50: Accumulated gas production for the methane hydrate equilibrium temperature as outer boundary condition (insulated, subscript \( \text{ins} \)) and the experimental outer boundary conditions (subscript \( \text{exp} \)).

The production data for this insulated case is given in Figure 51; without any significant heat flux from the outer boundary the depressurisation scheme at 6 MPa BHP does not lead to any gas production, despite the theoretical 12.2 kJ of specific heat available from the sediment. This suggests that the available dissociation energy in the form of the formation’s latent heat and the recovered volume is not strictly correlated, because some fraction of the freed gas remains trapped in the pore space. This phenomenon is enhanced in the experiments due to the impermeable outer boundary and hence the absence of a flow induced pressure profile. The only driving mechanism to transport the gas to the well is therefore the expansion and resulting pressure increase of the dissociated gas, which exceeds the set wellbore-pressure and induces a flow.
Figure 51: Produced gas after 90 min controlled methane hydrate dissociation with insulated outer boundary conditions compared with the constant temperature outer boundary conditions of the experiments.

The temperature- and saturation profiles for the insulated outer boundary case are given in Figure 52. In the depressurisation schemes, the temperatures are at equilibrium throughout, whereas the zone affected by the wellbore heating remains unchanged compared to the previous boundary conditions. In line with the latent heat governed dissociation in the $\Delta P_{4,n,\text{ins}}$ case, the zone’s hydrate saturation is uniformly reduced to 35% and remains constant over the entire testing period. In $\Delta P_{6} + \Delta T_{n,\text{ins}}$, on the other hand, the dissociation front extending over about 6 wellbore radii moves progressively outwards from the wellbore, suggesting that also in this insulated case, a combination of reduced pressure and wellbore heating is a more efficient dissociation driver in the long term, compared to a pure depressurisation.
6.6 Gas extraction rate

The production rate depends on the rate of dissociation. In the laboratory tests, the bottom-hole pressure is controlled by a spring loaded regulator with a defined cracking-pressure. The intermittency in the measured production rate for $\Delta P_6$ is due to the free gas being removed faster from the sample than it is being dissociated from the hydrate. In the numerical simulation the rate is defined solely by the amount of gas reaching the inner boundary. The gas production rates for each test are given in Figure 53; the calculated production rate in general matches well with the trend of the experiments. As one of the unique features of gas production from hydrates, the $\Delta P_4$
tests show that the production rate is high at the beginning but then decreases rapidly. This is because the large dissociation drive can be obtained from the initial temperature difference right after depressurisation, but that the drive subsequently reduces as the formation temperature drops, because of the endothermic hydrate dissociation process.

Figure 53: Production rates in SL per minute. Experimental data is shown in solid lines, and numerical simulations with constant (282 K) and hydrate equilibrium outer boundary condition are shown in dashed and dashed-dotted lines respectively.

For the insulated outer boundary conditions the production rate peaks at the beginning, identical to the simulated rate with the fixed temperature boundary conditions, but then ceases altogether for the depressurisation schemes and is reduced
to a fraction for the wellbore heating. This implies that the dissociation process is first
governed by the latent heat of the formation and later by the heat energy transferred to
the dissociating region, either by conduction or fluid convection from outer non-
dissociated regions, or by conduction from the heated wellbore.

6.7 Energy comparison

The tests results presented in section 6.4 show that the extracted gas volume can be
increased significantly with additional wellbore heating to 15°C at the same wellbore
pressure of 6 MPa. By lowering the wellbore pressure to 4 MPa, however, a
comparable amount of gas can be extracted during the test duration of 90 minutes.
The energy comparison presented in this section is based on the energy for heating the
miniature wellbore, the calorific value of the extracted methane (39.68 kJ/litre at
standard conditions) and the required pumping energy for pressure maintenance.
The energy balance between $\Delta P_6$ and $\Delta P_6 + \Delta T$ simply depends on the voltage input for
heating to production surplus ratio, as it is assumed that the pumping energy remains
unchanged for a constant wellbore pressure. To compare production scenarios with
different wellbore pressures on the other hand, the energy to remove the pore fluid
continuously has to be assessed. But this cannot be derived from the produced water
in the experiments, as the laboratory tests refer to a confined space with no flow at the
outer boundary, whereas in real reservoirs the source of water is essentially infinite.
Therefore, it is assumed that the same tests as described in the previous sections were
conducted at 1000 m depth, which allows a quantification of the required energy for
pumping, and in turn enables a comparison of tests with different bottom hole
pressures. The extracted gas- and water volumes of the tests conducted are tabulated
in Table 21. Since each production method was repeated to show their repeatability, average values of both tests are used for comparisons.

Table 21: Extracted gas- and water volumes during the 90 minutes production tests in litres at standard conditions (SL) and as a fraction of the total contained gas in hydrates.

<table>
<thead>
<tr>
<th>TEST</th>
<th>(\Delta P_6)</th>
<th>(\Delta P_6)</th>
<th>(\Delta P_4)</th>
<th>(\Delta P_4 + \Delta T)</th>
<th>(\Delta P_6 + \Delta T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produced gas [SL]</td>
<td>16.6</td>
<td>11.0</td>
<td>55.4</td>
<td>62.2</td>
<td>52.8</td>
</tr>
<tr>
<td>Produced water [L]</td>
<td>0.55</td>
<td>0.71</td>
<td>0.79</td>
<td>1.05</td>
<td>0.49</td>
</tr>
<tr>
<td>Recovery factor gas [%]</td>
<td>12.7</td>
<td>9.5</td>
<td>45.4</td>
<td>47.8</td>
<td>37.4</td>
</tr>
</tbody>
</table>

The required pumping energy \(E_p\) given in equation (6.2) is a function of the flow rate \(Q\) at which pore fluid reaches the wellbore, the pressure head \(\Delta P\) and the pump’s efficiency factor \(\eta_p\).

\[
E_p = \frac{Q \Delta P}{\eta_p}
\] (6.2)

The heating energy \(E_h\) as shown in equation (6.3) depends on the input voltage \(V\), the resistivity of the heating elements in the wellbore \(R\) and a reduction factor \(\eta_{gen}\) accounting for losses in electricity generation and –transmission.

\[
E_h = \frac{V^2}{R \eta_{gen}}
\] (6.3)

The water influx into the well is modelled by a perfect Darcian flow:

\[
Q = \frac{(P_x - P_{wb})k_0 2\pi}{\mu \ln \left(\frac{r_x}{r_{wb}}\right)}
\] (6.4)

The symbols are explained together with their values in
Table 22. The static- and hydraulic head of the reservoir fluid inside the production tubing is approximated by equation (6.5).

\[ \Delta P = \frac{32 f \rho z Q^2}{\pi^2 ID^3} + \rho gz \]  

(6.5)

A downhole separation of gas and water is assumed in this study, reflecting the well design used in the Mallik field tests. For the concerned flow rates \( Q \), the single phase water flow regimes inside the tubing remain laminar (Re < 2000), and thus the Fanning friction factor \( f \) is approximated as shown in equation (6.6). The calculated pressure drops in equation (6.5) show further that the pressure difference between the reservoir and the surface is in principle hydrostatic, as, the hydraulic term (first on the right in equation (6.7)) is remains below 1% of the static term for the investigated wellbore pressures.

\[ f = \frac{16}{\text{Re}} = \frac{16 \mu}{\rho U ID} = \frac{4 ID \pi \mu}{\rho Q} \]  

(6.6)

Which combined with equation (6.5) yields to:

\[ \Delta P = \frac{128 z \mu Q}{\pi ID^4} + \rho gz \]  

(6.7)

<table>
<thead>
<tr>
<th>Table 22: Input parameter used for the energy comparison.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well depth</td>
</tr>
<tr>
<td>Reservoir pressure</td>
</tr>
<tr>
<td>Initial permeability</td>
</tr>
<tr>
<td>Hydrate saturation</td>
</tr>
<tr>
<td>Toyoura sand</td>
</tr>
</tbody>
</table>
Wellbore radius \( r_{wb} \)  5 mm

\( P\)-unaffected radius \( r_\infty \)  10 m

Perforation length  0.18 m

Production tubing \( ID \)  8 mm

Water viscosity \( \mu \)  0.0013 Pa s

Pump efficiency \( \eta_p \)  0.4

Generator efficiency \( \eta_{gen} \)  0.9

Calorific value CH₄  39.68 kJ/SL

Water density \( \rho \)  1025 kg/m³

Figure 54: The correlation between in-situ permeability and hydrate saturation in water saturated silica (Toyoura) sand (modified from Oyama et al., 2009), on a logarithmic scale.

Data sets comparing the permeability and hydrate saturation in Toyoura sand are shown in Figure 54. It shows that in the hydrate saturation range between 40 to 90 %, the most attractive from a commercial production perspective, the permeabilities vary between 10 to 300 mD.
The theoretical energies for pressure maintenance and wellbore heating are calculated for the testing period of 90 minutes and compared to the calorific value of the extracted gas in each production scenario. The results are tabulated in Table 23: pressure maintenance at 6 and 4 MPa requires 640 and 965 kJ respectively, whereas heating of the miniature wellbore from 8 to 15°C requires 90 kJ.

Table 23: Energy balance after 90 min of production

<table>
<thead>
<tr>
<th>TEST</th>
<th>$\Delta P_6$</th>
<th>$\Delta P_6$</th>
<th>$\Delta P_4$</th>
<th>$\Delta P_6 + \Delta T$</th>
<th>$\Delta P_6 + \Delta T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produced gas</td>
<td>16.6</td>
<td>11.0</td>
<td>55.4</td>
<td>62.2</td>
<td>52.8</td>
</tr>
<tr>
<td>$E$ depress</td>
<td>-636</td>
<td>-636</td>
<td>-965</td>
<td>-965</td>
<td>-636</td>
</tr>
<tr>
<td>E heating</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-90</td>
</tr>
<tr>
<td>E gas</td>
<td>659</td>
<td>435</td>
<td>2197</td>
<td>2468</td>
<td>2096</td>
</tr>
<tr>
<td>E net</td>
<td>23</td>
<td>-201</td>
<td>1232</td>
<td>1503</td>
<td>1369</td>
</tr>
<tr>
<td>E net [%]</td>
<td>4 %</td>
<td>-46 %</td>
<td>56 %</td>
<td>61%</td>
<td>65 %</td>
</tr>
</tbody>
</table>

The net energy in Table 23 shows that the production scheme with sole depressurisation to 6 MPa ($\Delta P_6$) is not economical. But by moderately heating the wellbore at the same wellbore pressure ($\Delta P_6 + \Delta T$), the net energy gain is substantially increased to above 60%. Similarly, the $\Delta P_4$ tests also result in a net gain of around 60%, a little less efficient than $\Delta P_6 + \Delta T$.

