Natural Gas production and CO$_2$ Sequestration in a
Class 2 Hydrate Accumulation: A Numerical Simulation
Study

24/09/2010 R.H. Huneker
<table>
<thead>
<tr>
<th>Title</th>
<th>Natural Gas Production and CO₂ Sequestration in a Class 2 Hydrate Accumulation: A Numerical Simulation Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>R.H Huneker</td>
</tr>
<tr>
<td>Date</td>
<td>September 2010</td>
</tr>
<tr>
<td>Professor(s)</td>
<td>Prof. dr. P.L.J. Zitha</td>
</tr>
<tr>
<td>Supervisor(s)</td>
<td>Dr. E.S.J. Rudolph</td>
</tr>
<tr>
<td>TA Report number</td>
<td>AES/PE/10-31</td>
</tr>
</tbody>
</table>
| Postal Address | Section for Petroleum Engineering  
Department of Applied Earth Sciences  
Delft University of Technology  
P.O. Box 5028  
The Netherlands |
| Telephone | (31) 15 2781328 (secretary) |
| Telefax | (31) 15 2781189 |
Abstract

Large amounts of natural gas hydrates have been found in sub-oceanic deposits and beneath permafrost regions. It has the potential to become a major hydrocarbon resource in the near future. Research is needed to evaluate the production possibilities of this new resource. CH₄ hydrate dissociation and production is an endothermic process and a production challenge is the reservoir temperature reduction. CO₂ is thermodynamically favoured over CH₄ in the hydrate form and it has been suggested to use CO₂ to prevent cooling by replacement of CH₄ hydrates with CO₂ hydrates. This technique has three advantages: sequestration of CO₂, increased CH₄ production and maintaining formation stability.

The effect of CO₂ injection on the CH₄ production from a hydrate reservoir has been investigated by numerical simulations. A sensitivity analysis on the CH₄ production has been performed by varying the injection pressure, temperature, reservoir properties, hydrate blockage models, intrinsic kinetic rates for CO₂ hydrate formation and numerical parameters. The research has been performed by running numerical simulations using the kinetic simulator STARS from CMG. A 3D homogeneous class 2 hydrate reservoir was constructed with a production well completed in the hydrate zone and an injection well completed in the free water zone, injecting liquid CO₂ in the free water zone below the CH₄ hydrate zone. The injection and production well pressure were regulated to create CO₂ hydrate forming and CH₄ hydrate dissociation conditions in the reservoir.

The simulation results have shown that when CO₂ is injected, the cumulative CH₄ production can increase with 50-60 %, while storing significant amounts of CO₂ simultaneously. 2 % of the injected CO₂ was produced at the production well. CO₂ hydrates were formed directly under the CH₄ hydrates, supplying the dissociating CH₄ hydrates with a low grade heat source. No upward moving front of CO₂ was observed. It is concluded that CO₂ injection only increases CH₄ production when the temperature of the reservoir is too low to support further hydrate dissociation. The highest recovery rates are achieved with low injection pressures. Injection of CO₂ in the gas phase is favoured and the intrinsic kinetic formation rate for CO₂ hydrates is a major influence on the CH₄ production. It is concluded that CO₂ injection in a Class 2 hydrate reservoir could increase the CH₄ production under certain conditions.
# Table of Contents

Abstract ....................................................................................................................................... 3  
1 Introduction ........................................................................................................................ 7  
   1.1 What are Gas Hydrates? .............................................................................................. 7  
   1.2 Production Techniques.............................................................................................. 10  
   1.3 Objectives .................................................................................................................. 11  
2 Hydrate Behaviour ........................................................................................................... 13  
   2.1 Phase Diagrams ......................................................................................................... 13  
   2.2 Hydrate Saturation and Permeability Effects ............................................................ 17  
   2.3 Reaction Kinetics ....................................................................................................... 19  
3 Simulator and Model ....................................................................................................... 22  
   3.1 Introduction ............................................................................................................... 22  
   3.2 Model Properties ....................................................................................................... 22  
   3.3 Component Properties .............................................................................................. 25  
   3.4 Relative Permeability .............................................................................................. 26  
   3.5 Implementation of Reaction Kinetics ........................................................................ 29  
   3.6 Model Modifications ................................................................................................. 30  
   3.7 Operational Values and Parameters ......................................................................... 31  
4 Results .............................................................................................................................. 33  
   4.1 Base Case ................................................................................................................... 33  
   4.2 Case 1 - CH₄ Production in Combination with CO₂ Injection .................................... 36  
   4.3 Influence of Numerical Parameters ........................................................................ 42  
   4.4 Influence of Reaction Kinetics ................................................................................... 46  
   4.5 Influence of Injection Pressure ................................................................................. 53  
   4.6 Influence of Injection Temperature .......................................................................... 56  
   4.7 Influence of Permeability ......................................................................................... 58  
   4.8 Influence of Hydrate Blockage ................................................................................ 64  
   4.9 Influence of Porosity ................................................................................................. 69  
   4.10 Influence of Well Spacing ...................................................................................... 73  
5 General Discussion ........................................................................................................... 75  
   5.1 Simulations ................................................................................................................ 75  
   5.2 Method and feasibility .............................................................................................. 76  
   5.3 Model and Numerical Stability .................................................................................. 79  
6 Conclusion ........................................................................................................................ 81  
   6.1 Reservoir Behaviour without Injection ................................................................. 81  
   6.2 Reservoir Behaviour with CO₂ Injection ............................................................... 81  
7 Recommendations ........................................................................................................... 83  
8 Acknowledgements .......................................................................................................... 84  
9 References ....................................................................................................................... 85  
Appendix .................................................................................................................................. 88
1 Introduction

Natural gas hydrates can form a significant new hydrocarbon resource in the years ahead and has the potential to triple the world known natural gas resources. Production from this resource is however still in its infancy, and more research is needed on production methods. This report evaluates by means of numerical simulation the use of CO$_2$ to increase production from a CH$_4$ hydrate deposit.

1.1 What are Gas Hydrates?

Gas hydrates are crystalline solids, composed of multiple water molecules with a captured gas molecule, such as CH$_4$ or CO$_2$ and can form under high pressure and low temperatures. Gas hydrates have the appearance of ice and require heat to melt and release heat during formation. When gas hydrate forms, gas molecules are trapped within the water structure. The presence of the gas molecule stabilises the crystal, explaining the presence of these crystals above the normal freezing temperature. The size of the gas (or guest) molecule is therefore determining the structure of the gas hydrates.

Gas hydrates were first documented in 1810 by Sir Humphrey Davy, although Joseph Priestly was probably the first who encountered gas hydrates in 1778. He observed that vitriolic air (SO$_2$) causes water to freeze and re-freeze, while HCl and SiF$_4$ do not. During the following century, the knowledge about gas hydrates was expanded, ranging from adaptations of the hydrate number to the equilibrium conditions for several gases. Until 1934, gas hydrates were considered a purely scientific phenomenon. Hammerschidt discovered that natural gas hydrates were blocking gas transmission lines at temperatures above the freezing point. This discovery led to the regulation of the water content in pipelines. Gas hydrate research was mainly motivated by production and processing problems in colder regions, such as Alaska, Siberia, the North Sea and in deep ocean drilling.$^1$

In the 1960’s, the U.S.S.R. became interested in gas hydrates as a potential energy source. The Soviets discovered in 1967 the first major hydrate deposit in the Messoyakha field in Siberia.$^1$ Production from the free gas zone below the gas hydrate deposit was sustained longer than anticipated, mainly because of dissociation of the overlying gas hydrates. The Messoyakha field is still producing. In 1998, a production test was performed on a well in the gas hydrate Mallik field in Canada. Since then, research programs have started up in Japan, United States and India to investigate the feasibility of production from gas hydrate deposits.$^1$
Gas hydrates are located in cold environments; beneath the sea in the outer continental margins, in permafrost regions and on the oceanic floor. This report focuses on the subsurface hydrate deposits only. Figure 1.1 gives an overview of some of the locations where gas hydrates have been found or inferred from seismic. Figure 1.2 shows two diagrams of reservoir conditions. Both situations have a hydrate window, in which natural gas hydrates are stable. The depth at which gas hydrates are found is governed by reservoir conditions, water depth or the extent of the surface permafrost, but is usually ranging from 130 to 2000 m.

Natural gas hydrate accumulations are formed as seeping gas enters the hydrate stability zone. Most gas hydrates found in the earth consists mainly of methane, together with small amounts of ethane, carbon dioxide and hydrogen sulfide. Estimates on the total amount of natural gas hydrates are highly speculative and very variable. Knowledge on locations, depth, recoverability and saturations is low. Recent estimates obtained by applications of different methods are however converging on very large amounts of natural gas reserves, captured in hydrate form. Commonly, the amount of gas hydrates in the outer continental shelf is estimated to be two orders of magnitude larger than in the permafrost region. According to Kvenvolden, 1988, a total of $1.8 \times 10^{16}$ sm³ of methane is captured in hydrates, which is two orders of magnitude larger than the total amount of recoverable conventional natural gas. Even only a small percentage of recoverable gas hydrates could lead to a significant increase in recoverable fossil fuels reserves. Figure 1.3 shows the resources from gas hydrates compared to resources from other fossil fuels.

![Figure 1.1 Known and inferred locations of gas hydrates in either (○) outer continental margins and (■) permafrost regions. Locations numbers are in Appendix A.1.](image-url)
Figure 1.2 Depth-temperature zones and methane hydrate stability zones. (a) Permafrost Region; the top of the hydrate window is determined by the permafrost gradient. The base of the hydrate window is determined by the geothermal gradient. (b) Outer Continental Margin. In the direct subsurface below the sea floor, hydrates are stable until the temperature exceeds the hydrate phase boundary.

Figure 1.3 Size of organic carbon reservoirs, in Gigatons. The total amount of natural gas hydrates exceeds the recoverable and nonrecoverable fossil fuels by a factor two. This amount also includes the non-recoverable gas hydrates.
Natural hydrate accumulations can be divided into 4 classes. Each class has different characteristics and requires different production strategies.

Class 1 - Hydrate bearing layer above a free-gas zone. The lower hydrate stability boundary occurs at the free gas gas hydrate contact. The Messoyakha field in Siberia is an example of a Class 1 accumulation.

Class 2 - Hydrate bearing zone overlying a water bearing zone.

Class 3 - Hydrate bearing zone occupying the entire permeable formation.

Class 4 - Hydrate bearing zone with dispersed and low saturations, without confining overburden and underburden.

This thesis assumes a so-called Class 2 hydrate accumulation.

1.2 Production Techniques

In Figure 1.4, a simplified $H_2O + CH_4$ phase diagram is shown. For high pressures and low temperatures one finds hydrates; for low pressures and high temperatures one observes a liquid and a gas phase. The line depicts the phase equilibrium curve describing the coexistence of the hydrate, liquid and gas phase. Such a phase diagram helps to decide on the appropriate production method.

Production from gas hydrates is achieved by adjusting the pressure and temperature such that conditions are outside the hydrate stability zone. Production through depressurization is lowering the pressure isothermally until the hydrates are not stable, while hot water injection is increasing the temperature. By injecting an inhibitor, the hydrate equilibrium line is shifted so that gas hydrates are not stable at initial reservoir pressure and temperature anymore; i.e. in Figure 1.4, the stability line would be shifted upwards.

So far, only a few hydrate test wells have been drilled and the observed flow rates were not high enough to make development currently economically feasible. The main problem of gas production from gas hydrates is the large amount of heat required to dissociate the hydrates and the large volumes of coproduced water. The heat can either be withdrawn from the reservoir rock by slowly reducing overall temperature and dissociation or the heat can be supplied by hot water injection. Additionally, the permeability in the gas hydrate zone is too low to allow large production rates. This is a problem, but technologies exist to solve this. Production could be increased by drilling deviated or horizontal wells.

In Figure 1.4, point 1 corresponds to the initial temperature and pressure in a hydrate. When production starts through depressurization, the hydrates become unstable and start to dissociate (Point 2). Dissociating hydrates requires heat, and if the temperature decline is large, the equilibrium line might be reached, so that the dissociation stops (Point 3). Only further depressurization or a temperature increase can resume hydrate dissociation. Depressurization is usually constrained by operating limits, such as bottom hole pressure (BHP) and tubing head pressure (THP).
1.3 Objectives

The current view on global warming has lead to the initiative to reduce emissions of greenhouse gasses such as CO₂. One of the options for CO₂ reduction in the atmosphere is CO₂ sequestration in the subsurface, e.g. in depleted reservoirs or aquifers. In this work, it is investigated if CO₂ can be sequestered in the gas hydrate form, preferably with CH₄ production from a CH₄ gas hydrate bearing layer. Ohgaki et al, 1996, suggested using CO₂ to improve CH₄ gas hydrate recovery. From a thermodynamic point of view, the CH₄ hydrates could be replaced by CO₂ hydrates because the CO₂ hydrate HLV equilibrium line is found at lower pressures for T<10.4 °C. Two methods can be used: direct CH₄-CO₂ exchange in the hydrates, leaving the primary hydrate crystals intact. The other methods suggest forming new, secondary hydrates to form a low grade heat source for primary hydrate dissociation. The combined CH₄ hydrate production and CO₂ sequestration by gas hydrate formation possibly offers three additional benefits over conventional CH₄ hydrate production: storage of CO₂, increased CH₄ production and maintaining mechanical stability of the formation.\(^5\)
The objective of this MSc thesis is to simulate a Class 2 CH₄ hydrate reservoir with CMG STARS, capable of simulating both CH₄- and CO₂ hydrates. The feasibility of injecting CO₂ in the water bearing layer below a producing CH₄ gas hydrate layer is investigated, with the intent to increase CH₄ production. Depending on the injection conditions, the CO₂ is injected in either the liquid or the gas phase. CO₂ hydrates should form under the CH₄ hydrate layer and form secondary hydrates, providing a low grade heat source for the dissociating CH₄ hydrates through heat conduction. This concept is shown in Figure 1.5, where CO₂ hydrates are formed in the free water zone of a class 2 hydrate accumulation. The reaction of the system, the effect on the CH₄ production and the influence of several parameters on the production and injection rate will be evaluated. Parameters which will be investigated are permeability, porosity, $k_v/k_h$ ratio, CO₂ formation kinetics, grid block size, injection temperature and pressure, gas hydrate blockage and numerical parameters.