This energy comparison of different production methods clearly reflects only one case with specific boundary conditions and assumptions, thus the energy efficiency of different production methods is to be evaluated on an individual basis depending on the actual reservoir conditions and well design. But this study clearly shows that a proposed production scheme can be made feasible with additional wellbore heating.
The chosen permeability of 10 mD is the lower bound for the given hydrate saturation of 40%. Higher permeabilities lead to a larger pumping rate $Q$. It can therefore be examined for which permeability additional heating becomes more efficient compared to a further pressure reduction (assuming that all the remaining parameters remain unchanged). For the specified conditions in Table 22, this sensitivity check on the formation’s initial permeability shown in Figure 55 indicates that $\Delta P_6 + \Delta T$ becomes more energy efficient than $\Delta P_4$ for $k_0 > 3$ mD. At present commercially attractive gas hydrate deposits have all several of orders larger permeabilities (see Table 1), and therefore additional wellbore heating will in most cases be more energy efficient than a further pressure reduction.

![Graph showing required production energy for different permeabilities.](image)

Figure 55: Required production energy for different permeabilities for this study.

### 6.8 Conclusion

The novel experimental results with a heated miniature wellbore were successfully replicated by numerical simulations. The experimental tests show that gas production during the period of 90 minutes at the same wellbore pressure is on average increased
by 3.6 times by heating the wellbore when the wellbore pressure was 6 MPa. The numerical simulation shows an increase in produced gas of 1.8 times. The difference is due to differences in the temperature regime and hence the dissociation drive, as small discrepancies in heat fluxes from the heated wellbore and the outer boundary could be observed in the experiments and simulations. A lower wellbore pressure to achieve a similar production rate results in a substantially increased initial production rate but which later declines because of endothermic cooling. Hence a heated wellbore results in a more sustained dissociation drive compared to a lower wellbore pressure, despite their comparable initial production trend.

The dissociation process of hydrates in saturated sediments is governed by the radial heat flux from the environment into the dissociating zone, or in the case of a heated wellbore from both directions. In natural conditions, pore water feeds additional heat energy into the dissociating region by forced convection. The boundary conditions in a production scenario from a semi-infinite reservoir may hence lie between the here presented constant outer boundary temperature and the insulated case. The effect of heat convection depends on the larger reservoir’s geomechanical- and thermodynamic properties, and is therefore difficult to assess and account for in small scale experiments. The results further show that the formation’s specific heat is consumed rapidly, and thus contributes only at a very early stage to the dissociation process.

The energy balance shows that in this particular case, additional heating of the wellbore increases the net energy gain by about 60%. It also shows that moderate heating at 6 MPa is more efficient compared to a production scheme with a wellbore pressure of 4 MPa for an initial formation permeability $k_0$ greater than 3 mD, which is smaller than the conventional permeabilities of hydrate bearing sand.
7 Heat generation during depressurisation

7.1 Introduction

The majority of attractive natural gas hydrate reservoirs are partially hydrate and water saturated sandy formations, so called class 3 reservoirs. By applying practises from the conventional oil and gas industry, gas from those reservoirs will eventually be produced through wells drilled into it. The depressurisation of those wells will be the major hydrate dissociation driver, possibly combined with some degree of heating as discussed in chapter 6. Besides dissociation, the pressure gradient is also essential for the flow of the free gas to the wellbore.

Depressurisation experiments of partially hydrate and water saturated sediments have shown changes in temperature. Between the initial pressure and the start of hydrate dissociation at its phase boundary, distinct increases in temperature were observed in five independent test runs. The free pore water which coexists with the hydrate in the formation’s pore space is assumed to be fully saturated with natural gas, the same gas the hydrates consist of. The gas solubility of water is pressure-, and to a smaller degree, temperature dependent, with more gas dissolved in water at higher pressures and lower temperatures than at lower pressures and higher temperatures. The temperature change during the depressurisation ofhydrate bearing sediments is therefore governed by two consecutive reactions: By the endothermic effervescence of gaseous methane as the water solubility of gas decreases, and, since the conditions are still in the stable methane hydrate pressure-temperature region, by the exothermic hydrate formation of the same gas. Because the enthalpy change due to hydrate
formation is about three times greater than the absorbed heat energy during the effervescence, both reactions lead to a net energy surplus resulting in a temperature increase. For moderate depressurisation rates of less than 4 MPa/min, the freed methane has sufficient time to form hydrate.

This chapter discusses this heat generation during the depressurisation through the hydrate stability region, shown as (1) in the methane hydrate phase diagram in Figure 56. It analyses its origins, applies the derived theoretical model to a wider range of initial pressure and temperature conditions and puts possible implications forward.

![Figure 56: Temperature changes during depressurisation tests: (1) exothermic methane dissolution and hydrate formation; (2) endothermic dissociation along the methane hydrate phase boundary.](image)

Experimentally measured temperature changes during depressurisation are shown in the hydrate stability diagram in Figure 56 (1). The changes during depressurisation are important to consider for several reasons. A temperature increase leads to a dissociation start at a higher pressure as compared to the initial temperature equivalent equilibrium pressure. Furthermore, the additional hydrate formation from the dissolved gas increases the hydrate saturation just before the phase equilibrium is
reached. To which extent the temperature is increased during depressurisation depends on the thermophysical properties of the samples as well as on the initial and boundary conditions.

7.2 Thermophysical species properties

In this study, the relevant thermophysical properties are the methane solubility in water, the sample’s bulk heat capacity, the methane’s dissolution enthalpy, the heat of hydrate formation and the methane hydrate phase boundary. The hydrate phase boundary serves as a reference for the initial pressure and temperature conditions, and is repeated here from equation (1.1). The above listed properties suffice to quantify the theoretically released heat energy during depressurisation.

\[ P_{eq} = 1 + 1.6 \exp\left(0.132\left(T_{eq} - 273.15\right)\right) \]  

(7.1)

Where \( P_{eq} \) is the equilibrium pressure in [MPa] and \( T_{eq} \) the corresponding temperature in [K].

The study is based on the assumption of perfect heterogeneous conditions, with uniform porosity and hydrate saturation distribution throughout the sample. The source of heat origins in the water phase. Due to the relatively small scale of the sediment grain and stable hydrate, the heat transfer into these species is assumed to occur instantly compared to the heat generation, and thus only the specific heat of the bulk is considered while any possible heat transfer is ignored. This simplifies the system and enables an analysis per unit sample volume. The relevant properties of the species involved, sand, water and hydrate, are given in Table 24. The bulk density and specific heat are approximated with equations (5.8) and (5.9).
Table 24: Species properties used in this study.

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Water</th>
<th>Hydrate</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, $\rho$ [kg/m$^3$]</td>
<td>2620</td>
<td>1000</td>
<td>913</td>
<td>1958.1</td>
</tr>
<tr>
<td>Specific heat $C_p$ [J/(kg K)]</td>
<td>800</td>
<td>4190</td>
<td>2010</td>
<td>1305</td>
</tr>
<tr>
<td>Volume fraction</td>
<td>0.6</td>
<td>0.24</td>
<td>0.16</td>
<td>1</td>
</tr>
</tbody>
</table>

7.2.1 Methane solubility in water

The solubility of methane in water has strong pressure- and moderate temperature dependency. The currently available water solubility data of methane is scarce and requires further experiments in the stable hydrate region (Sloan and Koh, 2007, p. 205, Makogon, 1997, p. 66). The total amount of gas in the liquid and solid water phase increases sharply in stable hydrate conditions, as both react to form hydrates. The volume of gas dissolved in the free water, however, is assumed to remain unchanged without and in the presence of hydrates for constant pressure and temperature conditions. This is a simplification, as with time, the difference in partial pressure between the dissolved gas and the hydrate surface area drives the dissolved gas towards the solid hydrate where it eventually may form to hydrate (Makogon, 1997). But for a first approach the assumption of uniform solubility of methane in water is justifiable.

A comprehensive literature review on methane water solubilities and their modelling is given by Duan and Mao (2006). Solubility data between 273 and 303 K temperature and up to 40 MPa pressure is approximated by two different functions to achieve a better accuracy over the whole range. The first, equation (7.2), fits the solubility data in Figure 57 for pressures below 15 MPa and temperatures of around 282 K. This function was used to quantify the solubility changes in the conducted experiments described in section 7.3, as their initial temperature only varied between
281.3 and 283.7 K. As can be seen, for low pressures the temperature dependency on the solubility is small, but increases significantly with increasing pressure.

\[ m_{CH_4} = 3.5344 \times 10^{-4} P^2 + 1.5876 \times 10^{-2} P + 2.2121 \times 10^{-3} \]

for \( T = 282 \text{ K} \) and \( 0.1 \leq P \leq 15 \text{ MPa} \) (7.2)

Where \( m_{CH_4} \) is the methane solubility in water in [mol/kg].

Figure 57: Methane solubility \( m_{CH_4} \) in water at different pressures and temperatures (data from Chapoy et al., 2004, Wang et al., 2003, Duan and Mao, 2006, Handa, 1990, Duan et al., 1992) and the data fit for 282 K.

The second approximation serves to quantify the changes in solubility for various initial conditions (section 7.4). To see how the methane solubility in water changes at higher pressures and over a wider temperature range, the literature data plotted in Figure 58 are fitted by equation (7.3), both matching with an acceptably accuracy for pressures between 15 and 40 MPa. Pressure and temperature dependencies of the solubility are further illustrated in the surface plot in Figure 59.
Figure 58: Methane solubility \( m_{CH_4} \) data with curve fits for different temperatures (solid lines) obtained by equation (7.3) as well as the 282 K curve fit for lower pressures (dashed line)

\[
m_{CH_4} = \left[ 1 - \frac{T - 288.15}{60} \right] \left( -9.95653 \times 10^{-5} P^2 + 9.70603 \times 10^{-3} P + 4.93496 \times 10^{-2} \right) \quad (7.3)
\]

for \( 273.15 \leq T \leq 303.15 \) K and \( 15 < P \leq 40 \) MPa

Figure 59: Surface of methane solubility in pure water in [mol/kg] at different pressures and temperatures.
The water solubility of methane, compared to other gases, is relatively low. CO₂ for example is about ten times more soluble in water \( m_{CO_2} = 1.36 \text{ mol/kg at 10 MPa} \), and has a similar pressure dependency to methane. This means that pore water saturated with CO₂ releases more gas during depressurisation, which could result in an amplified temperature change due to hydrate formation during depressurisation. Methane is however less soluble in sea water, the natural environment of most hydrate bearing sediments.

### 7.2.2 Dissolution enthalpy

Dissolution is the process when a substance, in this case methane, dissolves into water. The contrary process, when gas comes out of the liquid solution is termed effervescence. The enthalpy changes for both processes depend on the solute and the solvent, but for gases dissolution is generally exothermic, and thus effervescence endothermic. For methane, the aqueous dissolution enthalpy decreases linearly with increasing temperature. Figure 60 shows the data of two references and the corresponding linear data fit which is stated in equation (7.4).

![Figure 60: Heat of solution of methane in water](image-url)

\[ \Delta H \text{ (kJ/mol)} \]

- Naghibi et al. (1986)
- Rettich et al. (1981)
- fit

Temperature [K]

-20
-18
-16
-14
-12
-10
-8
-6
-4
-2
0
2
4
6
8
10
12
14
16
18
20
220
240
260
280
300
320
340
360
380
400

Figure 60: Heat of solution of methane in water (data from Naghibi et al., 1986, Rettich et al., 1981)
\[-\Delta H_{\text{eff}} = \Delta H_{\text{dis}} = 0.2181 T_0 - 78.255 \quad (273.5 \leq T_0 \leq 323 \text{ K}) \tag{7.4}\]

where

- $\Delta H_{\text{eff}}$ is the change in enthalpy due to methane effervescence [kJ/(mol CH$_4$)]
- $\Delta H_{\text{dis}}$ is the change in enthalpy due to methane dissolution [kJ/(mol CH$_4$)]
- $T_0$ is the water temperature [K]

During depressurisation, the enthalpy change due to gas effervescence $\Delta H_{\text{eff}}$ is equal to $-\Delta H_{\text{dis}}$. For the testing range presented here, ethane has a significantly larger dissolution enthalpy (23.68 kJ/(mol C$_2$H$_6$) at 283 K) compared to the 16.5 kJ/(mol CH$_4$) of methane (Rettich et al., 1981). Also for CO$_2$ the dissolution enthalpy in water is larger, about 20 kJ/mol (Duan and Sun, 2003).

### 7.2.3 Hydrate formation enthalpy

The methane hydrate formation enthalpy is most widely used as a constant of 54.2 kJ/(mol CH$_4$), but which validity is given for only temperatures below 273 K (Handa, 1986). The change in enthalpy during hydrate formation however has a small temperature dependency, as given in the linear equation by Kamath and Holder (1987):

\[\Delta H_f = -56.57 + 0.01682 T_0 \quad (273.15 \leq T_0 \leq 298 \text{ K}) \tag{7.5}\]

where

- $\Delta H_f$ is the change in enthalpy due to methane hydrate formation [kJ/(mol CH$_4$)]
- $T_0$ is the water temperature [K]

Again, the formation enthalpy of higher alkenes like Ethane (71 kJ/mol), Propane (126 kJ/(mol)), or Isobutane (130.4 kJ/(mol)) are significantly higher than the enthalpy change during pure hydrate formation (Handa, 1986). The resulting increase
in hydrate saturation due to the additional hydrate is calculated based on the dissolved moles of methane per volume sample and the hydration number of 6.

7.3  Depressurisation tests

In this study, five independent depressurisation tests of water saturated hydrate bearing sediment samples were carried out. The initial pressure- and temperature conditions of about 14.5 MPa and 9°C in Table 25 are typical conditions for an offshore hydrate reservoir in deep water (see Figure 43).

The respective enthalpy changes for methane effervescence $\Delta H_{\text{eff}}$ during depressurisation and hydrate formation $\Delta H_f$ are determined with equations (7.4) and (7.5) based on the initial temperature $T_0$. The equilibrium pressure $P_{\text{eq}}$ is the pressure at which methane hydrate starts dissociating at the initial temperature $T_0$, and is calculated by equation (7.1). The pressure reduction shown as $\Delta P$ in Figure 61 is the difference between the initial- and equilibrium pressure $P_{\text{eq}}$, and determines how much methane comes out of the water solution before the phase boundary is reached. Since the equilibrium pressure increases by $\Delta P_{\text{eq}}$ during dissociation, and thus the originally assumed amount of dissolved methane is slightly overestimated, the changes are approximated iteratively by updating the actual equilibrium pressure based on the change in temperature. For these conditions, two iterations are sufficient to obtain convergence. The time between the beginning of the pressure reduction and the moment the phase boundary was reached is given in minutes.
Figure 61: Schematics of increase in temperature $\Delta T$ and equilibrium pressure $\Delta P_{eq}$ during depressurisation with respect to the initial in-situ conditions (exaggerated changes for illustration purposes).

Table 25: Initial- and testing conditions of the experiments in this study.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta P 1$</th>
<th>$\Delta P 2$</th>
<th>$\Delta P 3$</th>
<th>$\Delta P 4$</th>
<th>$\Delta P 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pressure $P_0$</td>
<td>14.64</td>
<td>14.51</td>
<td>14.88</td>
<td>14.62</td>
<td>14.48</td>
</tr>
<tr>
<td>Initial temperature $T_0$</td>
<td>283.69</td>
<td>282.24</td>
<td>282.24</td>
<td>282.39</td>
<td>281.27</td>
</tr>
<tr>
<td>CH$<em>4$ effervescence $\Delta H</em>{eff}$ [kJ/mol]</td>
<td>16.38</td>
<td>16.70</td>
<td>16.70</td>
<td>16.67</td>
<td>16.91</td>
</tr>
<tr>
<td>Methane hydrate formation $\Delta H_f$ [kJ/mol]</td>
<td>-51.80</td>
<td>-51.82</td>
<td>-51.82</td>
<td>-51.82</td>
<td>-51.84</td>
</tr>
<tr>
<td>Methane hydrate equilibrium pressure $P_{eq}$ [MPa]</td>
<td>7.80</td>
<td>7.00</td>
<td>7.12</td>
<td>6.93</td>
<td>6.46</td>
</tr>
<tr>
<td>Pressure reduction in stable hydrate region $\Delta P$ [MPa]</td>
<td>7.72</td>
<td>6.60</td>
<td>6.61</td>
<td>6.71</td>
<td>5.96</td>
</tr>
<tr>
<td>Depressurisation time [min]</td>
<td>6.92</td>
<td>7.91</td>
<td>8.27</td>
<td>7.91</td>
<td>8.52</td>
</tr>
<tr>
<td>$dP/dt$ [MPa/min]</td>
<td>-1.20</td>
<td>-1.34</td>
<td>-2.09</td>
<td>-2.32</td>
<td>-3.91</td>
</tr>
</tbody>
</table>
7.3.1 Theoretical changes during depressurisation

The moles of methane coming out of solution $\Delta m_{CH4}$ per litre of pore water are approximated by equation (7.2) and tabulated for each test in Table 26. The gas effervescence increases with increasing pressure reduction in stable hydrate conditions ($\Delta P$ in Figure 61). The released energy per litre pore water is obtained by multiplying the methane volume with the enthalpy changes due to effervescence (endothermic) and hydrate formation (exothermic). Subsequently, the released heat energy is expressed in Joules per unit weight of the bulk sample to enable quantifying the induced temperature increase $\Delta T$ by accounting for the bulk’s specific heat $C_{p,b}$.

The calculated increase in temperature during depressurisation varies between 0.23 and 0.38 K, and is larger for a smaller initial temperature as that prolongs the depressurisation in stable conditions and in turn increases the released amount of methane from the water.

Table 26: Calculated increase in temperature and hydrate saturation during depressurisation.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta P$ 1</th>
<th>$\Delta P$ 2</th>
<th>$\Delta P$ 3</th>
<th>$\Delta P$ 4</th>
<th>$\Delta P$ 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta m_{CH4}$ [mol/L]</td>
<td>0.056</td>
<td>0.069</td>
<td>0.071</td>
<td>0.068</td>
<td>0.076</td>
</tr>
<tr>
<td>kJ/(litre pore water)</td>
<td>1.99</td>
<td>2.41</td>
<td>2.48</td>
<td>2.39</td>
<td>2.66</td>
</tr>
<tr>
<td>kJ/(litre bulk sample)</td>
<td>0.48</td>
<td>0.58</td>
<td>0.59</td>
<td>0.57</td>
<td>0.64</td>
</tr>
<tr>
<td>J/(kg bulk sample)</td>
<td>477.85</td>
<td>295.12</td>
<td>303.59</td>
<td>292.33</td>
<td>326.13</td>
</tr>
<tr>
<td>Temperature increase $\Delta T$ [K]</td>
<td>0.38</td>
<td>0.24</td>
<td>0.24</td>
<td>0.23</td>
<td>0.26</td>
</tr>
<tr>
<td>Average $\Delta T$ [K]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.271</td>
</tr>
<tr>
<td>Change in equilibrium pressure $\Delta P_{eq}$ [MPa]</td>
<td>0.360</td>
<td>0.181</td>
<td>0.186</td>
<td>0.183</td>
<td>0.176</td>
</tr>
<tr>
<td>Average $\Delta P_{eq}$ [MPa]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.217</td>
</tr>
<tr>
<td>Increase in methane hydrate saturation $\Delta S_h$ [-]</td>
<td>0.018</td>
<td>0.022</td>
<td>0.023</td>
<td>0.022</td>
<td>0.025</td>
</tr>
<tr>
<td>Average $\Delta S_h$ [-]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.022</td>
</tr>
</tbody>
</table>
Based on the new equilibrium temperature, the phase boundary equation (7.1) can be used to determine to what extent the equilibrium pressure $\Delta P_{eq}$ increases. This leads to the above mentioned reduced gas effervescence and thus requires an iterative solution. These approximated $\Delta P_{eq}$ fall in a range between 0.18 and 0.36 MPa, with an average of about 0.22 MPa. The resulting increase in hydrate saturation $\Delta S_h$ ranges from 1.8 to 2.5%, with an average of the five tests equal to 2.2%. How these changes compare to the experimentally measured changes is discussed in the subsequent section.