STARS has previously been used by *Uddin et al., 2006*,⁶ to simulate production and injection of CH₄ and CO₂ into a hydrate bearing layer, however the CO₂ was modelled only in the gas phase and the use of CO₂ to assist the dissociation of CH₄ hydrate has not been investigated using STARS.

![Class 2 Hydrate Reservoir with secondary hydrate formation](image)

*Figure 1.5 Class 2 hydrate reservoir with secondary hydrate formation in the free water zone to increase the temperature in the primary hydrate zone.*
2 Hydrate Behaviour

2.1 Phase Diagrams

Gas hydrates are composed of water and gas molecules, arranged in a specific manner. The type of gas molecule determines the thermodynamic behaviour of the gas hydrate. One of the causes is the size of the gas molecule trapped in the crystal, giving the crystal more or less stability. A pentagonal dodecahedron ($5^{12}$) structure (a) in Figure 2.1 has a cavity which is almost spherical; with a radius of 3.95 Å in Structure I hydrates. CH$_4$, with a size of 4.36 Å, can occupy this type of cavity and stabilizes the crystal. The tetrakaidecahedron ($5^{12} 6^8$) structure (b) has a cavity with an average radius of 4.33 Å and can support molecules smaller than 6 Å in diameter, such as CO$_2$ (5.12 Å).

![Figure 2.1 Two gas clathrate hydrates crystals: (a) pentagonal dodecahedron ($5^{12}$), (b) tetrakaidecahedron ($5^{12} 6^8$).]

A structure I gas hydrate can form by linking five $5^{12}$ structures and two $5^{12} 6^8$ structures. More types of hydrate structures can form, depending on the size of the guest molecule, but CH$_4$ and CO$_2$ only form Structure I gas hydrates. Figure 2.2 shows an image of a Structure I gas hydrate.

![Figure 2.2 Five pentagonal dodecahedron ($5^{12}$) crystals together with two tetrakaidecahedron ($5^{12} 6^8$) crystals can form a Structure I hydrates.]

Both CH$_4$ and CO$_2$ can occupy any cavity in either the $5^{12}$ or the $5^{12} 6^8$ structure and have an ideal water/guest ratio of 5 ¾. The size of CO$_2$ is 5.12 Å, which is the upper size limit for occupying the small cavity. Therefore, some of the smaller cavities will remain empty in a CO$_2$ hydrate. The ideal water/guest ratio, also known as the hydration number, is almost never achieved. Experimental determination of the hydrate number is difficult and a wide range exists in literature. For CO$_2$ hydrates, 7.3 H$_2$O molecules per CO$_2$ molecule is suggested. For CH$_4$, the hydration number is six H$_2$O molecules for every CH$_4$ molecule. 1 m$^3$ of gas hydrate can be converted into 149-170 m$^3$ of gas at surface conditions, depending on the guest molecule.
The formation of a CH₄ hydrate is an exothermic process, releasing 5.186 KJ/mole of heat. All hydrates have a stability region, bounded by an equilibrium line (see also Figure 1.4). For pressures above the equilibrium line, the hydrate is stable and does not dissociate. When CO₂ is combined with water, CO₂ hydrates form in the same manner as CH₄ hydrates, however the equilibrium conditions are different. The formation of a CO₂ hydrate from CO₂(g) and H₂O is exothermic with a reaction enthalpy of 5.991 KJ/mole. Figure 2.3 shows the phase diagram for the H₂O + CO₂ and H₂O + CH₄ system with some experimental data taken from literature.\(^{11, 12, 13, 14, 15, 16, 17, 18}\) The difference in the phase behaviour of these two systems is due to the different phase behaviour of the pure components CO₂ and CH₄. The critical point of methane is found at lower temperatures and pressures than the freezing point of pure water while the critical point of pure CO₂ is found at a higher temperature and pressure than the freezing point of pure water.

The CO₂ + H₂O system has an upper quadruple point at 283.2 K and 4.4 MPa. At temperatures and pressures higher than the quadruple point conditions, the 3-phase equilibrium line changes from HLV to HL CO₂ LW, the gradient of the curve increases and crosses the CH₄-Hydrate equilibrium line at a temperature of 283.64 K and a pressure of 7.54 MPa. Above this temperature and pressure, CO₂ hydrates are less stable than CH₄ hydrates. The three-phase equilibrium curves can be described by empirical equations (see Table 2.1). These equations are derived from the so-called distribution or equilibrium coefficients, \(K_i\), which is derived from the equilibrium description by equalizing the fugacity of the coexisting phases (see equation(1)). In this study, \(P_e\) is the equilibrium pressure of the HLV or HL CO₂ LW equilibrium curve at the given reservoir temperature, while \(P_g\) is the pressure of the reservoir. This K-value is used for the description of hydrate equilibrium in the kinetic equations for gas hydrate formation and dissociation.

\[
\frac{P_e}{P_g} \times \frac{x_{i, H}}{y_i} = K_{i, \text{Hydrate}}^{\text{Equilibrium}}
\]  \(\text{Equation (1)}\)
Figure 2.3 phase equilibrium curve of CO₂-H₂O and CH₄-H₂O system Red crosses indicate experimental data.

Equilibrium lines can be described by the empirical equations given in Table 2.1.

<table>
<thead>
<tr>
<th>Line</th>
<th>Equation</th>
<th>Source:</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>A – B (-1.5 to +9 °C)</td>
<td>( \ln(P(kPa)) = -58100.96 + 8185.48 \cdot \ln(T + 273.15) + \frac{4430531.757}{T + 273.15} - \frac{3000893013}{(T + 273.15)^2} )</td>
<td>(Chen, 1972)⁹</td>
<td>(2)</td>
</tr>
<tr>
<td>A – B (+9 to +10 °C)</td>
<td>( \ln(P(kPa)) = 54.7181 - \frac{13114.75}{T(C) + 273.15} )</td>
<td>(Chen, 1972)⁹</td>
<td>(3)</td>
</tr>
<tr>
<td>A – D</td>
<td>( \ln(P(kPa)) = 15.3593 - \frac{1971.0352}{T(C) + 273.15} )</td>
<td>(Chen, 1972)⁹</td>
<td>(4)</td>
</tr>
<tr>
<td>A – E</td>
<td>( \ln(P(kPa)) = 13.37496 \cdot \frac{-19.9056}{T(C) - 6.007121} )</td>
<td>Based on experimental data¹⁵</td>
<td>(5)</td>
</tr>
<tr>
<td>B – C</td>
<td>( \ln(P(kPa)) = 18.1140 - \frac{3036.8980}{T(C) + 273.15} )</td>
<td>(Larson, 1955)¹⁶</td>
<td>(6)</td>
</tr>
<tr>
<td>F - G</td>
<td>( \ln(P(kPa)) = -2.373 - \frac{1170.96}{T(C) - 114.083} )</td>
<td>Based on experimental data¹¹, ¹², ¹³, ¹⁴</td>
<td>(7)</td>
</tr>
</tbody>
</table>

Table 2.1 Empirical equations describing the HLV and HL CO₂Lw equilibrium lines in Figure 2.3.
Mixed CH₄ – CO₂ - Hydrates

In CH₄ + CO₂ + H₂O systems, methane is also incorporated into gas hydrate even though the conditions are such that for the CH₄ + H₂O system no gas hydrate would form. This means that in the cavities of the formed gas hydrates both CH₄ and CO₂ are incorporated. In Figure 2.4 it is shown how it is modelled that the HLV equilibrium line shifts with increasing CH₄ content in the CH₄ + CO₂ + H₂O systems. It has been created with the Herriot-Watt Hydrate and Colorado School of Mines Hydrate equilibrium software packages HWHYD and CSMHYD. Unfortunately, no experimental data is published in the liquid CO₂ region and the chart has not been experimentally confirmed in the liquid region of CO₂. Even though CH₄ is also incorporated into the gas hydrates at conditions lower than the equilibrium curve of the system CH₄-H₂O, the incorporation of CO₂ is still favoured over CH₄. For CH₄ + CO₂ gas mixtures of at least 40 mol% CO₂, more than 90 % of the hydrates are CO₂ hydrates.

Unfortunately, STARS is not able to model this type of composition dependant equilibria. It is therefore not incorporated into the model.

![Figure 2.4 Phase equilibrium of binary systems water + CO₂, water + CH₄ and for the ternary system CH₄+CO₂ + water. The dashed lines give the HLV equilibrium curves with increasing CH₄ content; the increments are 0.1 mole fractions. The graphs were produced with the hydrate equilibrium software package HWHYD and CSMHYD.](image)

---

Natural Gas Production and CO₂ Sequestration in a Class 2 Hydrate Accumulation

16
2.2 Hydrate Saturation and Permeability Effects

Hydrate formation and dissociation leads to a change in effective permeability. Hydrates either block pore throats or occupy the pore space decreasing the permeability significantly. Equation (8) gives the relationship between the porosity, effective (fluid) porosity and the hydrate saturation.\textsuperscript{23} This relationship is the basis for empirical correlations relating the fluid porosity to the hydrate saturation. The porosity is then coupled by a Carman-Kozeny-kind relation to the permeability (equation (9) through (12)).

\begin{equation}
1 - S_h = \frac{V_f}{V_v} = \frac{V_w + V_g}{V_s + V_w + V_g} = \frac{\phi_f}{\phi_v}
\end{equation}

Equation (8) describes how with increasing hydrate saturation the effective porosity declines. There is hardly any experimental data available which would allow a derivation of the exact relationship between the porosity and the hydrate saturation. According to literature,\textsuperscript{24} hydrate formation in porous media is either within the capillary centre of the pores with a small film of water persisting on the grain surfaces or on the grain surfaces. The first is described by the Kozeny Capillary Centre formula, the latter by the Kozeny Grain Coating formula (see Table 2.2).

Modifications of these correlations exist, i.e., the modification as suggested by Masuda et al., \textit{1997}\textsuperscript{25}, which assumes n=3 in the Kozeny Grain Coating model or by Uddin et al., \textit{2006},\textsuperscript{6} which uses n=10. In Figure 2.5, the permeability ratio (permeability in the presence of gas hydrates over permeability without gas hydrates) as function of the hydrate saturation for the correlations given in Table 2.2 is shown. The graph shows that Uddin et al., \textit{2006},\textsuperscript{6} gives the most extreme permeability reduction with a permeability of almost zero at $S_h=0.4$. In the Kozeny Grain Coating model, the hydrate saturation has much less impact; only at $S_h=0.8$ the permeability approaches zero. For the further study, it was chosen to use the Carman-Kozeny model with n=5; the changes of the permeability values are less extreme than for the \textit{Uddin et al., 2006},\textsuperscript{6} model, but more extreme than for the Kozeny Grain Coating Model.
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kozeny Capillary Centre</td>
<td>$\frac{k(S_n)}{k_0} = \frac{(1-S_n)^n}{(1 + S_n^{0.5})^2}$</td>
</tr>
<tr>
<td></td>
<td>With $n=0.7S_n + 2.3$</td>
</tr>
<tr>
<td>Kozeny Grain Coating Model</td>
<td>$\frac{k(S_n)}{k_0} = (1-S_n)^{n+1}$</td>
</tr>
<tr>
<td></td>
<td>With $n=1.5$ for $0 &lt; S_n &lt; 0.8$ and diverges for $S_n &gt; 0.8$</td>
</tr>
<tr>
<td>Masuda et al., 1997\textsuperscript{25}</td>
<td>$\frac{k(S_n)}{k_0} = (1-S_n)^3$</td>
</tr>
<tr>
<td>Carman-Kozeny Model</td>
<td>$\frac{k(S_n)}{k_0} = (1-S_n)^{n} \left( \frac{1-\phi_c}{1-\phi_e} \right)^2$</td>
</tr>
</tbody>
</table>

*Table 2.2 Several formulas of different theories about hydrate blockage.*

*Figure 2.5 Permeability ratio as function of gas hydrate saturation. Correlations are given in Table 2.2.*
2.3 Reaction Kinetics

According to Kim et al., 1987, hydrate dissociation can be described by two processes:
1) Destruction of the clathrate lattice at the hydrate surface
2) Desorption of the guest molecules.

Above processes only take place at the interface between the clathrate and the liquid phase. Therefore, the rate of dissociation is a function of the size of the hydrate surface exposed to the liquid phase. The driving force is described by the difference in fugacity of the guest component in the hydrate and in the liquid phase. The rate of hydrate dissociation is then:

\[
\frac{dch}{dt} = k_d A_s (f_e - f)
\]

\( k_d \) Dissociation rate constant (mol/(m² Pa s))
\( A_s \) Hydrate surface per volume hydrate exposed to liquid phase. (m²/m³)
\( (f_e - f) \) Guest component fugacity difference between the bulk phase (equilibrium state) and the hydrate surface. (Pa)

According to Kim et al., 1987, equation (13) can generally be used for the description of the dissociation and the formation of gas hydrates and Uddin et al., 2006, used the same approach. However, because the size of the hydrate surface exposed to the liquid phase is crucial for the description of the formation and dissociation, they introduced are more detailed description of the surface. Equation (14) describes the hydrate surface for dissociation, while equation (15) is used to describe the surface for the formation of hydrates. In Figure 2.6, the hydrate surfaces per volume hydrate as function of the hydrate saturation as described by equations (14) and (15) are shown, with the assumption that \( S_g = 0 \). From these curves it can be concluded that during hydrate formation, the maximum surface is available for hydrate growth which is mainly determined by the first term at the rhs of equation (15). This is in fact describes the size of the vapour-liquid interface on which the hydrates prefer to grow. The size of the hydrate surface decreases with the hydrate saturation. The hydrates fill up the pore space so that the vapour-liquid interface becomes smaller.