### 7.3.2 Experimental measurements

It is important to validate these theoretical changes in temperature during depressurisation of a hydrate bearing sample with real experimental results. Table 27 lists the measured temperature changes at different radial locations during the five depressurisation experiments. The corresponding temperature and pressure histories are shown in Figure 62 to Figure 66. All samples were depressurised though the miniature wellbore located at the cylinder axis, except $\Delta T$ 1, which had to be depressurised through the top inlet (port 1 in Figure 17), because of sand clogging the miniature wellbore.

The temperature changes vary most at the sample’s extremes. It is generally higher at the centre ($r/r_0 = 1$) due to the relative surplus of free water in the wellbore’s annulus and copper mesh sand screen (and lower specific heat) compared to the sample’s pore space. At the samples’ inter-phase with the pressure vessel wall at $r/r_0 = 18$, the thermal inertia of the steel wall combined with the temperature fluxes from the cooling limit the local temperature increase.
Table 27: Measured temperature change $\Delta T$ [K] at different radii during depressurisation.

<table>
<thead>
<tr>
<th>$r/r_0$</th>
<th>$\Delta P_1$</th>
<th>$\Delta P_2$</th>
<th>$\Delta P_3$</th>
<th>$\Delta P_4$</th>
<th>$\Delta P_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.13</td>
<td>0.80</td>
<td>0.88</td>
<td>0.29</td>
<td>0.72</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.61</td>
<td>0.68</td>
<td>0.24</td>
<td>0.49</td>
</tr>
<tr>
<td>7</td>
<td>-0.24</td>
<td>0.56</td>
<td>0.63</td>
<td>0.29</td>
<td>0.51</td>
</tr>
<tr>
<td>10</td>
<td>1.41</td>
<td>0.56</td>
<td>0.52</td>
<td>0.24</td>
<td>0.97</td>
</tr>
<tr>
<td>14</td>
<td>-0.02</td>
<td>0.51</td>
<td>0.61</td>
<td>0.15</td>
<td>0.58</td>
</tr>
<tr>
<td>18</td>
<td>0.67</td>
<td>0.11</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average per sample [K]</td>
<td>0.38</td>
<td>0.52</td>
<td>0.56</td>
<td>0.21</td>
<td>0.55</td>
</tr>
<tr>
<td>Average $\Delta T$[K]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.443</td>
</tr>
<tr>
<td>Change in equilibrium pressure $\Delta P_{eq}$ [MPa]</td>
<td>0.354</td>
<td>0.409</td>
<td>0.437</td>
<td>0.163</td>
<td>0.379</td>
</tr>
<tr>
<td>Average $\Delta P_{eq}$ [MPa]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.348</td>
</tr>
</tbody>
</table>

Water is generally assumed to be incompressible. It has been observed, however, that a flow of the pore water is induced during depressurisation, which is most likely a combination of expanding dissolving gas and some degree of expansion. In $\Delta T_1$, where the pore water flow was towards the inlet (essentially a point depressurisation), the local temperature evolutions are distorted by the flow, which explains its comparative anomalies. When the pressure is reduced at the wellbore (test $\Delta P_2$ to $\Delta P_5$), the rate at which the temperature increases at different radii is almost uniform. This shows that the initial internal temperature gradients within the sample do not change, and as a result that shows that the assumption of negligible heat transfer is legitimate.

The averages of the measured local temperature increases vary between 0.21 and 0.56 K. They exceed the theoretical changes given in Table 26 by up to 56%, except for $\Delta T$
4, where the predicted temperature increase is 12% higher than was actually measured. These discrepancies show that the model can only approximately predict the temperature change during the depressurisation of samples with methane saturated pore water. The conservative predictions can be attributed to the combination of the presence of free gas in the pore space at depressurisation start (only partial gas conversion during hydrate formation), free surplus water at the inner boundary and inaccuracies in the methane solubility data fit.

The tests show also that changes in depressurisation rate between 1.2 and 3.9 MPa/min are rather insignificant for the average temperature increase, which confirms that the dissolved methane bubbles are small with a high surface to volume ratio, and thus the hydrate forms rapidly. This is in line with the quantitative statement by Makogon (1997, page 346) about the same process.

The equilibrium pressure increase in the experiments varies between 0.16 and 0.44 MPa, again greater than the model predictions. These changes might seem more insignificant than they actually are: if in a gas production scenario from hydrates, the wellbore has to be depressurised less by 0.5 MPa in order to initiate hydrate dissociation, the pumping energy required for pressure maintenance is much less than initially assumed (see energy comparison, section 6.7).

A second advantage of the methane effervescence effect is that the resulting hydrate formation increases the initial hydrate saturation in the sediment $S_h$. Based on the moles of methane released, the change in hydrate saturation $\Delta S_h$ is calculated by:

$$
\Delta S_h = \Delta m_{\text{CH}_4} \frac{10^3 M_h}{\rho_h n}
$$

(7.6)

where

$\Delta m_{\text{CH}_4}$ is the amount of moles freed from the pore water [mol/(litre H$_2$O)]
\( M_h \) is the molar mass of methane hydrate, 0.1169 kg/mol

\( \rho_h \) is the density of methane hydrate, 913 kg/m³

\( n \) is the porosity of the sediment

In these experiments, the initial hydrate saturation of 0.40 was increased to about 0.42 during depressurisation, a net gain of 5%. From a production perspective, the effect on the increase in recoverable gas is probably of less significance than the changes to the initial permeability.

Figure 62: \( \Delta P \) 1 depressurisation test to atmospheric pressure: temperature histories at different sample radii (left) and pressure evolution compared to the methane hydrate equilibrium pressure (right).

Figure 63: \( \Delta P \) 2 depressurisation test to 6 MPa: temperature histories at different sample radii (left) and pressure evolution compared to the methane hydrate equilibrium pressure (right).
Figure 64: ΔP 3 depressurisation test to 4 MPa: temperature histories at different sample radii (left) and pressure evolution compared to the methane hydrate equilibrium pressure (right).

Figure 65: ΔP 4 depressurisation test to 4 MPa: temperature histories at different sample radii (left) and pressure evolution compared to the methane hydrate equilibrium pressure (right).

Figure 66: ΔP 5 depressurisation test to 4 MPa: temperature histories at different sample radii (left) and pressure evolution compared to the methane hydrate equilibrium pressure (right).
Even for only small variations in the initial conditions, these results show that the heat generation during depressurisation depends on the initial in-situ temperature and pressure. How sensitive these changes in equilibrium pressure and initial hydrate saturation are to the in-situ starting conditions, is elaborated in the subsequent section.

7.4 Sensitivity to initial in-situ conditions

The experiments were conducted within a narrow range of initial conditions in order to achieve comparability during the dissociation process. But the simple physical model describing the observed processes in section 7.3.1, can now be applied to a wider range of initial in-situ pressure and temperature conditions, to determine which effect they have on the heat generation during depressurisation.

The investigated range of initial conditions covers most in-situ conditions of gas hydrate fields which are or could become of commercial interest. The pressure is varied between 10 and 30 MPa, equivalent reservoir depths of up to 3000 m. Temperatures between 273 and 295 K are also deemed to be sufficient, as the upper bound already requires a minimum pressure of 34 MPa for the hydrate to be stable. Changes in water solubility of methane at different pressures and temperatures are approximated with equation (7.3). The results are derived for the same sediment properties as the samples tested experimentally and specified in Table 24, with a porosity of 0.4, an initial hydrate saturation of 0.4 and with the remaining pore space filled with water.
7.4.1 Change in temperature

How the temperature changes for different initial conditions is straightforward. The higher the initial pressure, the more gas is initially dissolved in the pore water. At the same time the change in pressure within the hydrate stability region is proportional to the initial pressure, which means that more gas comes out of solution and in turn heat is generated during depressurisation. Changes in initial temperature affect the depressurisation length $\Delta P$ within the stability zone, shortening it for higher initial temperatures. The resulting temperature change during depressurisation within the hydrate stability zone is therefore most pronounced for high initial pressure and low temperature conditions, and a sensitivity check on variations in $P_0$ and $T_0$ is shown in Figure 67:

![Figure 67: Temperature change $\Delta T$ during depressurisation in the stable hydrate region for varying initial pressure $P_0$ and -temperature $T_0$ conditions.](image)

Not only does this increase in temperature depend on the initial conditions, but also on the fraction of methane saturated water per unit sample or formation volume. Because water has an about five times higher specific heat than silica sand and twice as high as methane hydrate, the bulk conductivity $C_{p,b}$ increases with increasing water
saturation. But so does the released methane from water per unit volume, resulting in a larger increase in temperature $\Delta T$ for higher water saturations.

### 7.4.2 Change in equilibrium pressure

The importance of the temperature change due to the exothermic processes during depressurisation lies in the resulting change in the hydrate equilibrium conditions. An increase in temperature ($\Delta T$ in Figure 61) leads to an increase in equilibrium pressure $\Delta P_{eq}$. That means that hydrate dissociation starts at a higher pressure $P_{eq,2}$ as compared to the initial temperature corresponding equilibrium pressure $P_{eq,1}$. The implication of that are significant: if a well driven into a hydrate field is depressurised, leading to the shift in equilibrium conditions described here, gas starts to be dissociated from the hydrate at a higher wellbore pressure.