The available hydrate surface for dissociation is much smaller than for formation (see Figure 2.6). This is because it is assumed that gas hydrates occupy the pore centres. Dissociation commences thus in the pore throats, consequently the maximum hydrate surface size is closely related to the effective porosity. Because of the direct relation to the pore throat size the variation of the available hydrate surface for decomposition is only changing slightly (Figure 2.6).
\[ A_s = \phi_e^2 S_h S_w A_{si} \quad \text{(decomposition)} \]  

\[ A_s = \phi_e S_w A_{si} + \phi_e^2 S_h S_w A_{si} \quad \text{(formation)} \]

Figure 2.6 Active surface exposed to the fugacity difference for the formation and dissociation of hydrates. The graph on the right is a magnification of the dissociation surface in the left graph.

Combining equation (13) with equation (14) allows the description of the dissociation kinetics in equation (16). When equation (13) is combined with (15), the description for the formation kinetics is obtained in equation (17). The complete derivation of these equations can be found in Appendix B.

\[ \frac{dc_h}{dt} = r_{k1} e^{-\frac{E}{RT}} \left( \phi_e \rho_h S_h \right) \left( \phi_e S_w \rho_w \right) \left( y, p_g \left( 1 - \frac{1}{K} \right) \right) \]  

(16)

\[ \frac{dc_b}{dt} = r_{k2} e^{-\frac{E}{RT}} \left( \phi_e \rho_w S_w \right) \left( y, p_g \left( \frac{1}{K} - 1 \right) \right) + r_{k3} e^{-\frac{E}{RT}} \left( \phi_e \rho_h S_h \right) \left( \phi_e S_w \rho_w \right) \left( y, p_g \left( \frac{1}{K} - 1 \right) \right) \]  

(17)

With the kinetic rate constants:

\[ \frac{k_0 A_{si}}{\rho_h \rho_w} = r_{k1} \]  

(18)
The intrinsic rates $k^o_f$ and $k^o_d$ differ for different gases and hydrates structures and can be taken from literature (see Table 2.3). For example, the dissociation rate of CH$_4$ hydrates were determined from bulk phase experiments and is equal to $3.11 \times 10^{12}$ mol/(day.kPa.m$^2$).$^{27}$ For the formation of CH$_4$ hydrates, reported values$^{28}$ range from $4.75 \times 10^6$ to $5.62 \times 10^6$ mol/(day.kPa.m$^2$). The lowest value is found at a temperature of 277.15 K where the water density has a maximum. In this study the formation rate of CH$_4$ hydrates is taken to be $5.01 \times 10^6$ mol/(day.kPa.m$^2$) because the temperatures of simulations are around or above 280 K.

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$ hydrate</th>
<th>CO$_2$ hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature Range</strong></td>
<td>Intrinsic Rate</td>
<td>Temperature Range</td>
</tr>
<tr>
<td>Dissociation Rate</td>
<td>273.15 - 350 K</td>
<td>$3.11 \times 10^{12}$</td>
</tr>
<tr>
<td>Formation Rate</td>
<td>275 K and lower</td>
<td>$5.62 \times 10^6$</td>
</tr>
<tr>
<td></td>
<td>275-277 K</td>
<td>$4.75 \times 10^6$</td>
</tr>
<tr>
<td></td>
<td>277-280 K</td>
<td>$4.92 \times 10^6$</td>
</tr>
<tr>
<td></td>
<td>280 K and higher</td>
<td>$5.01 \times 10^6$</td>
</tr>
</tbody>
</table>

Table 2.3 Intrinsic Rates and Kinetic Rates for CH$_4$ hydrates and CO$_2$ Hydrates.$^{27, 28, 29, 30}$

The kinetic parameters taken from literature$^{28, 30}$ were determined in the bulk phase. According to this data, CO$_2$ hydrate formation is slower than CH$_4$ hydrate formation. However, recent experiments show that the formation of CO$_2$ hydrates$^{31, 32, 33, 34}$ is around 50 times faster than the formation of CH$_4$ hydrates. In this work we have assumed that CO$_2$ hydrate formation is 50 times faster and have used the intrinsic kinetic rate of $3.37 \times 10^7$ mol/(day.kPa.m$^2$). The derivation for this value is found in Appendix B.
3 Simulator and Model

3.1 Introduction

For the numerical simulations, the program STARS 2008.12 from CMG has been used. STARS is a thermal simulator and has been designed to process and simulate enhanced oil recovery processes such as steamflooding, combustion, water flooding, chemical/polymer injection and other thermal processes. Hydrate formation and decomposition is simulated by modifying the chemical reaction module which was originally designed to model combustion processes.

3.2 Model Properties

The reservoir geometry is described by a Cartesian grid of 20 by 20 blocks in the x and y direction and 20 in the z direction (Figure 3.1). Each grid block is 30 by 30 by 5 meters. The top of the reservoir is located at a depth of 700 m. The top 10 layers from 700 m to 750 m depth contain CH₄ hydrates with a saturation of $S_h=0.6$, a water saturation of $S_w=0.2$ and a gas saturation of $S_g=0.2$. The 10 lower layers from 750 m to 800 m depth are fully saturated with water. The total volume of the reservoir is 36 million m³ with $5.57 \times 10^8$ m³ gas originally present in the reservoir (at standard conditions) of which $8.152 \times 10^7$ m³ exist as free gas and $4.75 \times 10^8$ m³ as hydrate.

Two vertical wells are modelled; one 40 m long producer, completed in the top of the hydrate bearing layer from 700 m to 740 m depth and a 50 m long injector, completed from 750 m to 800 m depth in the free water zone. The wells are located in opposite corners of the reservoir near the edge (see Figure 3.1). For the description of the fluid and energy flow between the well and the first grid blocks Peaceman’s equations are applied. For the production well, a constant bottom hole pressure (BHP) of 3 MPa was assumed. This value was chosen such that the HLV equilibrium temperature of the CH₄ + H₂O system is 1.4 °C. In this way, ice formation during the simulations is avoided. For the injection well, injection only starts after the pressure in the near well bore area is lower than 5 MPa. The injection well is using the downstream gridblock mobility for its well index. The injection temperature is 13 °C, so that at the given pressure CO₂ is injected as a liquid.

The initial temperature gradient in the reservoir is 3.5 °C/100 m, with a temperature at the top of the reservoir of 7 °C. The initial pressure gradient is at hydrostatic pressure with the pressure at the top of the reservoir equal to 7 MPa. For the simulations it is assumed that the reservoir is homogeneous with a porosity of 0.25 and a horizontal permeability of 200 md. The vertical permeability has been set at 20 md, to simulate of the presence of small shale layers often encountered in sandstones. The effect of hydrates on the permeability is modelled by the Carman-Kozeny type of model with $n=5$ (see equation (12)).
Figure 3.1 Reservoir geometry. On the left hand side is the producer well, on the right hand side the injector well. The different colours indicate CH₄ hydrate bearing layers (brown) and the fully water saturated layers (blue)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Hydrate Zone</th>
<th>Water Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal Permeability ( k_{oh} ) (md)</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Vertical Permeability ( k_{ov} ) (md)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Porosity ( \Phi )</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Water Saturation</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>Gas Saturation</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>Hydrate Saturation</td>
<td>0.6</td>
<td>0</td>
</tr>
</tbody>
</table>

**Heat Capacity \((J/m^3-K)\)**
- Rock: \(2.120 \times 10^6\)
- Hydrate: 1600

**Thermal Conductivity \((J/m\cdot day\cdot K)\)**
- Rock: \(1.296 \times 10^5\)
- Hydrate: \(3.395 \times 10^4\)
- Water: \(5.183 \times 10^5\)
- Gas: \(5.183 \times 10^5\)

Table 3.1 Reservoir Properties.

STARS models the hydrate phase as part of the solid matrix and this solid reduces the porosity. Equation (19) gives the relationship between the saturations. It is thus possible that the combined liquid and hydrate saturation exceeds one.

\[
S_o = \frac{V_h}{V_v} = 1 - \frac{\phi_h}{\phi_v} \leq 1 \\
S_g = \frac{V_g}{V_v - V_h}, S_l = \frac{V_l}{V_v - V_h}, S_o = \frac{V_o}{V_v - V_h} \\
S_o + S_l + S_g = 1 \\
S_h + S_o + S_l + S_g \geq 1
\] (19)
A semi-analytical model is used for the heat transfer from the over- and underburden layers. Only when the temperature difference between the overburden and the adjacent block exceeds 0.1 °C, heat transfer accounted for; heat transfer with the surrounding rock in the horizontal direction is not incorporated. The temperature profile in the overburden layer as function of the time $t$ and the depth $z$ is described by the empirical equation (20). The initial temperature of the over- and underburden are the same as the initial reservoir temperatures in the adjacent gridblocks.

$$T(t,z) = \left( \theta + pz + qz^2 \right) e^{-\frac{z}{d}}$$

$$d = \sqrt{\frac{\lambda t}{2}}$$

(20)
3.3 Component Properties

For the simulations 5 components were accounted for: water, CH₄, CO₂, CH₄-hydrates and CO₂ hydrates. They exist in either gaseous, liquid (dissolved) or in the solid phase (hydrates) (Table 3.2). In general, water can be present as solid, liquid or gas. The permeability reduction due to ice formation is described in the same way as due to hydrate formation. Methane is only present as gas. Because of its low solubility of around of 0.2 mole % it was assumed that no methane is dissolved in the aqueous phase.

CO₂ is present as liquid, gas or dissolved in the aqueous phase. To allow distinguishing between the liquid aqueous phase and liquid CO₂, the liquid CO₂ is regarded as an oil phase. For the description of the distribution of CO₂ over the gas and the liquid phase, but also for the distribution of the gas or liquid phase and the liquid aqueous phase, so-called distribution factors (K-values) are used. These K-values are based on the description of phase equilibria, e.g., the equality of the chemical potential of CO₂ in the different coexisting phases, and are given in equations (21), (22), (23). The viscosities of the liquid phases are described by correlations. The viscosity of the components in the gas phase is assumed to be constant, since no suitable correlation for STARS could be found for CO₂ and CH₄. The temperature range used in the simulations is relatively small; from 1.4 °C to 18 °C, constant values for the gas viscosity can therefore be used. Values and correlations are listed in appendix E.

\[
K_{CO_2}^{G\rightarrow L} = \frac{CO_2(Gaseous)}{CO_2(Oleic)} = \frac{P_{vap,CO_2}}{P}
\]  

(21)

\[
K_{CO_2}^{L\rightarrow A} = \frac{CO_2(Aqueous)}{CO_2(Oleic)}
\]  

(22)

\[
K_{CO_2}^{G\rightarrow A} = \frac{CO_2(Gaseous)}{CO_2(Aqueous)}
\]  

(23)

<table>
<thead>
<tr>
<th>Component</th>
<th>Gas</th>
<th>Aqueous</th>
<th>Oleic</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>CH₄ hydrate</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>CO₂ hydrate</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

*Table 3.2 Components and phases used in the simulations.*
The temperature dependence of the heat capacities of the gas and liquid phases are described by correlations.\textsuperscript{23,37} A constant value of 1600 J/(m\(^3\) K) for the heat capacity of the hydrate phase is used. For the description of the heat release upon the phase transition from the vapour phase to the liquid phase, the vaporization enthalpies at 25 °C for water (44.6 KJ/mole) and for CO\(_2\) (5712 J/mole) are used. The vaporization enthalpies are not constant, but are a function of the heat capacity of the gas and liquid. The correlations and values are found in Appendix E.

The thermal conductivity of the different phases and the matrix within one grid block is described as one (mixed) conductivity by a simple linear model given in equation (24). The values of the thermal conductivity of the different phases can be found in Table 3.1.

\[
K = \phi \left[ S_w K_w + S_g K_g + S_s K_s \right] + (1 - \phi) K_r
\]  

(24)

### 3.4 Relative Permeability

For the simulations, the relative permeability to the different existing phases (water, liquid CO\(_2\), gas (CO\(_2\) or CH\(_4\))) needs to be described. In Figure 3.2, the relative permeability for the liquid phase and gas, as function of the liquid phase saturation (sum of the water and liquid CO\(_2\) saturation) is shown. For the description of the curves the empirical relations in equation (25) was used, with the input parameters given in Table 3.3.

Unfortunately, no data exists in literature to derive a realistic description of the relative permeability curve to water and to liquid CO\(_2\) as function of the water saturation. However, because in most cases of the performed simulations the injected CO\(_2\) is in liquid state, an equation needed to be derived. The behaviour of liquid CO\(_2\) is clearly different than the behaviour of an oil phase. In Figure 3.3a, the relative permeability to water and to supercritical CO\(_2\) is shown.\textsuperscript{38} Even though supercritical CO\(_2\) behaves differently than liquid CO\(_2\), the shape of the curves was taken as base for the description of the relative permeability curves to liquid CO\(_2\). Most evident difference is that for liquid CO\(_2\) an end point relative permeability was assigned (see Figure 3.3a). In Table 3.3, the input parameters for the calculation of the relative permeability curves in equation (25) are given.
Figure 3.2 Relative permeability to gas and liquid as function of liquid saturation. The liquid saturation is the sum of the liquid CO$_2$ and the water saturation.

Figure 3.3 (a) Relative Permeability to supercritical CO$_2$ and water at 350 K and 20 MPa. (b) Relative permeability curves to water and liquid CO$_2$ as used for simulations.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Connate Water Saturation</td>
<td>0.2</td>
</tr>
<tr>
<td>Critical Water Saturation</td>
<td>0.2</td>
</tr>
<tr>
<td>Irreducible Oil Saturation</td>
<td>0.05</td>
</tr>
<tr>
<td>Residual Oil Saturation</td>
<td>0.05</td>
</tr>
<tr>
<td>Connate Gas Saturation</td>
<td>0.05</td>
</tr>
<tr>
<td>$k_{rw}$ at Connate Water Saturation</td>
<td>0.8</td>
</tr>
<tr>
<td>$k_{rw}$ at Irreducible Oil Saturation</td>
<td>0.8</td>
</tr>
<tr>
<td>$k_{rg}$ at Connate Liquid Saturation</td>
<td>1</td>
</tr>
<tr>
<td>$k_{rg}$ at Connate Gas Saturation</td>
<td>0.8</td>
</tr>
<tr>
<td>Exponent $n$</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3.3 Parameters for the computation of relative permeabilities with equation (25). The subscript $o$ represents the liquid CO$_2$ phase.

\[
k_{rw} = k_{rw,ro} \left( \frac{S_w - S_{w,\text{crit}}}{1 - S_{w,\text{crit}} - S_{o,ir}} \right)^n
\]

\[
k_{ro,w} = k_{ro,cw} \left( \frac{S_o - S_{o,r}}{1 - S_{w,con} - S_{o,r}} \right)^n
\]

\[
k_{rg} = k_{rg,rg} \left( \frac{S_g - S_{w,con} - S_{w,con}}{1 - S_{g,con} - S_{o,r} - S_{w,con}} \right)^n
\]

(25)
3.5 Implementation of Reaction Kinetics

In STARS, the rate of hydrate dissociation is described by equation (26) and the rate of hydrate formation by equation (27).

\[
\frac{-dc_h}{dt} = r_k e^{-\frac{E}{RT}} \prod_{i=1}^{n_c} C_i^{r_{ki}} \left(1 - \frac{1}{K}\right)
\]

(26)

\[
\frac{dc_h}{dt} = r_k e^{-\frac{E}{RT}} \prod_{i=1}^{n_c} C_i^{r_{ki}} \left(\frac{1}{K} - 1\right)
\]

(27)

In these equations the description of the phase equilibrium, \( K \), is directly related to the description of the kinetics. The \( K \)-value originates from equation (1) with \( K > 1 \) for dissociation conditions and \( K < 1 \) for formation conditions. The concentrations of the different components are described by:

\[
C_i = \phi_e \rho_i S_i \quad (28)
\]

\[
C_g = y_i p_g \quad (29)
\]

\[
C_h = \phi_v c_h \quad (30)
\]

For the calculation of the hydrate concentration the total porosity \( \phi_v \) and the saturation of hydrates in mole per m\(^3\) of void porespace, \( c_h \), is used. Incorporating equations (28) to (30) into equations (16) and (17) gives the equations to describe the hydrate dissociation (equation (31)) and hydrate formation (equation (32)) in STARS. Table 3.4 lists the constants used in equations (31) and (32).

\[
\frac{-dc_h}{dt} = r_{k1} e^{-\frac{E}{RT}} (\phi_e \rho_w S_w) (\phi_v c_h) (y_i p_g) \left(1 - \frac{1}{K}\right)
\]

(31)

\[
\frac{dc_h}{dt} = r_{k2} e^{-\frac{E}{RT}} (\phi_e \rho_w S_w) (y_i p_g) \left(\frac{1}{K} - 1\right)
\]

\[
\frac{dc_h}{dt} = r_{k3} e^{-\frac{E}{RT}} (\phi_e \rho_w S_w) (\phi_v c_h) (y_i p_g) \left(\frac{1}{K} - 1\right)
\]

(32)

The rate of hydrate formation is determined by the mass transfer rate of CO\(_2\) or CH\(_4\) to the liquid-hydrate interface. The CH\(_4\) and CO\(_2\) are assumed to be dissolved in the water and hydrates will form at the hydrate-liquid interface. Liquid CO\(_2\) is expected to have a lower mass transfer rate than gaseous CO\(_2\). Therefore the rate of hydrate formation for liquid CO\(_2\) is lowered by a factor 100. Table 3.4 gives the hydrate formation rates \( r_{k2} \) and \( r_{k3} \) for both liquid and gaseous CO\(_2\) of hydrates.
### Table 3.4 Hydrate Physical and Kinetic Properties

<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>CH₄ hydrate</th>
<th>CO₂ hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>kg/gmole</td>
<td>0.124133</td>
<td>0.1755195</td>
</tr>
<tr>
<td>Molar Density</td>
<td>kg/m³</td>
<td>919.7</td>
<td>1112</td>
</tr>
<tr>
<td>Volumetric Density</td>
<td>gmole/m³</td>
<td>7408.99</td>
<td>6335.48</td>
</tr>
<tr>
<td>Dissociation Rate</td>
<td>gmole/(day.kPa.m³)</td>
<td>3.11·10¹²</td>
<td>6.05·10¹²</td>
</tr>
<tr>
<td>Formation Rate</td>
<td>m³/(gmole.day.kPa)</td>
<td>5.01·10⁶</td>
<td>3.37·10⁷</td>
</tr>
<tr>
<td>Rk₁ (gaseous)</td>
<td>1/(day.kPa)</td>
<td>3.39·10⁻⁷</td>
<td>2.28·10⁻⁸</td>
</tr>
<tr>
<td>Rk₂ (gaseous)</td>
<td>m³/(gmole.day.kPa)</td>
<td>4.58·10⁻³</td>
<td>3.59·10⁻⁴</td>
</tr>
<tr>
<td>Rk₃ (liquid)</td>
<td>1/(day.kPa)</td>
<td>N/A</td>
<td>2.28·10⁻⁶</td>
</tr>
<tr>
<td>Specific Area Aₙ</td>
<td>m²/m³</td>
<td>375000</td>
<td>375000</td>
</tr>
<tr>
<td>Activation Energy</td>
<td>J/gmole</td>
<td>81084.2</td>
<td>81084.2</td>
</tr>
<tr>
<td>Reaction Enthalpy (Gas)</td>
<td>J/gmole</td>
<td>51858</td>
<td>59910</td>
</tr>
<tr>
<td>Reaction Enthalpy (Liquid)</td>
<td>J/gmole</td>
<td>N/A</td>
<td>54198.36 (at 25 °C)</td>
</tr>
<tr>
<td>Hydration Number</td>
<td>-</td>
<td>6</td>
<td>7.3</td>
</tr>
</tbody>
</table>

### 3.6 Model Modifications

In the simulations from literature, the presence of a liquid phase rich in CO₂ is not accounted for. For the simulation of CO₂ sequestration in gas hydrates, it is crucial to incorporate the description of a CO₂-rich liquid phase. The temperatures and pressure occurring during sequestration might exceed the quadruple temperature and pressure (10.05 °C and 4.4 MPa) so that a different phase transition, namely from LL to HL, needs to be described. In the adjusted model, the phase transition from gaseous to liquid CO₂ is incorporated by introducing the heat of vaporization. The liquid CO₂ exists as a separate liquid phase next to the water phase. Additionally, it can be accounted for the fact that CO₂ is injected as a liquid, while CO₂ is produced as a gas.

There are hardly any literature data on permeability variation due to the presence of hydrates. Additionally, the scarce data available even contradict each other. Uddin et al, 2006 used equation (12) with n=10 to describe the change of the absolute permeability with the hydrate saturation, while Masuda et al, 2002 describe a less severe permeability reduction. In this work the permeability was described by equation (12) with n=5, which lays in between the descriptions of literature data.
3.7 Operational Values and Parameters

The main focus of this work is to evaluate the feasibility of combined CH₄ production from and CO₂ sequestration in gas hydrate bearing layers. Therefore, several simulations were performed to get a better understanding of the different processes. Where appropriate, both a simple depressurization scenario and a scenario with CO₂ injection was simulated under same conditions to allow for a direct comparison. In the following the parameters which have been varied for the different simulations are listed. A full list of all parameters and scenario names can be found in Appendix C. Except for the mentioned parameters, the simulations are equal to the base case.

**Numerical aspects**

The sensitivity of the results on the time step and the effect of the grid size around the well have been evaluated. A simulation has been run with a maximum time step of 0.05 day. The base case is using 0.3 days as maximum time step. The base case has a run time of 8 hours, while for the smaller time step the runtime is 60 hours. Another scenario was run using a refined grid around the wellbores. This scenario has a run time of 90 hours.

**Reaction Kinetics:**

The intrinsic kinetic rate for the formation of CO₂ hydrates has been changed to investigate its influence. The rate has been increased by a factor 7 and lowered by factor 20, 50 and 100. Additionally, values from literature have also been used. In one scenario it is assumed that the mass transfer rates to the liquid-hydrate interface is equal for liquid and gaseous CO₂. The rates and scenario names are given in Table 3.5.

<table>
<thead>
<tr>
<th></th>
<th>Case 4</th>
<th>Case 5</th>
<th>Case 6</th>
<th>Case 7</th>
<th>Case 8</th>
<th>Published Values</th>
<th>Case 9</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formation Rate</strong></td>
<td>gmole/(day.kPa.m²)</td>
<td>7 x faster</td>
<td>20 x slower</td>
<td>50x slower</td>
<td>100 x slower</td>
<td>Published Values</td>
<td>Equal Mass Transfer</td>
</tr>
<tr>
<td><strong>R_k2 (gaseous)</strong></td>
<td>1/(day.kPa)</td>
<td>2.51 x 10⁸</td>
<td>1.69 x 10⁸</td>
<td>6.74 x 10⁶</td>
<td>3.37 x 10⁶</td>
<td>4.55 x 10⁵</td>
<td>3.37 x 10⁷</td>
</tr>
<tr>
<td><strong>R_k3 (gaseous)</strong></td>
<td>m³/(gmole.day.kPa)</td>
<td>2.29 x 10⁵</td>
<td>1.80 x 10⁵</td>
<td>7.18 x 10³</td>
<td>3.59 x 10²</td>
<td>4.86 x 10²</td>
<td>3.59 x 10⁴</td>
</tr>
<tr>
<td><strong>R_k2 (liquid)</strong></td>
<td>1/(day.kPa)</td>
<td>1.70 x 10⁷</td>
<td>1.14 x 10⁷</td>
<td>4.56 x 10⁴</td>
<td>2.28 x 10²</td>
<td>3.08 x 10⁶</td>
<td>2.28 x 10⁸</td>
</tr>
<tr>
<td><strong>R_k3 (liquid)</strong></td>
<td>m³/(gmole.day.kPa)</td>
<td>2.29 x 10⁵</td>
<td>1.80 x 10⁵</td>
<td>7.18</td>
<td>3.59</td>
<td>4.86 x 10²</td>
<td>3.59 x 10⁴</td>
</tr>
</tbody>
</table>

*Table 3.5 CO₂ hydrate formation rates used in the simulations.*

**Injection pressure:** The BHP of the injection well has been varied with 4 MPa, 5.5 MPa, 6 MPa, 7 MPa and 8 MPa. At 4 MPa, gas was injected, since CO₂ is in the gas phase at this pressure.

**Injection Temperature:** The temperature has been varied with 8 °C, 10 °C, and 15 °C. Above 15 °C, CO₂ is in the gas phase at 5 MPa. To investigate the effect of warm water injection, water was injected at 5 MPa with the temperature variations of 13 °C, 18 °C, 25 °C and 30 °C.
**Permeability:** The absolute permeability has been varied from $k=1$ D to $k=2$ D. The ratio of the vertical and horizontal permeability, $k_v/k_h$, was changed from 0.01 to 1.

**Hydrate Blockage:** The effect of the chosen hydrate blockage model has been investigated by changing the parameter ‘$n$’ in the Carman-Kozeny type equation (12). The following values for $n$ were tested: $n=5$ (the base case) to $n=3$ (less hydrate blockage) to $n=8$ (more hydrate blockage) and to $n=10$ (severe hydrate blockage).

**Porosity:** The porosity was varied from $\phi=0.2$ to $\phi=0.3$.

**Grid Block Size:** The grid block size has been varied. Subsequently, the distance between the wells has changed. The wells of the base case are 636 meters apart with a gridblock size of 30 by 30 by 5 m.

1) Gridblock size 10 m by 10 m by 5 m, distance between the wells: 212 m.
2) Gridblock size 20 m by 20 m by 5 m, distance between the well: 424 m.
3) Gridblock size 40 m by 40 m by 5 m, distance between the well: 848 m.
4) Gridblock size 50 m by 50 m by 5 m, distance between the well: 1060 m.
4 Results

The model is validated by comparing the results with the work of Uddin et al., 2006,6 and Hong and Pooladi-Darvish, 2003.40 The results of this validation can be found in Appendix F.

4.1 Base Case

The base case serves as a reference case and the comparison of the results of the other simulations with the results of the reference case allows for estimation of the feasibility of CO₂ sequestration. Gas and water from dissociation of the gas hydrates by depressurization is produced through one production well with a BHP of 3 MPa, completed in the top 40 m of the 50 m thick hydrate bearing zone. Figure 4.1 shows the pattern of the CH₄ hydrate dissociation. The results agree well with literature data.¹, 39 Initial average temperature and pressure are 7.8 °C and 7200 kPa for the hydrate zone. Since some permeability is present in the hydrate zone, the pressure in this zone is reduced to near the BHP of 3000 kPa in 28 years. Subsequently, hydrates are dissociated in the entire reservoir. After 35 % of the CH₄ hydrates have dissociated, the temperature in all layers of the hydrate zone is at 1.4 °C and the pressure at 3000 kPa, which is on the HLV equilibrium curve (see Figure 2.3).