The methane hydrate equilibrium pressure increases exponentially with temperature. Therefore, if a hydrate bearing sediment is depressurised at a higher initial temperature, any temperature increase results in a larger change in equilibrium pressure $\Delta P_{eq}$ compared to depressurising it from a lower initial temperature. Thus the change in equilibrium pressure caused by the dissolution of methane from the water depends on the initial temperature. But there is a tradeoff: as explained in section 7.4.1, the lower the initial temperature, the lower the corresponding equilibrium pressure. Therefore, the release of heat during depressurisation increases with decreasing initial temperature. Both counteracting trends with changes in initial temperature suggest that there must be a critical point where the change in equilibrium pressure $\Delta P_{eq}$ reaches a maximum. Figure 68 plots $\Delta P_{eq}$ for varying initial conditions, and the expected local maxima are well defined. It can be seen that the $\Delta P_{eq}$ increases with increasing initial temperature $T_0$ due to the positive curvature of
the methane hydrate phase boundary. The rate at which $\Delta P_{eq}$ increases is larger for higher initial pressures, as there the reduction of depressurisation length $\Delta P$ within the hydrate stability zone is less significant as for lower initial pressures.

Figure 68: Change in equilibrium pressure $\Delta P_{eq}$ during depressurisation of methane saturated water in hydrate conditions for varying initial pressure and temperature conditions.

The maximum change in equilibrium pressure varies between 0.17 MPa for an initial pressure of 10 MPa, and 0.74 MPa for initial in-situ pressures of 30 MPa. From a gas production perspective, a wellbore pressure maintenance 0.7 MPa higher than initially predicted results in energy savings in downhole pumping as well as surface gas compression, since the gas is recovered at a higher pressure.

7.4.3 Change in hydrate saturation

The difference in methane solubility between the initial- and equilibrium pressure, is the amount of methane which, once separated from the water, reforms to methane hydrate. This newly formed hydrate adds to the initial hydrate saturation in the pore space. Like the temperature increase during depressurisation, the change in hydrate saturation increases with increasing depressursation length within stable hydrate
conditions. In other words, the higher the initial pressure and the lower initial temperature, the more hydrate forms during depressurisation.

![Figure 69: Increase in methane hydrate saturation $\Delta S_h$ due to the formation of the dissolving gas during depressurisation for varying initial pressure and temperature conditions.](image)

A quantitative assessment of the saturation changes is shown in Figure 69. For low initial temperatures, the change in hydrate saturation can be as high as 8.6% for the initial conditions being 30 MPa and 274 K. Even for lower initial pressures and higher temperatures, the increase in hydrate saturation can be substantial.

The implications of this increase in hydrate saturation are an increased gas production from hydrates, but also a reduction in initial permeability of the host formation. The benefits of an increased gas concentration in place are obvious. The permeability decrease due to the additional solid hydrate in the pore space can have two effects. On one hand it reduces the required pumping rate for the well-pressure maintenance, as the flow rate of the pore fluid flowing into the well is reduced (see energy comparison in section 6.7). On the other hand it may change the initial pore pressure profile, limiting the degree to which the reservoir can be depressurised from a single wellbore. The increase in hydrate saturation is proportional to the fraction of methane saturated...
heat generation during depressurisation water per unit volume, as it does not depend on any changes in any thermophysical properties like the temperature. That means that the increase in hydrate saturation is higher for an initial smaller hydrate saturation (thus more water per volume) and vice versa. Whether a small increase to a highly saturated or a larger increase to smaller saturated formation has a greater impact on the water’s relative permeability is not clear. The data by Oyama et al. (2009) in Figure 54 show a relatively scattered correlation between different hydrate saturations and their respective initial permeabilities without suggesting any particular trend.

7.5 Conclusion

The effects of heat generation during depressurisation are beneficial from a production perspective. The increased temperature raises the equilibrium pressure at which the increased amount of gas hydrate can be dissociated. Compared to the endothermic effects during dissociation, the impact of these exothermic reactions is however secondary, as they will only affect the initial dissociation conditions but not the dissociation process itself.

More experimental tests with a wider range of initial pressure, temperature and saturation conditions would be desirable for benchmarking the analytical model. A subsequent implementation of these exothermic processes into numerical code would allow determining their effect in a large scale gas production scenario from hydrates.
8 Conclusion and Future Work

8.1 Conclusion

The main contribution of this study is the finding that gas can be extracted from hydrate bearing sediments more efficiently by a combination of depressurisation and wellbore heating. A moderate heating is sufficient to increase the extracted gas rate by several times (3.6 experimentally, 1.8 numerically) as compared to depressurisation only, because it creates a constant disequilibrium around the wellbore reducing the limiting endothermic cooling effects during hydrate dissociation. An energy comparison shows that for an initial permeability $k_0$ greater than 3 mD and a reservoir depth greater than 1000 m, additional heating is more efficient as compared to a lower wellbore pressure.

The hydrate dissociation process in the pore space of the host formation is governed by the heat energy supplied to it. The formation and pore water’s specific heat is used up very rapidly during dissociation by a pressure reduction, and therefore the governing dissociation drivers become heat conduction through the sediment (especially in the case of a heated wellbore) and forced convection through the fluid phase from the radially outer dissociation boundary. The bulk thermal conductivity of stable water saturated hydrate bearing layers with a porosity of 40% has been measured as 2.6 W/mK. In contrast to what the theoretical mixing models suggest, the bulk conductivity only slightly decreases in partially saturated sediment. No effects natural (free) convection were observed in the stable- and dissociated hydrate zones. Only in fully gas saturated sediments convective heat transfer could be measured for
gas pressures above 5.5 MPa. Since the hydrate dissociation rate is governed by the heat transferred to it, the widely used Kim-Bishnoi model which describes the dissociation kinetics of the hydrate itself is only of secondary importance for production pressure- and temperature conditions. However, gas hydrate layers can become heat conductive during dissociation if their hydrate dissociation is sufficiently reduced, which in the case of a heated wellbore extends its influence zone after the initial insulative behaviour. The required dissociation energy for these sample and boundary conditions could be approximated with a uniform energy consumption rate on the order of $10^4$ W/m$^3$.

The depressurisation of water saturated methane hydrate bearing samples lead to two sequential exothermic processes: the methane solubility in water is reduced with decreasing pressure, and comes out of solution in the water ($\Delta H = 16.5$ kJ/(mol CH$_4$)). Consecutively, the freed gas together with the pore water forms hydrate ($\Delta H = 54.2$ kJ/(mol CH$_4$)) before the phase boundary is reached by the ongoing pressure reduction. The resulting temperature increase raises the hydrate equilibrium pressure where dissociation commences. This is beneficial from a production perspective, as on one hand it increases the initial hydrate saturation in place, and on the other it reduces the necessary wellbore pressure reduction in order to initiate the dissociation process.

### 8.2 Future work

This work should only be the beginning. The developed test rig lends itself to a wide range of hydrate related research, with little or no modification. The capabilities of working with real methane hydrates puts NUS in a favourable position, compared to
research on artificial ‘model’ carbon dioxide hydrates, or numerical dissociation analysis not coupled to experiments. The current setup is the first combining dissociation by depressurisation and simultaneous electrical heating from a miniature wellbore, probably the most effective production scheme for a wide range of class 3 hydrate deposits. The most attractive hydrate deposits are in class 3 sediments (Nankai Trough, Mallik, Alaskan North Slope), and therefore they should remain the main research subject. Research on natural gas hydrates involves so many aspects that collaborations with complementing groups are essential. While the main focus should remain on small scale experiments, the results can however in future be verified with the Hydrate Reservoir Simulator code in Fortran.

In a production scenario from hydrates, the hydrate dissociation rate is governed by the heat transfer from non-dissociating regions into the dissociation zone, as the specific heat of the formation itself is used up very rapidly if no external heat is supplied. The general conclusion drawn from the two full-scale tests at the Mallik site is that the most efficient production method is depressurisation. This might be true for that particular well design with a perforation length of 12 metres; but in a commercial production scheme, where perforation lengths of 100 m are proposed, the heat transfer into the dissociating region will no longer be axial from the over- and underburden, but radial from the stable hydrate reservoir itself, which will in most cases lead to comparably smaller and decreasing heat fluxes as dissociation progresses. Supplying heat is thus essential to achieve a sustained dissociation process, while a corresponding pressure reduction at the well is necessary to drain the freed gas from the formation.

With exploration and production, and hence the offshore industry as a whole moving into deeper waters, the likelihood of encountering hydrates on the seabed increases. In
deep waters, production facilities are most commonly anchored with friction piles, driven into the seabed, or shallower suction caissons. In moderate climates, natural gas hydrate is stable in water depth of equals or greater than 400 metres, and can extend from the seabed surface to several hundreds of metres depth. Such shallow hydrate deposits jeopardise the foundation's stability, as their dissociation can result in significant friction- and bearing capacity losses. Dissociation can easily be triggered by the transportation of hot reservoir fluids through wells, flow- and pipelines. Seabed hydrates have also been encountered in South East Asian waters, in deep water projects offshore Sabah (Kenneth et al., 2004), where they are a hazard to seabed and wellbore stability. It is therefore of great importance to quantify the soil’s response to hydrate dissociation to improve the design and reduce the failure risk of deepwater foundations.

The widely applied Kim-Bishnoi model describing the hydrate dissociation rate includes an empirical rate constant, which in the literature varies by two orders of magnitude, as well as the hydrate surface area which is difficult to determine. If we therefore succeed in describing the rate at which gas is freed from hydrate molecules based on the porosity, saturation, bulk thermal properties and the dissociation drive (defined as the distance normal to the hydrate equilibrium phase boundary in pressure and temperature), we would make a major contribution to the present knowledge of hydrate dissociation in sediments.