After these conditions have been reached, further hydrate dissociation requires to either lower the pressure further or to increase the temperature. Lowering the pressure is not possible, as this is the minimum BHP of the production well. Consequently, CH₄ hydrate dissociation is only observed near the top and the bottom of the hydrate zone due to heat influx from the surrounding strata. In Figure 4.2 the cumulative CH₄ gas production as function of time is shown. Initially the cumulative production rate is smaller because the permeability around the producer is still low due to the high gas hydrate saturation (see also Figure 2.5). When the hydrate saturation around the producer has decreased sufficiently, the production rate increases because of the increased permeability in the near well bore area. However, after around 28 years the gradient of the cumulative CH₄ production decreases again because now the conditions of the HLV equilibrium line have been reached.

In Figure 4.3 the hydrate saturation and the temperature as function of time are given for layers 8 to 10 and for layer 11 (only temperature). Layers 8 to 10 are in the initial gas hydrate bearing region while layer 11 is the top layer of the initially completely water saturated zone. The temperature in all depicted layers drops fairly uniform in all layers due to hydrate dissociation. The hydrate dissociation rate in layer 10 is however much faster than in layers 8 and 9. The drop in temperature in layer 11 gives proof that the increased hydrate dissociation rate in layer 10 is caused by the heat influx from the water bearing layers.
After 30 years of production the temperature in layer 8 and 9 has reached 1.4 °C, the HLV equilibrium temperature at the BHP of 3000 kPa. At this point, hydrate dissociation in layer 8 is stopped, as no energy for hydrate dissociation is available anymore. When all hydrates in layer 10 have dissociated after 24 years, the heat from the water bearing zone and the underburden is conducted through layer 10 to layer 9; this increases the temperature in layer 10. The conducted heat from the water bearing zone increases the dissociation rate in layer 9 immediately after all hydrates in layer 10 have dissociated. The same process is seen after 46 years, when all hydrates have dissociated in layer 9 and the rate of dissociation in layer 8 is increased.

In Figure 4.3, it can be seen that after all hydrates have dissociated in layer 10, its temperature is an average of the temperature of layers 8 and 10. As the heat supply from the water bearing zone and the underburden is not constant, but a function of time and depth (see equation (20)), the heat supply from the water bearing zone is slowly reduced as its temperature drops. This causes the temperature of layer 11 and 10 to slowly drop as hydrate dissociation continues in layer 9. Comparable behaviour is observed in the top layers of the hydrate bearing zone where heat influx from the overburden layers is enhancing the dissociation of gas hydrates.

Figure 4.1 Base case: Production, no CO₂ injection. CH₄ hydrate saturation after 0, 10, 20, 30, 40 and 50 years simulation times. Producer is located at the left hand side, the injector at the right hand side, but is not used. In appendix G, a copy of this image can be found with a more detailed scale.
Figure 4.2 Base case and case 1: Cumulative production of CH₄ and cumulative sequestrated CO₂ as a function of time. The cumulative CH₄ production is 58% higher when CO₂ is injected. At the conditions of the simulations 1.8 million tonnes of CO₂ are sequestrated in the reservoir.

Figure 4.3 Base case: CH₄ hydrate saturation and temperature as function of time within layer 8, 9, 10, and 11. Layers 8 to 10 are layers within the gas hydrate bearing zone (initially). Layer 11 is the first (top) layer in the fully water saturated region.
4.2 Case 1 - CH$_4$ Production in Combination with CO$_2$ Injection

In these simulations, gas is initially produced from the gas hydrates by depressurisation. When the pressure at the injection well has been lowered to 5 MPa, injection of liquid CO$_2$ commences (after around 10 years of production, see Figure 4.2). In Figure 4.2 the cumulative CH$_4$ production and the cumulative sequestered CO$_2$ as function of the time are given. Differently than in the base case there is no decline in the slope of the cumulative production curve if the CH$_4$ production is combined with CO$_2$ injection. Consequently, the cumulative CH$_4$ production is 58 % higher. From saturation profiles and production profiles (see Figure G.2 and G.3 in Appendix G), it can be seen that after 20 years of CO$_2$ injection (thus a total time of around 30 years), a small amount of the injected CO$_2$ is produced. However, after 30 years of injection (40 years of total simulation time), almost no CO$_2$ is produced anymore. After 50 years, 1.8 million tonnes of CO$_2$ is sequestered in the reservoir, of which 0.72 million tonnes in hydrate form. Only 2 mol% of the injected CO$_2$ was produced through the production well.

The injected liquid CO$_2$ travels upwards in the reservoir due to its smaller density than water. Only a small amount of the injected CO$_2$ gets dissolved in the aqueous phase because the mixing and the mass transfer of CO$_2$ into water is a slow process. When the temperature and pressure conditions in the layers are in the CO$_2$ hydrate stability zone, CO$_2$ hydrates start to form above the injection well (see Figure 4.8). Immediately after injection, CO$_2$ hydrate formation starts in the layers where already CH$_4$ hydrates have been dissociated. The formation of CO$_2$ hydrates release heat, so that further CH$_4$ hydrate dissociation is promoted in the gridblock itself and adjacent grid blocks. This is visible when Figure 4.1 and Figure 4.7 are compared.

After the initial CO$_2$ hydrate formation above the injection well, the liquid CO$_2$ spreads horizontally in direction of the production well, thus underneath the CH$_4$ hydrate zone (see also Figure 4.10 and Figure G.3 in appendix G). This is due to the lower effective permeability in the hydrate bearing zone. With the spread of the liquid CO$_2$, the CO$_2$ hydrates also extend towards the production well. The majority of the CO$_2$ hydrates are formed in the region where CH$_4$ hydrates have been decomposed. Thereby, the formation of CO$_2$ hydrates is promoted by the dissociation of the CH$_4$ hydrates while the formation of CO$_2$ hydrates enhances further dissociation of CH$_4$ hydrates due to the released heat. Consequently, the CH$_4$ saturation decreases faster if CO$_2$ is injected than if no CO$_2$ is injected (see Figure 4.1 and Figure 4.7).

In Figure 4.4 the temperature, pressure, CH$_4$ hydrate and CO$_2$ hydrate saturation as function of time are depicted for layer 8. Therein, it can be seen how the temperature continuously decreases due to CH$_4$ hydrate dissociation in layer 8, but also in the adjacent lower layer. The temperature stays approximately constant when CO$_2$ hydrates start to form. The heat consumed to dissociate CH$_4$ hydrates is compensated by the heat released when CO$_2$ hydrates are formed. After all CH$_4$ hydrates in layer 8 have been dissociated the temperature and the CO$_2$ hydrate saturation increase strongly. When the temperature reaches its
maximum of around 8.5 °C, it can be seen that the gradient describing the CO₂ hydrate saturation increase decreases slightly. Temperature is then lowered again and fluctuates between 7.5 and 8.2 °C.

In Figure 4.5 and Figure 4.6 the CH₄- and CO₂ hydrate saturation in layers 5 to 8 and the temperature profile in layer 8 are shown. From these graphs it becomes obvious how the temperature fluctuations observed in layer 8 are also influenced by the CH₄ hydrate dissociation in the upper layers. The temperature decrease is related to a strong decrease in CH₄ hydrate saturation in layer 7. An increase in the temperature is observed when in all CH₄ hydrates in layer 7 have been decomposed. It is interesting to note that CO₂ hydrates start to form in the lowest layer first. The hydrate saturation after 50 years is around 0.8. In the layers 5 to 7 the CO₂ hydrate formation is less and after 50 years the CO₂ hydrate saturation reaches values below 0.2. CO₂ hydrate growth reduces the effective permeability and blocks the upward flow of CO₂. This can be also seen in the distribution of liquid CO₂ in the reservoir after 50 years (see Figure 4.10). The small amount of CO₂ hydrate growth in the layers 5-7 does assist in the dissociation of CH₄ hydrates, as observed in Figure 4.6. In Figure 4.7, the change of the CH₄ hydrate saturation until 50 years of simulation is seen. When compared to the base case, the CH₄ hydrate saturation in the reservoir after 50 years is much lower when CO₂ is injected.

Small amounts of CO₂ hydrates are also formed in the free water zone as the liquid CO₂ displaces the water towards the production well. The initial average temperature in this zone is 9.45 °C, while the injected CO₂ has a temperature of 13 °C. No CO₂ hydrates will form above 10.1 °C, therefore the CO₂ hydrate saturation in the free water zone remains very low and does not exceed \( S_h = 0.05 \).

When CO₂ is injected, the amount of water produced increases significantly by a factor 3.8, as shown in Figure 4.9. This is caused by displacement of the water by liquid CO₂ in the free water zone (see Figure 4.10). Additionally, the water saturation is very low in region where CO₂ hydrates have been formed.

It can be concluded that injection of CO₂ increases the cumulative CH₄ production with 58 % after 50 years, while significant amounts of CO₂ can be stored in hydrate form. Less than 2 mol% of the injected CO₂ is produced. A significant extra amount of water is produced when CO₂ is injected, potentially reducing the feasibility of this method.
Figure 4.4 Case 1: Hydrate saturation, pressure and temperature as a function of time in a gridblock in layer 8 in the middle of the reservoir. When the CO$_2$ hydrate saturation increases, the CH$_4$ hydrate saturation decreases until it is zero. The temperature then rises quickly and the gridblock starts heating the layer above.

Figure 4.5 Case 1: CH$_4$ hydrate saturation of layers 5 to 8 and temperature of layer 8 as function of time. Note: layer 10 is the lowest layer of the initial hydrate bearing zone, layer 1 is the top layer of the hydrate bearing zone.
Figure 4.6 Case 1: CO₂ and CH₄ hydrate saturation as function of time in layers 5 to 8.

Figure 4.7 Case 1: CH₄ hydrate saturation after 0, 10, 20, 30, 40, and 50 years simulation times. Cross sections of the reservoir between the injection (right) and production well (left). CO₂ injection starts after 10 years. The scale indicates the CH₄ hydrate saturation.
Figure 4.8 Case 1: CO₂ hydrate saturation after 0, 10, 20, 30, 40 and 50 years simulation times. Cross sections of the reservoir between the production (left) and injection well (right). CO₂ injection starts after 10 years. The scale indicates the CO₂ hydrate saturation.

Figure 4.9 Cumulative water production as function of time for base case and case 1.
Figure 4.10 Case 1: Liquid CO₂ saturation after 50 years.
4.3 Influence of Numerical Parameters

The sensitivity of the simulation results to the chosen grid block size and time step was investigated by changing the maximum time step to 0.05 days (Case 2) and by refining the gridblock size around the wellbore by dividing the 30 by 30 by 5 m well gridblock into smaller gridblocks of 6 by 6 by 1.667 m. In Figure 4.11 to 4.16, the effect of changing the time step and of refining the grid block size around the wellbores is depicted for the cumulative CH$_4$ production and the cumulative sequestrated CO$_2$. The results of the simulations from case 2 and case 3 are compared to the results of case 1 (CH$_4$ production with CO$_2$ injection).

By decreasing the maximum time step from 0.3 days in case 1 to 0.05 days in case 2 the run time of the simulation increased from 8 hours to more than 60 hours. In Figure 4.11 the cumulative CH$_4$ production as function of time is depicted for case 1, case 2 and case 3. Initially, the cumulative CH$_4$ production is equal. After CO$_2$ injection starts around 10 years, the curves diverge, indicating that the simulation is sensitive to time step changes when CO$_2$ hydrates are present. Less CH$_4$ is produced when the time step is decreased. This is due to the fact that less CO$_2$ is sequestrated when the time step is decreased (see Figure 4.17). This might be explained by the fact that for smaller step sizes more CO$_2$ hydrates are formed in the layers below the CH$_4$ hydrates (see Figure 4.12), limiting upward CO$_2$ mobility. When comparing Figure 4.13 with Figure 4.7, it can be seen that less CH$_4$ hydrates have been dissociated. The CO$_2$ hydrate saturation after 50 years for case 2 is shown in Figure 4.14. Due to the extremely longer simulation run times when decreasing the maximum timestep size this was not further investigated in this project.

![Figure 4.11 Cumulative CH$_4$ Production as function of time for the base case, case 2 (max time step of 0.05 days) and case 3 (refined grid blocks around the wells).](image-url)
Figure 4.12 CH₄ – CO₂ hydrate saturation and temperature as a function of time in a grid block in the middle of the reservoir in layer 8 for case 1 and case 2.

Figure 4.13 Case 2: CH₄ hydrate saturation after 50 years. Maximum time step is 0.05 days.

Figure 4.14 Case 2: CO₂ hydrate saturation after 50 years. Maximum time step is 0.05 days.
In case 3, the grid blocks around the two wells were refined, by dividing the grid blocks around the wells into 75 smaller evenly sized grid blocks. This increased the simulation run time from 8 hours to more than 90 hours. By refining the grid blocks around the injector and producer the hydrate formation and dissociation can be described more precisely. This is in particular of interest in the near well bore areas because in these regions the pressure drops and the temperature fluctuations are the strongest. In this way also the skin effects are reduced which can be seen by the slightly increased cumulative CH₄ production for the simulations with a refined grid block in the first 15 years (see Figure 4.11). Figure 4.15 shows that after 5 years, the 10 meters around the producer are cleared of hydrates. After 5 years, the producer in case 1 is still completely surrounded by some hydrates. However, after 15 years, the production rates of case 3 and case 1 are the same indicating that also for case 1 the producer is not surrounded by hydrates anymore.

Figure 4.15 Case 3: CH₄ hydrate saturation after 5 years. Grid around the injection and production wellbore is refined.

Figure 4.16 Case 3: CO₂ hydrate saturation after 50 years. The grid around both wellbores is refined.
A refined grid size around the injectors and producers results in an increased cumulative amount of sequestrated CO₂ (see Figure 4.17). This is most likely because the pressure changes more realistically around the well bores, because the skin around the wells is less. The lower pressure front from the production well propagates faster into the reservoir, enabling earlier CO₂ injection (see Figures G.4 and G.5 in appendix G). Figure 4.17 shows that after 50 years the total amount of CO₂ sequestrated is nearly equal for all scenarios.