The overall scope of the proposed future work can therefore be divided into two major areas of the natural gas hydrate research field – the exploitation of gas hydrates as a form of energy and their geohazardous potential in deep water. The work would focus on gas production from hydrate reservoirs as well as soil investigation of hydrate bearing seabed.
It is proposed to examine various production schemes from a single- and dual wellbore, to optimise the gas extraction/production by balancing depressurisation with local heating in order to moderate the constraining cooling effect. The geohazardous potential of shallow natural gas hydrates can be addressed by modified cone penetrometer tests as well as pile response analysis in stable- and partially dissociating hydrate bearing sediment. The targeted outcome of the proposed studies would be to find:

1. Balance between wellbore heating rate and pressure reduction to optimise the gas recovery from hydrates, applicable to a single- and dual wellbore scheme
2. Mechanical soil response to local hydrate dissociation from a cone penetrometer
3. Analytical hydrate dissociation model describing the dissociation rate of gas hydrate in a variety of seabed conditions
4. Reduction in pile capacity due to local hydrate dissociation on its surface

The dissociation model (3) would be the first to describe hydrate dissociation in sediment, where the heat transfer is expected to govern the process. To date, almost all analytical and numerical models are based on the dissociation model proposed by Bishnoi and co-workers (1987), which was derived for pure hydrate grains in a stirred tank to eliminate the effect of heat transfer, and is therefore only partially applicable to in-situ dissociation (refer to chapter 5). The dissociation model can be derived from heating tests in the line dissociation setup shown in Figure 70. It could then be directly applied to the soil investigation tests proposed in (2) and (4), with which sensitivity tests on hydrate saturation and sediment conditions would allow to correlate the soil’s response to controlled heat dissociation and the in-situ properties.
The hydrate dissociation experiments from a line source with measurements of local pressure, -temperature and -density can be the design-basis for a downhole offshore site-investigation device, incorporating operational parameters and leading dimensions and operating parameters, and advanced to the point where it could be taken over by a site investigation companies.

The proposed experiments will be conducted on the basis of the existing testing facilities at NUS described in chapter 4. Modifications will have to be made to the internal equipments of the pressure vessel. With the incorporation of the dual wellbore scheme, a second internal sample holder is required. An additional in-line gas flow meter would allow the determination of low gas flow rates, which govern later stages of production by depressurisation. An extra flange cap containing a second piston will be needed to load the pile. To facilitate soil investigation at seabed conditions, a modified cone penetrometer with a resistivity heated tip will be fabricated together with a miniature pile. To gather stress-displacement patterns and load redistribution data, strain gauges and displacement transducers will be placed at the cone’s shaft and pile’s length while stress mats could be incorporated within the sample. As such, additional modules will be required for the data acquisition system. The existing piping and analogue pressure readings will have to be modified in order to accommodate the new devices.

8.2.1 Gas production from hydrate reservoirs

The current setup shown in Figure 70 (left) is designed for small scale production tests with a combined heated and depressurised wellbore. The research with the single wellbore is however far from exhausted, as variations in
- The initial hydrate saturation $S_h$
- Sediment properties, e.g. the effect of tight clay layers
- The vertical effective stress, $\sigma_v'$, load and loading sequence
- The wellbore pressure and temperature

strongly affect the hydrate dissociation process and hence the systems efficiency. The aim should be to extend the currently obtained correlations of gas extraction from hydrates by simulating more diverse and complex scenarios, like varying saturation and heterogeneity. The constant vertical effective stress represents the overburden of in-situ deposits and, depending on the geological history, is applied before- or after hydrate is formed. This determines the load the pore-filling hydrates carry, and in turn affect the formation’s strain development during their dissociation. A potential limitation of a single wellbore scheme is that heat is supplied to the dissociation zone purely by conduction through the sediment, against the forced convection induced by the pore fluid flowing towards the well.

Once gas production from hydrates starts off on a commercial scale, it would therefore be of great interest to see how the heat transfer can be improved in a dual wellbore production scheme (see Figure 70), in which the forced convection would be turned into an advantage. In a multiple wellbore scheme, with regularly spaced production and heat injection wells, this forced convection through the pore fluid could be utilised to supply energy into the dissociating zone. A dual wellbore separating production from injection is nothing new to the petroleum industry, but this would be a novel setup for hydrate gas production tests.
Figure 70: Small scale production schemes with combined heating and depressurisation: with a single wellbore a in the current setup (left); with the proposed dual wellbore scheme (right).

The current experimental setup would therefore be modified to accommodate two miniature wellbores as shown in Figure 70 (right). In this particular setup, a decentralised production well reduces the necessary bending radius of the gas extraction hose, reducing the tripod height, enabling tests on longer cylindrical samples and therefore reducing axial boundary effects. Care would have to be taken that the set wellbore pressure corresponds to the initial- and outer boundary temperature equilibrium pressure, to eliminate artificial heat fluxes in either direction.

Local temperature measurements will indicate the location and duration of dissociation; from the gamma ray transmissivity readings bulk density changes can be derived. This gives insight into several things: it enables the allocation of a moving dissociation front in dissociation tests by heating (as the transmissivity changes due to free gas, even though the mass is conserved), and it shows patterns where residual gas accumulates in the sample during production testing. The latter would be of particular
interest in the dual wellbore scheme, as the rotational symmetry of the piston plate enables gamma ray measurements from perpendicular to in-line to the heater-production well plane (compare density orientation in both schematics of Figure 70).

8.2.2 Soil investigation of hydrate bearing seabed

The existing pressure vessel can be used for geomechanical testing of hydrate bearing soil. The piston currently used to apply effective stress would be modified to simulate penetrations into a hydrate sediment. To assess its mechanical properties, such as bearing capacity, shear resistance and compound stability throughout the installation and lifetime of a structure, a miniature cone will first be penetrated into a stable hydrate soil (see Figure 71, right). The soil’s response to hydrate dissociation would then be examined by locally heating, either from the cone’s tip (direct), or from the accessible gamma ray guide pipe (indirect). The sample can host up to ten thermocouples, sufficient to accurately measure the special extend of heating and hence to quantify the dissociated volume, necessary to validate any changes in mechanical response. Depending on the sediment permeability and hence the local excess pore pressure dissipation, it is expected that the soil loses much of its shear strength immediately after the hydrate is dissociated. This is of particular importance in heterogeneous ground with almost impermeable clay layers.
A further proposal is to measure the response of piles to dissociating hydrate on their surface, as shown schematically in Figure 71 (right). The reduction in skin friction would be examined either by local heat dissociation again through the gamma ray guide pipe or by heating the pile’s surface directly. The bearing capacity clearly depends on the soil’s stress state. Unlike conventional pile testing, experiments with gas hydrates cannot practically be studied in a centrifuge because of their demanding pressure and temperature stability conditions. Thus, the stress application has to be achieved in 1g, by axial compression of the sediment sample, similar to the production tests. The pile would be loaded by a smaller piston from the opposite flange, where care has to be taken that the clearance between the miniature pile and the sample support does not relax stresses around the pile.

Both the cone’s shaft and the miniature pile would be strain gauged, which together with the measured displacement would enable to derive general stress-displacement
pattern for a respective dissociation weakened soil. Additional stress mats could be placed within the sample to better assess load redistribution.

The correlation between the assessed properties of the hydrate bearing sediment, derived from the local heat dissociation tests, and its resulting stability for standard foundations and -loadings would be an essential contribution to the offshore industry.
References


REFERENCES


Appendix A – Design

Pressure vessel design

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1 Shell Thickness
Design Pressure, N/mm²  
Allowable Stress, N/mm²  
Outside Diameter, mm  
Outside Radius, mm  
Joint Efficiency (longitudinal stress)  
Joint Efficiency (circumferential stress)  
Corrosion Allowance, mm  
Nominal Shell Thickness, mm  
Internal Radius, mm  
Calculated Shell Thickness, mm

Longitudinal Stress [Sect UG-27(c)(2)]

\[ 1/2 \, R = 45 \, \text{mm} \]
\[ t_{n} = 1/2 \, R \]
\[ 1.25\, E_{1} = 144 \, N/mm² \]
\[ P < 1.25 \, E_{1} \]
\[ t = \frac{PR}{[2SE_{1}+0.4P]} + c, \, \text{mm} \]
\[ = 5.7 \]

Circumferential Stress [Sect UG-27(c)(1) & Appendix 1-1 (1)]

\[ 0.385\, E_{2} = 98 \, N/mm² \]
\[ P < 0.385 \, E_{2} \]
\[ t = \frac{PR}{[SE_{2}+0.4P]} + c, \, \text{mm} \]
\[ = 13.6 \]

Minimum required thickness
Actual shell thickness
Excess thickness
Shell thickness is therefore adequate
APPENDIX

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Integral Flange Calculations

Using the rules in Appendix 2 of VIII-1

Design Pressure, psi \( p \) = 2175 psi
Design Temperature, Deg F \( T \) = 122 Deg F
Flange Material is Type 3/6L
Bolting Material is A193 B7
Gasket is O Ring Viton Type
Corrosion Allowance, in \( b \) = 0 in
Allowable bolt stress (gasket seating) \( S_a \) = 20000 psi
Allowable bolt stress (operating) \( S_b \) = 20000 psi
Allowable flange stress (gasket seating) \( S_{fa} \) = 16700 psi
Allowable flange stress (operating) \( S_{fb} \) = 16700 psi
Gasket Width \( w \) = 0.594 in
\( b = w + b = 0.049 \) in

Diameter of gasket reaction \( D \) = 8.558 in
Gasket Factor \( m \) = 0
Gasket unit seating load \( y \) = 0

Bolt loadings and the number and diameter of bolts are
Total Hydrostatic End Force \( H \) = 134061 lb
Total joint contact surface compression Load \( H_p \) = 0 lb
min required bolt load (operating) \( W_{m1} \) = 134061 lb
min required bolt load (gasket seating) \( W_{m2} \) = 0 lb
\( W_{m1}/S_b \) = 6.70 in2
\( W_{m2}/S_a \) = 0.00 in2
\( A_m \) = 0.70 in2
Using 8 bolts of 1 1/4-in diameter
\( A_b \) = 7.432 in2
\( >A_m \) (OK)

Gasket seating \( W_a = 0.5(A_m + A_b)/S_b \) = 141351 lb
operating \( W_b = W_{m1} \) = 134061 lb
Therefore flange design bolt load \( W \) = 141351 lb