![Figure 4.17 Cumulative CO₂ sequestrated as a function of time for case 1, 2 and 3.](image)

It can be concluded from the results of these simulations that numerical stability is definitely an issue. The main cause for the numerical instability is most likely the complicated phase behaviour of the CO₂ + H₂O system in the temperature and pressure region encountered during this study. The temperatures encountered in the simulations are around 10 °C, the pressure varies from 3 to around 5 MPa. In this temperature and pressure window the CO₂ + H₂O system displays its upper quadruple point. This means one needs to account for the phase changes between hydrate, CO₂ liquid phase, CO₂ gas phase and aqueous liquid phase. These phase changes are accompanied by heat release and consumption which then influence also the dissociation of CH₄ hydrates. Simulations describing solely gas production from CH₄ hydrates can be performed with a maximum time step of 0.3 days. However, for the simulation of gas production coupled to CO₂ sequestration, a maximum time step of 0.05 days might still be too large. A smaller grid size, in particular around the well bores, is advisable as in this region the real behaviour can be described better. However, care must be taken to keep the simulation runtime within a reasonable timeframe.
4.4 Influence of Reaction Kinetics

As mentioned in Chapter 2, there is no consensus in the literature on exact values of the intrinsic kinetic rate constants for the formation of CO$_2$ hydrate. In this work, the effect of changing the reaction kinetics of CO$_2$ hydrate formation on the simulation results has been investigated. For this reason, the reaction rate for CO$_2$ hydrate formation has been varied (see Table 4.1 and Table 3.4). The results of case 4 to 9 are compared to the results of case 1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formation Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 4</td>
<td>7x faster</td>
</tr>
<tr>
<td>Case 5</td>
<td>20x slower</td>
</tr>
<tr>
<td>Case 6</td>
<td>50x slower</td>
</tr>
<tr>
<td>Case 7</td>
<td>100x slower</td>
</tr>
<tr>
<td>Case 8</td>
<td>Published values</td>
</tr>
<tr>
<td>Case 9</td>
<td>Equal formation rates for gas/liquid CO$_2$</td>
</tr>
</tbody>
</table>

*Table 4.1 CO$_2$ hydrate formation rate and the scenario name.*

In Figure 4.18, the cumulative CH$_4$ production for case 1 and 4 up to 8 is shown. For the case 1, the recovery after 50 years is the highest at $4.5 \times 10^8$ m$^3$ of methane, while for case 7, the recovery is $2.5 \times 10^8$ m$^3$. As the kinetic rate of formation of CO$_2$ hydrates decreases, the maximum CO$_2$ hydrate saturation observed in the simulation also decreases, as can be seen in Figure 4.21, Figure 4.23 and Figure 4.25. As a result, the hydrate blockage effect of the CO$_2$ hydrate layer formed below the CH$_4$ hydrate layer is not as severe as in case 1. The upward mobility of the CO$_2$ is high enough to ensure CO$_2$ flow to the top of the reservoir for all slower formation rate scenarios. However, to achieve full dissociation of the CH$_4$ hydrates in a region, it needs to be replaced by at least 85 %mol of CO$_2$ hydrates. The CH$_4$ hydrate saturation is $S_h=0.45$ after the reservoir has cooled down, and the saturation for CO$_2$ hydrates has to exceed $S_h=0.40$ to supply enough heat to dissociate all CH$_4$ hydrates. In case 5, the CO$_2$ hydrate saturation at the top of the reservoir is less than 0.3, and not all CH$_4$ hydrates have dissociated, as can be seen in Figure 4.20. The CO$_2$ hydrate saturations of case 6, 7 and 8 are even lower and less CH$_4$ hydrates are dissociated (see Figure 4.18).

In case 4, with an increased kinetic formation rate, an intriguing phenomenon occurs. Shown in Figure 4.19, a reduction of the CO$_2$ hydrate saturation is observed after 26 years, although no heat source is present capable of dissociating the hydrates at such rate. When the enthalpy difference between gaseous and liquid CO$_2$ and subsequently the difference of the CO$_2$ hydrate formation enthalpies is set to zero in the simulator, the phenomenon disappears. At the pressure and temperature present in the gridblock, the CO$_2$ + H$_2$O system is near its quadruple point and the pressure and temperature conditions are exactly on the HLV equilibrium curve, causing the CO$_2$ + H$_2$O system to switch from dissociating to formation between each timestep. The cause of this phenomenon is thus the phase switching of CO$_2$ from gas to liquid and vice versa. The increased kinetic formation rate increases this effect.
The effect of a reduced formation rate for liquid CO₂ due to the lower mass transfer rate of liquid CO₂ can be seen in Figure 4.30, where the cumulative CH₄ production of case 1 and 9 are compared. In case 9, the formation rate of gaseous and liquid CO₂ are equal and a thicker CO₂ hydrate layer forms below the CH₄ hydrates. This results in less upward mobility for the CO₂ and less CO₂ hydrates can be formed in the CH₄ hydrate zone. In Figure 4.29, the cumulative CH₄ production of this simulation is compared with case 1. Less CH₄ is produced after 50 years and less CO₂ is injected. The effect is not very large, but it is not negligible.

The amount of sequestered CO₂ is within 5 %mol of the base case for all scenarios and less than 5 %mol of the CO₂ is produced together with the CH₄. This indicates that the same amount of CO₂ is present in the pores of the reservoir, but the formation rate of CO₂ hydrates is too slow to form CO₂ hydrates and is thus not providing the CH₄ hydrates with heat for dissociation.

From this study on formation kinetics, it can be concluded that the effect is significant when the overall formation rate is reduced. The rate reduction for liquid CO₂ has less impact on the total amount of recovered CH₄ after 50 years, but is not negligible.

Figure 4.18 Comparison of the cumulative CH₄ production for case 1, 4-8 as a function of time.

Figure 4.18 Comparison of the cumulative CH₄ production for case 1, 4-8 as a function of time.
Figure 4.19 Case 4: Hydrate saturation, pressure and temperature as a function of time in a gridblock in the middle of the reservoir. A reduction of CO$_2$ hydrate saturation is observed after 26 years. No external heat source is nearby, capable of dissociating the hydrates at such rate.

Figure 4.20 Case 5: CH$_4$ hydrate saturation with a 20x slower formation rate scenario after 50 years.
Figure 4.21 Case 5: CO₂ hydrate Saturation with the 20 x slower formation rate scenario after 50 years.

Figure 4.22 Case 6: CH₄ hydrate saturation with the 50 x slower formation rate after 50 years.

Figure 4.23 Case 6: CO₂ hydrate Saturation with the 50 x slower formation rate scenario after 50 years.
Figure 4.24 Case 7: CH₄ hydrate saturation with the 100 x slower formation rate after 50 years.

Figure 4.25 Case 7: CO₂ hydrate saturation with a 100 x slower CO₂ hydrate formation rate after 50 years.

Figure 4.26 Case 8: CH₄ gas hydrate saturation with the literature values for CO₂ hydrate formation rate after 50 years.
Figure 4.27 Case 8: CO₂ hydrate Saturation with the literature values for CO₂ hydrate formation rate after 50 years.

Figure 4.28 Case 4: CO₂ hydrate saturation with a 7 x faster CO₂ hydrate formation rate after 50 years.
Figure 4.29 Cumulative CH$_4$ production and CO$_2$ sequestered as a function of time for case 1 and case 9 with equal formation rates for liquid and gaseous CO$_2$.

Figure 4.30 Case 9: CO$_2$ hydrate concentration after 50 years for the scenario with equal formation rates for liquid and gaseous CO$_2$. 
4.5 Influence of Injection Pressure

The BHP pressure of the injection well has been varied with 4 MPa, 5.5 MPa, 6 MPa, 7 MPa and 8 MPa to investigate the influence of the BHP. The results are compared to Case 1 which has a BHP of 5 MPa.

<table>
<thead>
<tr>
<th>Name</th>
<th>Injection BHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 10</td>
<td>4 MPa</td>
</tr>
<tr>
<td>Case 11</td>
<td>5.5 MPa</td>
</tr>
<tr>
<td>Case 12</td>
<td>6 MPa</td>
</tr>
<tr>
<td>Case 13</td>
<td>7 MPa</td>
</tr>
<tr>
<td>Case 14</td>
<td>8 MPa</td>
</tr>
</tbody>
</table>

*Table 4.2 Scenario names and injection BHP.*

It can be seen from Figure 4.31 that as the injection pressure increases, the recovery rate is lowered. This is caused by the pressure increase in the reservoir above the injection well, increasing the dissociation temperature. At pressures above 6.5 MPa, CH₄ hydrates are stable at temperatures up to 11 °C, while CO₂ hydrates are stable up to 10.4 °C. Therefore, the CO₂ hydrates cannot supply the heat required for CH₄ hydrate dissociation and the injection of CO₂ is useless in this regard. This effect is clearly seen in Figure 4.31, where for injection pressures from 5 to 6 MPa, the CH₄ production rates are very similar. For case 13 and 14 with an injection pressure of 7 to 8 MPa, the CH₄ production rate is significantly reduced and is actually lower than the production with the depressurization method in the base case.

After 45 years, case 10 with 4 MPa BHP has produced all CH₄ hydrates. At 4 MPa and 13 °C, CO₂ is in the gas phase and is injected as such into the reservoir. Gaseous CO₂ is modelled to have a 5.4 x higher mobility than liquid CO₂ and is also modelled to form CO₂ hydrates 100 x faster than liquid CO₂, due to higher mass transfer rate of gaseous CO₂ over liquid.

Injecting liquid CO₂ at different pressures does not change the amount of sequestered CO₂. Almost 1.91 million tonnes CO₂ is sequestered at all injection pressure scenarios. When gas is injected, the amount of stored CO₂ is less than 1 million tonnes. The amount of produced CO₂ is increasing with higher pressures and is very high at 7 MPa and 8 MPa. Above 7 MPa, less CO₂ is converted into hydrate form, since the temperature is not lowered by the dissociation of CH₄ hydrates.

The cumulative production for case 10 with CO₂ gas injection at 4 MPa is much higher than case 1, however less CO₂ is injected. This is caused by the higher mobility of the gas, rising up at a faster rate than liquid CO₂. As a result, 73 mol% of the injected CO₂ is converted into CO₂ hydrates for case 10. In case 1, only 40 mol% is converted into CO₂ hydrates. Another positive effect is that in case 10, much less water is produced. This supports the observation that the gaseous CO₂ rises up into the CH₄ hydrates, instead of displacing the water like the liquid CO₂ in case 1.
It can be concluded that the injection pressure should not exceed 6 MPa BHP for CO₂ injection to be successful. Increasing the BHP to 7 MPa and higher does not increase the amount of stored CO₂, but more CO₂ and less CH₄ is produced. Injecting the CO₂ as a gas at even lower pressures increases the recovery rate significantly.

![Cumulative CH₄ production as a function of time for case 1 and case 10-14. With 4 MPa in case 10, CO₂ is injected in the gas phase.](image1)

![Cumulative CO₂ sequestered as a function of time for case 1 and case 10-14.](image2)
**Figure 4.33** Case 10: CO$_2$ hydrate saturation after 50 years. The CO$_2$ is injected as a gas at 4 MPa.

**Figure 4.34** Case 12: CO$_2$ hydrate saturation after 50 years with 6 MPa BHP.

**Figure 4.35** Case 12: Pressure distribution after 50 years with 6 MPa BHP. A large pressure gradient exists between the CH$_4$ hydrate zone and the free water zone, caused by the CO$_2$ hydrate layer.
4.6 Influence of Injection Temperature

The influence of the injection temperature has been investigated by changing the temperature of the liquid CO\textsubscript{2}. An attempt was made to inject CO\textsubscript{2} in the gas phase at higher temperatures, but this was numerically unstable. Only at 15 °C, a slight increase in cumulative production was observed, but this is negligible (Figure 4.36).

To investigate the effect of thermal injection, warm water is injected with temperatures ranging from 13 °C to 30 °C, injected at 5 MPa. The cumulative CH\textsubscript{4} recovery (Figure 4.37) is less than the base case with depressurization only. Only a slight positive effect on the cumulative recovery is seen when the injection temperature is increased to 30 °C. Figure 4.38 shows that the warm water front has progressed 200 m into the reservoir, increasing the CH\textsubscript{4} hydrate dissociation rate above the injection well, however the increased reservoir pressure due to injection cause less CH\textsubscript{4} hydrates to dissociate.

![Figure 4.36 Cumulative CH\textsubscript{4} production as a function of time for case 1, 15 – 17.]

![Figure 4.37 Cumulative CH\textsubscript{4} production as a function of time for case 18-21. Only warm water was injected.]

Figure 4.38 Case 21: Temperature profile after 50 years. The hot water has warmed the reservoir around the injection well.
4.7 Influence of Permeability

The influence of permeability has been investigated by increasing the permeability of the reservoir to $k_h=1$ D and $k_h=2$ D. Four permeability ratio scenarios from $k_w/k_h = 0.01$ to $k_w/k_h = 1$ have been run to investigate the permeability ratio effect. The results from case 22 to 29 (Table 4.3) are compared to the results of the base case and case 1, which have a permeability of $k_h=200$ md and a $k_w/k_h=0.1$.

<table>
<thead>
<tr>
<th>Name</th>
<th>$k_h$</th>
<th>$k_w/k_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 22</td>
<td>1 D</td>
<td>with CO$_2$ injection</td>
</tr>
<tr>
<td>Case 23</td>
<td>1 D</td>
<td>without CO$_2$ injection</td>
</tr>
<tr>
<td>Case 24</td>
<td>2 D</td>
<td>with CO$_2$ injection</td>
</tr>
<tr>
<td>Case 25</td>
<td>2 D</td>
<td>without CO$_2$ injection</td>
</tr>
</tbody>
</table>

Table 4.3 Name of the permeability scenarios.