Total Flange Moment (Gasket)
Flange Load \( H_g \) = 141351 lb
Bolt Centre Diameter \( C \) = 12.25 in
Lever Arm \( 0.5(C-C) \) \( h_g \) = 1.73 in
Flange Moment \( W_{mg} \) = 244659 in-lb

The total flange moment for operating condition is:
Inner flange diameter \( B \) = 7.087 in
Flange Loads
Gasket Load \( W_{H-H} \) \( H_{g} \) = 85799 lb
thickness of hub at the back of flange \( g_1 \) = 0.768 in
thickness of hub at small end \( g_0 \) = 0.768 in
Lever Arms
BCD to where Hd acts \( d_{h} \) = 2.24
Gasket to BCD \( h_{g} \) = 1.59
HT to BCD (prescribe Table 2-6) \( h_{t} \) = 2.18

Flange Moments
\( M_d \) = 192541 in-lb
\( M_g \) = 12627 in-lb
\( M_t \) = 104070 in-lb
APPENDIX

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| J6528 | 310148 in-lb | Page 3 of 3 |

Use the absolute value in the calculation

Calculation of flange stresses

Inside Diameter of flange

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From Fig 2.7.1 of VIII-1

| T    | 1.55 |
| Z    | 1.75 |
| Y    | 2.95 |
| U    | 3.20 |
| g1/g0| 1    |
| h0   | 2.33 |
| h    | 0    |
| h / h0| 0   |

From Appendix 2 of VIII-1

| F   | 0.0069 |
| V   | 0.8501 |
| f   | 1     |
| e   | 0.39  |
| d   | 8.00  |

Analyse moment at operating condition since this is larger (M = 313004 in-lb)

| flange thickness | t    | 2.8 in |
| Longitudinal hub stress | Sh = 16773 psi |
| Radial Flange stress | Sr = 3543 psi |
| Tangential stress | St = 10700 psi |

Combined Stresses

\[
0.5(Sh + Sr) = 11158 \text{ psi} \\
0.5(Sh + St) = 14766 \text{ psi}
\]

Allowable stresses

\[
\begin{align*}
Sh &< 1.5Sf \\
Sh < Sf &< 3543 < 16700 \text{ (OK)} \\
St &< Sf < 10700 < 16700 \text{ (OK)} \\
0.5(Sh+Sr) < Sf &< 11158 < 16700 \text{ (OK)} \\
0.5(Sh+St) < Sf &< 14766 < 16700 \text{ (OK)}
\end{align*}
\]

Required Thickness of blind = 2.53 inch

Ref. \( t - \sqrt{[\gamma(CP/SE) + (1.9Whg/SEc^2)]} \)

Reviewed by:

NG TONG LENG
Ministry of Manpowers (Singapore)
Authorised Inspector

CHAN YOK HAN
334
SINGAPORE
APPENDIX 158

ORIENTATION VIEW

CIRCUM SEAM (CS#1, CS#2)

DETAIL A (BOLTS HOLES)

DETAIL B (O-RING GROOVE)

ELEVATION VIEW

DETAIL OF NOZZLE N1, N2

NOZZLE SCHEDULE

219mm O.D. x 420mm S.L. STORAGE TANK

DESIGN DATA

<table>
<thead>
<tr>
<th>DESIGN CODE</th>
<th>ASME SECT VIII DIV 1 2007 ED 2008 ADD</th>
</tr>
</thead>
<tbody>
<tr>
<td>DESIGN PRESSURE</td>
<td>1500 kN/m² (217 PSIG)</td>
</tr>
<tr>
<td>DESIGN TEMPERATURE</td>
<td>93 °C</td>
</tr>
<tr>
<td>HYDROTEST PRESSURE</td>
<td>1558 kN/m² (2258 PSI)</td>
</tr>
<tr>
<td>FILL</td>
<td>AIR / WATER</td>
</tr>
<tr>
<td>INSPECTOR</td>
<td>MOM SINGAPORE AUTHORIZED SURVEYOR</td>
</tr>
<tr>
<td>RADIOGRAPHY</td>
<td></td>
</tr>
<tr>
<td>CORROSION ALLOWANCE</td>
<td>0.05 mm</td>
</tr>
<tr>
<td>DENT EFFICIENCY</td>
<td>100% SHELL 100% HEADED</td>
</tr>
<tr>
<td>CAPACITY</td>
<td>10 LITRES</td>
</tr>
<tr>
<td>WEIGHT (EMPTY)</td>
<td>380 KG (WITH BLINDS)</td>
</tr>
<tr>
<td>TTY REQUIRED</td>
<td>011 ONE</td>
</tr>
</tbody>
</table>

BILL OF MATERIALS

<table>
<thead>
<tr>
<th>ITEM</th>
<th>DESCRIPTION</th>
<th>MATERIAL</th>
<th>QTY</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>BLIND FLANGE OD 390 x 65mm THK</td>
<td>A176 ST37</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>FLANGE OD 390 x 10 OD 380 x 70mm THK</td>
<td>A176 ST37</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>SHELL OD 379 x ID 380 x 195mm THK</td>
<td>A172 ST37</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>NAMEPLATE &amp; BRACKET</td>
<td>SS304</td>
<td>1</td>
</tr>
</tbody>
</table>

GENERAL NOTES

1. ALL DIMENSIONS ARE IN MM UNLESS OTHERWISE NOTED.
2. FLANGE BOLT HOLES TO STRAIGHT VESSEL NORMAL CENTER LINE.
3. PRIOR TO FINAL INSPECTION AND PAINTING, ALL SLAG, DIRT, WELD SPATTER AND OTHER FOREIGN MATTER SHALL BE REMOVED FROM INSIDE AND OUTSIDE OF VESSEL.
4. FILLET WELD SIZE ARE MINIMUM AS INDICATED.

PAINTING SPECIFICATION

INTERNAL: BARE AND UNPOLISHED
EXTERNAL: BARE AND UNPOLISHED

N5 | 1/4" | 600# | SCREW | PNPT | 22 | CONNECTOR |
N4 | 1/2" | 600# | SCREW | PNPT | 22 | CONNECTOR |
N3 | 1/4" | 600# | SCREW | PNPT | 22 | CONNECTOR |
N2 | 3/4" | 600# | SCREW | PNPT | 25 | CONN PXRPDL SEAL |
N1 | 1/2" | 600# | SCREW | PNPT | 22 | CONN PXRPDL HIGH DENSITY |

MATERIAL: | SIZE | RATING | PREC | PROD |

Client: NATIONAL UNIVERSITY OF SINGAPORE

Fabricator: VANSIN TRADING & ENGINEERING PTE. LTD.

Title: 219mm O.D. x 420mm S.L. STORAGE TANK

Drawn: WILSON OHIA

Date: 19-05-2010

Scale: ASSMWM

Checked: D. K. LTD

Drawing No: A3-6928

Sheet: 1

Revision: 0

Approved: Y. H. CHAN
High strength flange design

Pressure vessel cap design: BS5500:2009

Material: SUS 329 J4
Yield stress $f_y = 560$MPa (acc. Inspection Certificate Daido Steel Co., Ltd.)
BS equivalent: 321020 to 147831
DIN equivalent: X8 CrNiMo275

Blind flange with gasket entirely within the belt circle (Fig.3.5-35(c)):

Minimum flange thickness $e$:

$$ e = \sqrt{\frac{0.3D^2 p}{S_{FE}} + \frac{1.909 W_{ml} h_G}{DS_{Fe}}} $$  \hspace{1cm} (1)

Where:

- $D$ is the diameter between the gasket (225mm)
- $p$ is the design pressure (15 MPa)
- $W_{ml}$ is the minimum bolt load $H_G + H$
- $m$ is the gasket design factor (0.25)
- $S_{FE}$ is the normal design stress (MPa)
- $b$ is the width of the gasket (13.7mm)
- $h_G$ is the radial distance from the bolt circle to the gasket

$$ W_{ml} = H_G + H = 596 + 72.6 = 668.6 \text{ MN} $$

$$ H = 0.785D^2p = 0.785 * 2252 * 15 = 596 \text{ MN} $$

$$ H_G = 2b^* \pi \cdot Dnp = 2 * 0.0137 \pi \cdot 0.225^* 0.25^* 15 = 0.073 \text{ MN} $$

$$ h_G = \frac{C - D}{2} = 0.044 \text{ m} \hspace{1cm} (3) $$

With the nominal design stress $S_{FE}$ equals the yield stress $f_y$, the minimum flange thickness is calculated to 29mm. (<30mm of our design)

Yamaha Works Co., Ltd

Professional Engineer Toshikide Yamaga
PCD=313.0
8等配

14×M5T、深さ7.0

8×φ36スクリーニング

A-A
φ390.0

NPT1/4

8×φ36

NPT1/4

NPT1/4 現合部品あり

ガスハイドレート室内試験
校正容器（R）上部キャップ
SUS-329-J4，1ヶ
S=1/2
Gamma ray source guide pipe

<table>
<thead>
<tr>
<th>Project: Methane Hydrate</th>
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<tbody>
<tr>
<td>Drawing no.: MH23, Soi&amp;R 1</td>
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<tr>
<td>Title: Pressure Vessel and Flange Cap</td>
</tr>
<tr>
<td>Scale: 1:4</td>
</tr>
<tr>
<td>Constructor: sf</td>
</tr>
<tr>
<td>Date: 11.10.2010</td>
</tr>
</tbody>
</table>
Gamma ray detector
Appendix B – Numerical codes