Increasing the permeability has a positive effect on CH$_4$ production. Without CO$_2$ injection, this positive effect is reduced after 35% of the GIIP is produced. Figure 4.39 shows that for case 23 and case 25, the cumulative CH$_4$ production is identical after 13 years. At this point, the reservoir has cooled down to hydrate equilibrium conditions. Only heat from the over- and underburden is dissociating the CH$_4$ hydrates. This shows that the permeability is the limiting production factor for the first 35% production of the GIIP. After this point, the gas production rate is not connected to the permeability.

When CO$_2$ is injected, a short drop in the gas rates is observed in Figure 4.41 for case 22 and 24. This drop in the gas rate is caused by the increasing pressure around the injection well, increasing the stability of the overlying CH$_4$ hydrates. When the CO$_2$ has reached the CH$_4$ hydrate zone, this effect disappears as the formation of CO$_2$ hydrates increases the temperature. The increase in production rate is not proportional to the permeability.

The amount of CO$_2$ stored (Figure 4.40) in the reservoir is equal for case 22 and case 24, but more than in case 1. The reason for this difference can be seen in Figure 4.42 and Figure 4.43, where the CO$_2$ hydrate is more evenly spread over the entire CH$_4$ hydrate zone. In the base case, a CO$_2$ hydrate layer is formed below the CH$_4$ hydrate zone and blocks any upward mobility of CO$_2$. In the higher permeability scenarios, the mobility is higher and the CO$_2$ does migrate to the top of the reservoir, increasing the CH$_4$ hydrate dissociation rate. For case 24, less than 12 mol% of the injected CO$_2$ is produced together with the CH$_4$ until all CH$_4$ hydrates have been produced, significantly more than the 2 mol% for the base case. Another effect seen in Figure 4.40 is that the total amount of sequestrated CO$_2$ does not
increase after all the CH₄ hydrates have been produced, even if CO₂ injection and gas production continues. This indicates that the temperature in the reservoir is too high to form any additional CO₂ hydrates and the amount of injected CO₂ is immediately produced at the production well. When all CH₄ hydrates have been produced, the released heat of formation of CO₂ hydrates cannot be used for dissociating CH₄ hydrates anymore, but is instead heating up the reservoir, until the HLV equilibrium for the CO₂ + H₂O system is reached in the entire reservoir and no additional CO₂ hydrate are formed.

Figure 4.39 Cumulative CH₄ production as a function of time for the base case, case 1 and case 22-25. After 10 years, the cumulative CH₄ production of case 23 and 25 match each other.

Figure 4.40 Cumulative CO₂ sequestrated as a function of time for case 1, case 22 and 24. After all CH₄ is produced in case 22 and 24, no additional CO₂ is sequestrated and all injected CO₂ is backproduced.
Figure 4.41 CH₄ Gas rates as a function of time for the base case, case 1 and case 22-25.

Figure 4.42 Case 22: CO₂ saturation with $k_h=1$ D after all CH₄ hydrates have produced.

Figure 4.43 Case 24: CO₂ saturation for case 24 with $k_h=2$ D after all CH₄ hydrates have produced.
The results on the four permeability ratio scenarios, named case 26 to 29, can be found in Figure 4.44, where the cumulative CH₄ production for these cases is observed. For the base case, case 27 and 29, the cumulative CH₄ production after 50 years is almost equal. Initial CH₄ production for case 26 and 27 is however low. This is probably caused by the modelling of large gridblocks around the well. The dip is not caused by extra water production from the water zone; only a slight difference in water production in the first 10 years is observed between the case 26 to 29 and the base case.

The higher vertical mobility in case 26 results in a more even spread of CO₂ hydrates in the reservoir. Figure 4.45 shows that only directly above the injection well some CH₄ hydrate is remaining. This part of the reservoir is bypassed by the CO₂ due to a saturated CO₂ hydrate layer (Figure 4.46) caused by a rapid upward movement of CO₂ immediately after injection commenced. At this point, the CH₄ hydrate saturation is too high for the CO₂ to migrate upwards and a saturated CO₂ hydrate layer is formed directly above the injection well. CO₂ then moved horizontally in the direction of the production well. The CH₄ hydrate saturation in the middle of the reservoir is lower due to more dissociation and CO₂ is able to migrate upward into the CH₄ hydrate zone.

In case 28, the vertical mobility of CO₂ is very small and the CO₂ is confined to the horizontal layers below the CH₄ hydrate. Figure 4.48 shows that the CO₂ hydrate is not contributing much to the CH₄ hydrate dissociation when compared to case 29.

It can be concluded that without injection, the permeability is the limiting production factor until 35% of the GIIP has been produced. At this point, the heat influx from the over and underburden controls the rate of hydrate dissociation. If CO₂ is injected, the production rates are maintained in a similar fashion as in case 1.

From the permeability ratio results, it can be concluded that when the vertical mobility is low, CO₂ is unable to migrate upwards and is not able to form enough CO₂ hydrates to assist in CH₄ hydrate dissociation. If the vertical mobility is high, more CO₂ hydrates are formed in the CH₄ hydrate zone and the cumulative CH₄ production is higher.
**Figure 4.44** Cumulative CH₄ production as a function of time for the base case, case 1 and case 26-29.

**Figure 4.45** Case 26: CH₄ hydrate saturation with kᵢ/kₚ=1 injection after 50 years of production. The CH₄ hydrates in the top right corner are bypassed and isolated by the CO₂ hydrates.

**Figure 4.46** Case 26: CO₂ hydrate saturation with kᵢ/kₚ=1 after 50 years of production.
Figure 4.47 Case 28: CH₄ hydrate saturation with \( k_v/k_h = 0.01 \) after 50 years of production.

Figure 4.48 Case 28: CO₂ hydrate saturation with \( k_v/k_h = 0.01 \) after 50 years of production. The low vertical permeability prevents upward CO₂ flow.
4.8 Influence of Hydrate Blockage

Hydrate saturation has a negative impact of the effective permeability. To investigate the sensitivity of the simulations, the variable ‘n’ in equation (33) is changed (Table 4.4). The effect of hydrates on the permeability ratio is shown in Figure 4.49, where n=3 has the least impact and n=10 the largest. The base case scenario is using n=5. The results of case 30 to 35 have been compared to the results from the base case and case 1.

\[
\frac{k(S_h)}{k_o} = (1 - S_h)^n \left( \frac{1 - \phi_e}{1 - \phi_i} \right)^2
\]

(33)

<table>
<thead>
<tr>
<th>Name</th>
<th>‘n’</th>
<th>(k(S_h = 0.6))</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>5</td>
<td>1.42 md</td>
<td>with CO(_2) injection</td>
</tr>
<tr>
<td>Base Case</td>
<td>5</td>
<td>1.42 md</td>
<td>without CO(_2) injection</td>
</tr>
<tr>
<td>Case 30</td>
<td>3</td>
<td>8.8 md</td>
<td>with CO(_2) injection</td>
</tr>
<tr>
<td>Case 31</td>
<td>3</td>
<td>8.8 md</td>
<td>without CO(_2) injection</td>
</tr>
<tr>
<td>Case 32</td>
<td>8</td>
<td>0.091 md</td>
<td>with CO(_2) injection</td>
</tr>
<tr>
<td>Case 33</td>
<td>8</td>
<td>0.091 md</td>
<td>without CO(_2) injection</td>
</tr>
<tr>
<td>Case 34</td>
<td>10</td>
<td>0.016 md</td>
<td>with CO(_2) injection</td>
</tr>
<tr>
<td>Case 35</td>
<td>10</td>
<td>0.016 md</td>
<td>without CO(_2) injection</td>
</tr>
</tbody>
</table>

Table 4.4 Names and variables for the hydrate blockage scenarios. The permeability gives the initial effective permeability in the hydrate zone for \(S_h = 0.6\).

Without CO\(_2\) injection, the gas production rate is initially higher for case 31 compared to the base case and case 33 due to the higher effective permeability in the hydrate zone, as seen in Figure 4.50. After 50 years, the cumulative CH\(_4\) production for the base case and case 30 is almost equal. This is caused by low reservoir temperature, which is at the HLV equilibrium temperature of 1.4 °C at 3 MPa after 35% of the GIIP has been produced. From this point on, CH\(_4\) hydrate dissociation only takes place due to heat influx from the surrounding strata and
permeability is no longer the limiting factor for production. The same effect is seen in Chapter 4.7. For case 33 and case 35, the reservoir temperature has not yet dropped to its CH₄ hydrate equilibrium temperature of 1.4 °C at 3 MPa and the reservoir temperature is not yet the limiting factor for hydrate dissociation. In case 30, when CO₂ is injected, cumulative CH₄ production is much higher when compared to case 31 and after 50 years, all CH₄ hydrates have been produced. CO₂ injection starts after 5 years, 5 years earlier than in case 1. This is caused by the rapid depressurization of the reservoir due to a higher effective permeability. Due to the higher mobility of the CO₂ in case 30, the CO₂ spreads more effectively into the CH₄ hydrate zone, as shown in Figure 4.52. The CH₄ hydrate zone is saturated with CO₂ hydrates after 50 years of production.

In case 32 and case 34, injection starts much later due to the slower pressure drop. Only a slight positive effect on the CH₄ production is observed for case 32. In both scenarios, the temperature of the reservoir has not cooled down to equilibrium temperatures. The lower effective permeability leads to a lower mobility for the CO₂ and the CO₂ is confined to the area below the CH₄ hydrates, as seen in Figure 4.53 in Figure 4.54.

In case 34, the depressurization front from the injection well moves very slowly and after 50 years, it has propagated less than 600 m into the reservoir, as can be seen in Figure 4.56. A layer of CH₄ hydrates is visible in Figure 4.55 just below the production well, which dissociates at a slower rate than the above layers. This is caused by the pressure from the water zone below, keeping the CH₄ hydrates stable. Due to the low effective permeability, the hydrates are almost an impermeable layer. In Figure 4.57, the pressure difference can be seen between three overlying gridblocks below the production well. A pressure difference of 2 – 2.5 MPa is present over 10 m.

![Figure 4.50 Cumulative CH₄ production as a function of time for the base case, case 1 and case 30-35.](image)
In case 30, more CO₂ can be injected as can be seen in Figure 4.51, but three times more CO₂ was produced than in case 1. An explanation is the higher effective permeability, reducing the blocking effect of CO₂ hydrates around the production well. However, most CO₂ was produced when almost all CH₄ was produced.

![Figure 4.51 Cumulative CO₂ sequestrated as a function of time for case 1, 30, 32 and 34.](image)

![Figure 4.52 Case 30: CO₂ hydrate saturation after 50 years with n=3.](image)
Figure 4.53 Case 32: CO$_2$ hydrate saturation after 50 years with n=8.

Figure 4.54 Case 34: CO$_2$ hydrate saturation after 50 years with n=10.

Figure 4.55 Case 34: CH$_4$ hydrate saturation after 50 years with n=10.
It can be concluded that when the hydrate blockage effect is too large, CO₂ injection is less efficient. The low permeability of the hydrates reduces the upward mobility of the CO₂, reducing the effectiveness of CO₂ injection. It is seen that CO₂ injection only increases the cumulative CH₄ production when the reservoir temperature is the limiting production factor.
4.9 Influence of Porosity

The effect of reservoir porosity on the CH₄ production has been investigated by changing the porosity, as listed in Table 4.5. Due to the nature of the equation used to describe the hydrate blockage effect (equation (33)), changing the porosity has a minor effect on the effective permeability, listed in Table 4.5. The results from case 36 to 39 have been compared to the base case and case 1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Porosity φ</th>
<th>k(Sₘ = 0.6)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>0.25</td>
<td>1.42 md</td>
<td>with CO₂ injection</td>
</tr>
<tr>
<td>Base case</td>
<td>0.25</td>
<td>1.42 md</td>
<td>without CO₂ injection</td>
</tr>
<tr>
<td>Case 36</td>
<td>0.2</td>
<td>1.55 md</td>
<td>with CO₂ injection</td>
</tr>
<tr>
<td>Case 37</td>
<td>0.2</td>
<td>1.55 md</td>
<td>without CO₂ injection</td>
</tr>
<tr>
<td>Case 38</td>
<td>0.3</td>
<td>1.30 md</td>
<td>with CO₂ injection</td>
</tr>
<tr>
<td>Case 39</td>
<td>0.3</td>
<td>1.30 md</td>
<td>without CO₂ injection</td>
</tr>
</tbody>
</table>

Table 4.5 Names and porosities with its effective permeability for several simulation scenarios.

Initial hydrate saturation is 0.6 for all scenarios and a lower porosity results in less CH₄ hydrate per m³ of reservoir rock. More reservoir rock is thus available to give of heat to dissociate less hydrates. The increased energy capacity of the reservoir results in faster dissociation rates for case 37 as shown by Figure 4.58. The effective permeability is also higher. The GIIP is however lowered by the porosity reduction. This results in initially higher production rates, shown by Figure 4.58. After 30 years of production without CO₂ injection, the cumulative CH₄ production is equal for the base case, case 37 and 39. This indicates that the faster dissociation rate for case 36 is offset by the higher cumulative production potential of the base case and case 39. This is shown in Figure 4.59 and Figure 4.61. In case 37, 38 % of the CH₄ hydrates are remaining, while for case 39, 60 % of the hydrates are remaining in the reservoir after 50 years (Table 4.6).

When CO₂ is injected in case 36 and 38, CH₄ production rates do not drop after 35% of the CH₄ is produced. After 50 years, almost 92 % of the GIIP is produced in case 36 and Figure 4.60 shows that only a small amount of CH₄ hydrates are remaining (Table 4.6). In case 38, only 63 % of the GIIP has been produced after 50 years of production, as shown in Figure 4.62. This indicates that case 38 still has production potential left. Table 4.6 shows that after 50 years, when case 36 and 38 are compared, CO₂ injection will eventually be responsible for more CH₄ production. It can therefore be said that CO₂ injection is more effective for higher porosity scenarios.
Table 4.6 GIIP and production after 50 years with and without CO₂ injection. After 50 years, a larger percentage of the GIIP is produced for case 36-37.