Transient heat conduction in MATLAB

```matlab
function T17_trans_5
% conduction in partially dissociated hydrate
% control volume
m = 1;
x = (0.005:0.001:0.090);
t = (0.4:0.005:230);
sol = pdepe(m,@pdeTpde,@pdeTic,@pdeTbc,x,t);
u1 = sol(:,:,1);

% input parameters
global rho_b k_b c_b n S_h rho_s rho_w rho_h rho_g k_s k_w k_h k_g
c_s c_w c_h c_g...
S_w = 0.6+0.927*(0.4-S_h); % water saturation
S_g = (0.4-S_h)*(1-0.927); % gas saturation
n = 0.4; % porosity
S_h = 0.4; % hydrate saturation
P = 7.8; % pore pressure [MPa]
R = 8.314; % Gas constant [(m^3 Pa)/(K mol)] or [J/(mol K)]
mw = 16; % molar weight methane [g/mol]
T = 282; % initial temperature [K]
K_0 = 3.6e+5*60*1e+6; % intrinsic dissociation rate constant [mol/(MPa min m^2)]
AE = 81e+3; % activation energy [J/(mol CH4)]
K_d = K_0*exp(-AE/(R*T)) % dissociation rate constant [mol/(Pa s m^2)]
A_hd = 1e+4*n*S_h; % hydrate surface area approx after Klar and Soga
T_eq = 7.5757*log((P-1)/1.6)+273.15; % equilibrium temperature for actual pore pressure[K]
H_d = 54.2e+3; % dissociation enthalpy [J/(mol CH4)]
P_eq = 1+1.6*exp(0.132*(u-273));
rho_s = 2600; % density sand [kg/m^3]
rho_w = 1000; % fresh water
rho_h = 913; % hydrate
rho_g = P*1E+6/(R*T)*mw/1000 % methane
rho_b = rho_s*(1-n)+rho_w*n*S_w+rho_g*n*S_g+rho_h*n*(S_h) % bulk density
k_s = 3.92; % thermal conductivity sand [W/(m K)]
k_w = 0.56; % fresh water
k_h = 0.62; % hydrate
k_g = 0.034; % methane
k_b = k_s*(1-n)*k_w^n*S_w^k_g^n*S_g^k_h^n*(S_h) % bulk density
k_b = 1.841;
```
c_s = 800; % specific heat capacity sand [J/(kg K)]
c_w = 4190; % fresh water
c_h = 2010; % hydrate
c_g = 2120; % methane
c_b = c_s*(1n)*rho_s/rho_b+c_w*(n*S_w)*rho_w/rho_b+c_h*(n*S_h)*... 
 rho_h/rho_b+c_g*n*S_g*rho_g/rho_b

a = 1/(rho_b*c_b)

%figure;
subplot(3,2,1);
hold on;
plot(t,u1(:,1));

subplot(3,2,3);
hold on;
plot(t,u1(:,16));

subplot(3,2,5);
hold on;
plot(t,u1(:,31));

subplot(3,2,2);
hold on;
plot(t,u1(:,40));

subplot(3,2,4);
hold on;
plot(t,u1(:,66));

subplot(3,2,6);
hold on;
plot(t,u1(:,86));

% function [c,f,s] = pdeTpde(x,t,u,DuDx)
% global a k_b T_eq P K_d A_hd H_d
% c = (a*60)^(-1);
% f = k_b*DuDx;
% s = 0;%-1.5e3;%exp(t/60);%-K_d*A_hd*H_d*((1+1.6*exp(0.132*(u-273)))-
P);% heat sink due to dissociation [(W min)/m^3]

% function u0 = pdeTic(x)
u0 = 275.4;

% function [pl,ql,pr,qr] = pdeTbc(xl,ul,xr,ur,t)
if ul < 288;
    pl = 100; %heat flux [W/m]
    ql = 2*3.16*0.005;
else
    pl = 0;
    ql = 0;
end
pr = ur-275.4;
qr = 0;
% 

Dissociation heat sink modelling in MATLAB

function T16_trans_dissoc_sink_fit_2
% conduction in partially dissociated hydrate
% control volume
m = 1;
x = (0.005:0.001:0.090);
t = (0.5:0.01:60);

sol = pdepe(m,@pdeTpde,@pdeTic,@pdeTbc,x,t);
u1 = sol(:,:,1);

% input parameters
global rho_b k_b c_b n S_h rho_s rho_w rho_h rho_g k_s k_w k_h k_g
c_s c_w c_h c_g ...
a S_w S_g T_eq P R K_d A_hd H_d K_0 AE Tr5 Tr15 Tr25 Tr35 Tr45
Tr55 r\%P_eq

n = 0.4; % porosity
S_h = 0.4; % hydrate saturation
S_w = 0.6; % water saturation
S_g = 0; % gas saturation
P = 7.8; % pore pressure [MPa]
R = 8.314; % Gas constant [(m^3 Pa)/(K mol)] or [J/(mol K)]
mw = 16; % molar weight methane [g/mol]
T = 282; % initial temperature [K]
K_0 = 3.6e+5*60*1e+6; % intrinsic dissociation rate constant
[mo\l/(MPa min \text{m}^2)]
AE = 81e+3; % activation energy [J/(mol CH4)]
K_d = K_0*exp(-AE/(R*T)) % dissociation rate constant [mol/(Pa s \text{m}^2)]
A_hd = 1e+4*n*S_h; % hydrate surface area approx after Klar and Soga
T_eq = 273+(7.575*log(P-1)-3.56); % equilibrium temperature for actual pore pressure[K]
H_d = 54.2e+3; % dissociation enthalpy [J/(mol CH4)]

rho_s = 2600; % density sand [kg/m^3]
rho_w = 1000; % fresh water
rho_h = 913; % hydrate
rho_g = P*1E+6/(R*T)*mw/1000 % methane
rho_b = rho_s*(1-n)+rho_w*n*S_w+rho_g*n*S_g+rho_h*n*(S_h) % bulk density

k_s = 7.7; % thermal conductivity sand [W/(m K)]
k_w = 0.56; % fresh water
k_h = 0.62; % hydrate
k_g = 0.034; % methane
%k_b = k_s*(1-n)*k_w*(n*S_w)*k_g*(n*S_g)*k_h*(n*S_h)
k_b = 2.6;
\[
c_s = 800; \quad \text{% specific heat capacity sand [J/(kg K)]}
\]
\[
c_w = 4190; \quad \text{% fresh water}
\]
\[
c_h = 2010; \quad \text{% hydrate}
\]
\[
c_g = 2120; \quad \text{% methane}
\]
\[
c_b = c_s(1-n)\rho_s/\rho_b + c_w(n\rho_w/\rho_b) + c_h(n\rho_h/\rho_b) + c_g(n\rho_g/\rho_b)
\]
\[
a = k_b/(\rho_b c_b) \quad \text{% thermal diffusivity [m^2/s]}
\]
\[
Tr5=[u1(500,1);u1(500,6);u1(500,11);u1(500,16);u1(500,21);u1(500,26);
\ldots
u1(500,31);u1(500,36);u1(500,41);u1(500,46);u1(500,51);u1(500,56);
\ldots
u1(500,61);u1(500,66);u1(500,71);u1(500,76);u1(500,81);u1(500,86)];
\]
\[
Tr15=[u1(1500,1);u1(1500,6);u1(1500,11);u1(1500,16);u1(1500,21);u1(1500,26);
\ldots
u1(1500,31);u1(1500,36);u1(1500,41);u1(1500,46);u1(1500,51);u1(1500,56);
\ldots
u1(1500,61);u1(1500,66);u1(1500,71);u1(1500,76);u1(1500,81);u1(1500,86)];
\]
\[
Tr25=[u1(2500,1);u1(2500,6);u1(2500,11);u1(2500,16);u1(2500,21);u1(2500,26);
\ldots
u1(2500,31);u1(2500,36);u1(2500,41);u1(2500,46);u1(2500,51);u1(2500,56);
\ldots
u1(2500,61);u1(2500,66);u1(2500,71);u1(2500,76);u1(2500,81);u1(2500,86)];
\]
\[
Tr35=[u1(3500,1);u1(3500,6);u1(3500,11);u1(3500,16);u1(3500,21);u1(3500,26);
\ldots
u1(3500,31);u1(3500,36);u1(3500,41);u1(3500,46);u1(3500,51);u1(3500,56);
\ldots
u1(3500,61);u1(3500,66);u1(3500,71);u1(3500,76);u1(3500,81);u1(3500,86)];
\]
\[
Tr45=[u1(4500,1);u1(4500,6);u1(4500,11);u1(4500,16);u1(4500,21);u1(4500,26);
\ldots
u1(4500,31);u1(4500,36);u1(4500,41);u1(4500,46);u1(4500,51);u1(4500,56);
\ldots
u1(4500,61);u1(4500,66);u1(4500,71);u1(4500,76);u1(4500,81);u1(4500,86)];
\]
\[
Tr55=[u1(5500,1);u1(5500,6);u1(5500,11);u1(5500,16);u1(5500,21);u1(5500,26);
\ldots
u1(5500,31);u1(5500,36);u1(5500,41);u1(5500,46);u1(5500,51);u1(5500,56);
\ldots
u1(5500,61);u1(5500,66);u1(5500,71);u1(5500,76);u1(5500,81);u1(5500,86)];
\]
\[
r= \text{linspace}(1,18,18);
\]
\[
% Figure
\]
\[
subplot(3,2,1);
hold on;
plot(r,Tr5);
title('5 min')
% Appendix 167

```matlab
subplot(3,2,3);
hold on;
plot(r,Tr15);
title('15 min')

subplot(3,2,5);
hold on;
plot(r,Tr25);
title('25 min')

subplot(3,2,2);
hold on;
plot(r,Tr35);
title('35 min')

subplot(3,2,4);
hold on;
plot(r,Tr45);
title('45 min')

subplot(3,2,6);
hold on;
plot(r,Tr55);
title('55 min')

% -------------------------------------------------------------------

function [c,f,s] = pdeTpde(x,t,u,DuDx)
    global a k_b T_eq P K_d A_hd H_d
    c = (a*60)^(-1);
    f = DuDx;
    if u>276.45;
        s = -1e4*60*0.01; \[W/(m^3)\]
    else
        s = 0;
    end

% -------------------------------------------------------------------

function u0 = pdeTic(x)
    u0 = 276;

% -------------------------------------------------------------------

function [pl,ql,pr,qr] = pdeTbc(xl,ul,xr,ur,t)
    if ul < 288;
        pl = 100.0; \%heat flux [W/m]
        ql = 2*3.16*0.005;
    else
        pl = 0;
        ql = 0;
    end
    pr = ur-275.8;
    qr = 0;
```

% -------------------------------------------------------------------