<table>
<thead>
<tr>
<th>Porosity φ</th>
<th>GIIP (SC m³)</th>
<th>Produced after 50 years</th>
<th>Production increase through CO₂ injection</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>With Injection</td>
<td>Without Injection</td>
</tr>
<tr>
<td>0.20</td>
<td>4.46 x 10⁸</td>
<td>92 %</td>
<td>62 %</td>
</tr>
<tr>
<td>0.25</td>
<td>5.57 x 10⁸</td>
<td>80 %</td>
<td>50 %</td>
</tr>
<tr>
<td>0.30</td>
<td>6.96 x 10⁸</td>
<td>63 %</td>
<td>40 %</td>
</tr>
</tbody>
</table>

Figure 4.58 Cumulative CH₄ production as a function of time for the base case, case 1 and case 37-40.

It can be concluded that the porosity does influence production rates with and without CO₂ injection. A lower porosity and thus less hydrates per m³ have less impact on the reservoir temperature and a larger percentage of the CH₄ hydrates can be produced by temperature reduction from the reservoir. CO₂ injection is responsible for a smaller percentage of CH₄ production in lower porosity scenarios and thus less effective. It therefore can be said that the effectiveness of CO₂ injection in terms of the percentage of increased production increases with porosity.
Figure 4.59 Case 37: CH₄ hydrate saturation after 50 years of production with $\phi=0.2$ without injection.

Figure 4.60 Case 36: CH₄ hydrate saturation after 50 years of production with $\Phi=0.2$ with injection.

Figure 4.61 Case 39: CH₄ hydrate saturation after 50 years of production with $\Phi=0.3$ without injection.
Figure 4.62 Case 38: CH₄ hydrate saturation after 50 years of production with $\Phi=0.3$ without injection.
4.10 Influence of Well Spacing

To investigate the influence of the distance between the injection and production well, four alternative scenarios have been run, in which the horizontal size of the gridblocks has been varied. Table 4.7 lists all scenarios used to investigate the influence of well spacing. The results from case 40 to 47 have been compared with the results from the base case and case 1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Reservoir Size</th>
<th>Distance between wells</th>
<th>Production After 50 years (% of GIIP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With Injection</td>
<td></td>
<td>Without Injection</td>
</tr>
<tr>
<td>Case 40</td>
<td>200 x 200 m</td>
<td>212 m</td>
<td>95 %</td>
</tr>
<tr>
<td>Case 41</td>
<td>200 x 200 m</td>
<td>212 m</td>
<td>-</td>
</tr>
<tr>
<td>Case 42</td>
<td>400 x 400 m</td>
<td>424 m</td>
<td>95 %</td>
</tr>
<tr>
<td>Case 43</td>
<td>400 x 400 m</td>
<td>424 m</td>
<td>-</td>
</tr>
<tr>
<td>Case 44</td>
<td>600 x 600 m</td>
<td>636 m</td>
<td>85 %</td>
</tr>
<tr>
<td>Base Case</td>
<td>600 x 600 m</td>
<td>636 m</td>
<td>-</td>
</tr>
<tr>
<td>Case 45</td>
<td>800 x 800 m</td>
<td>848 m</td>
<td>53 %</td>
</tr>
<tr>
<td>Case 46</td>
<td>1000 x 1000 m</td>
<td>1060 m</td>
<td>37 %</td>
</tr>
<tr>
<td>Case 47</td>
<td>1000 x 1000 m</td>
<td>1060 m</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.7 Names and recovery rates for several scenarios with varying grid sizes. The thickness of all scenarios is 100 m; 50 m thick hydrate zone and 50 m free water zone.

It can be observed from Table 4.7 and Figure 4.64 that without CO2 injection, the cumulative CH4 production after 50 years as ratio of the GIIP is lower as the reservoir size increases. A cause might be the increase in size of the wellbore gridblock, increasing the skin effect of hydrates around the wellbore. As the gridblock size increases, more time is needed to fully dissociate the hydrates around the wellbore and thus reduce the skin effect. In Figure 4.64, an increase in CH4 production rate is observed for case 46 after 28 years, while for case 44 the rate is increased after 20 years.

When CO2 is injected, it is observed in Figure 4.63 that for case 40 and 42, all of the CH4 hydrates have been produced after 50 years. As the size of the reservoir increases, the effect of CO2 injection is lowered. For case 46, CO2 injection has a negative effect on CH4 production. This is caused by the high pressure around the injection well, increasing the stability of CH4 hydrates. It is also observed that CO2 injection starts much later in case 46, CO2 injection commences after 25 years and the CO2 has therefore less time to compensate for the pressure increase. CO2 injection might have a larger impact if simulations would have continued. Only 8 % of the CO2 injected in case 40 is produced, more than the 2 % from case 1. This is primarily caused by the shorter distance between the wells.
Figure 4.63 Cumulative CH₄ production as a function of time for case 1, 40, 42, 44 and 46 with CO₂ injection. The cumulative CH₄ production has been scaled to compensate for the difference in the GIIP of the scenarios, with the base case as reference.

Figure 4.64 Cumulative CH₄ production for the base case, case 41, 43, 45 and 47 - Without CO₂ injection. The cumulative CH₄ production has been scaled to compensate for the difference in the GIIP of the scenarios, with the base case as reference.

From the simulations with different sizes and distances between the wells, it is observed that a very short distance between the injector and the producer does not seem to have a negative impact on the CH₄ recovery. When the distance between the two wells is too large, no effect is seen. The cause of this is the delayed start of injection, larger gridblocks and the larger distance between the two wells.
5 General Discussion

5.1 Simulations

In this work it was shown that CH₄ production from gas hydrate bearing layers in combination with CO₂ sequestration is feasible under certain conditions. Therefore, the pressure in the reservoir needs to be low enough for CH₄ hydrates to dissociate and high enough for CO₂ hydrates to form. The presence of an aquifer below the CH₄ hydrate bearing layer acts also as a low grade heat source and compensates partly for the heat consumption during gas hydrate dissociation and thus promotes CH₄ hydrate dissociation. The aquifer provides a conduit for the CO₂ to flow upwards towards the CH₄ hydrates, where secondary CO₂ hydrates are formed, providing heat for further CH₄ hydrate dissociation. When the upward mobility of CO₂ is high enough, CO₂ hydrates also form in the zone of the initial CH₄ gas hydrates itself. Due to the heat release originating from the CO₂ hydrate formation, CH₄ hydrate dissociation and thus also the CH₄ recovery rate improves.

Previous work⁵,⁷ has confirmed the feasibility of combined CH₄ production from natural gas hydrates and CO₂ sequestration by means of CO₂ hydrate formation. However the reservoir set up and the used simulator was different. White et al., 2009⁹ have simulated injection of CO₂ in the gas, liquid and supercritical phase into a depressurized Class 1 hydrate reservoir with STOMP-HYD.⁴¹ This simulator is capable of using both the kinetic method and the phase equilibrium method. In these simulations CO₂ was injected with various pressures in the range from 6 to 10 MPa and at different temperatures ranging from 20 to 50 °C. CO₂ was injected directly into the CH₄ gas hydrate zone, exchanging CH₄ with CO₂ in the hydrates. According to their result liquid CO₂ is formed in the reservoir at CH₄ hydrate dissociation conditions regardless of the state of the injected CO₂. This is also seen in our simulations. Liquid CO₂ should therefore always be incorporated when simulating combined CH₄ production from and CO₂ sequestration in gas hydrates.

White et al., 2009⁹ state that a higher CO₂ injection pressure of above 10 MPa leads to CO₂ hydrate formation at undesired places so that pore plugging is observed which reduces the efficiency of CH₄ production. The same was concluded from the results of this work. However, in this work the efficiency of CH₄ production already decreased at pressures around 7 MPa and higher and the efficiency reduction was significantly higher. This might be explained by the different models applied to describe the effective permeability as function of hydrate saturation and the different kind of hydrate reservoir (class 1 instead of class 2). In the simulations of this work, the pressure front from the injection well propagates fast into the CH₄ hydrate bearing zone. Due to the increased pressure, the temperature required to dissociate the CH₄ hydrates increases. Another difference between the simulations of White et al, 2009⁹ and this work, is that in this work, CO₂ is injected into the aquifer below the hydrate bearing zone. The pressure travels faster through the water saturated zone so that over a longer distance away from the injector the increase of pressure becomes visible. This has a negative effect on the production of CH₄.
Because of the simultaneous dissociation of CH\textsubscript{4} hydrates and formation of CO\textsubscript{2} hydrates, the present gas phase contains both CO\textsubscript{2} and CH\textsubscript{4}. Consequently, so-called mixed gas hydrates are formed (see also Chapter 2). These mixed gas hydrates have intermediate equilibrium lines which lay between those of the single gas + water systems (see Figure 2.3). Simulations published in the literature\textsuperscript{5} however incorporate equilibrium data for mixed hydrates. Unfortunately, CMG STARS is not capable of handling compositional dependant equilibrium lines. It is not known how sensible the results of the simulations would be if this shift is incorporated into the model.

The effect of not incorporating the shift of the equilibrium line due to changes in the gas phase composition might be low. For example, for an equimolar CO\textsubscript{2}/CH\textsubscript{4} gas mixture, the mixed gas hydrate consists for a large fraction of CO\textsubscript{2} hydrates.\textsuperscript{22} Subsequently, the fraction of CO\textsubscript{2} in the gas mixture decreases to a smaller value, e.g., to 30 mol%. At this gas mole fraction, the equilibrium line is shifted upwards towards the HLV equilibrium line of the CH\textsubscript{4} + H\textsubscript{2}O system. As the pressure is still below the equilibrium pressure, more CH\textsubscript{4} hydrates dissociate so that CH\textsubscript{4} content in the gas phase increases. At the same time the pressure is still high enough to form CO\textsubscript{2} gas hydrates so that the CO\textsubscript{2} content in the gas phase keeps decreasing, until only CH\textsubscript{4} is present in the gas phase. So, by not incorporating the shift of the HLV equilibrium line for mixed gas hydrates the amount of sequestrated CO\textsubscript{2} of dissociated CH\textsubscript{4} computed might be too high. However, incorporating the shift of the HLV curve would enhance the numerical instability of the system which might give erroneous results. It is therefore important to do experiments so that the simulation results can be verified.

\section*{5.2 Method and feasibility}

The concept of injecting CO\textsubscript{2} in a CH\textsubscript{4} gas hydrate layer has been simulated by several researchers.\textsuperscript{5, 7} Thereby, CH\textsubscript{4} is replaced by CO\textsubscript{2} in the hydrates. Even though this process is possible from a thermodynamic and kinetics aspect, it is expected that it is a very slow process with a low efficiency. In this work, it has been investigated if production of CH\textsubscript{4} from CH\textsubscript{4} hydrate bearing layers is feasible when CO\textsubscript{2} is injected into an aquifer situated below the hydrate bearing layer after some of the CH\textsubscript{4} hydrates have already been dissociated by depressurization. The injected CO\textsubscript{2} is then sequestrated in form of CO\textsubscript{2} hydrates (secondary hydrates). The heat originating from the hydrate formation supports further CH\textsubscript{4} hydrate (primary hydrates) dissociation. To make this concept feasible, sufficient pore space needs to be available for secondary hydrate formation and the distance between the primary and secondary hydrates needs to be small enough so that heat transfer is effective. In theory, all classes of hydrate deposits could qualify for the proposed concept of enhanced methane recovery from gas hydrate bearing layers through secondary CO\textsubscript{2} gas hydrate formation. A Class 1 hydrate deposit, with a depleted gas reservoir underneath the hydrate bearing zone is a prime candidate for CO\textsubscript{2} injection. As shown in Figure 5.1, a class 1 hydrate reservoir has sufficient pore space for secondary hydrate formation below the CH\textsubscript{4} hydrates. Additionally, the permeability is high enough so that CO\textsubscript{2} can be injected and can spread to make the
sequestration also efficient. The low reservoirs pressures due to the earlier gas production allow for large volumes of CO₂ to be injected directly at the start of the project. CO₂ injection is more effective in this situation, as the results of this work have shown that CO₂ injection is only feasible at low pressures and when the reservoir has cooled down to hydrate equilibrium temperature at the given pressure. This is the case in a Class 1 hydrate reservoir with a depleted gas zone.

In a Class 3 hydrate deposit, the CH₄ hydrate zone is surrounded by two impermeable layers (Figure 5.2). Permeable layers might exist below the impermeable layer and could be used for CO₂ sequestration by CO₂ hydrate formation. The CH₄ production from the hydrate bearing zone is then thermally stimulated. An advantage of this method is that higher injection pressures could be used, in particular, if pressure communication between the permeable layers is low so that the amount of captured CO₂ is higher. A disadvantage is that the heat has to be conducted through a non-permeable shale layer and the effect on the gas production form gas hydrate bearing layers by injecting CO₂ is smaller.

![Class 1 Hydrate Reservoir with secondary hydrate formation](image)

*Figure 5.1 Schematic of enhanced gas recovery from gas hydrate bearing layers with injection and sequestration of CO₂: Class 1 Hydrate deposit; hydrate bearing zone with underlying depleted gas zone.*
Figure 5.2 Schematic of enhanced gas recovery from gas hydrate bearing layers with injection and sequestration of CO$_2$: Class 3 Hydrate deposit; hydrate bearing zone with under- and overlying impermeable layer. Below underlying impermeable layer a permeable zone with sufficient pore space for CO$_2$ hydrate formation.
5.3 Model and Numerical Stability

For the simulation of hydrate formation and dissociation, two methods are commonly used: the kinetic approach or the phase equilibrium approach. In this work the kinetic approach was applied. This means that the hydrate formation is described by chemical reactions accounting for the reaction rates for dissociation (equation (34)) and formation (equation (35)). In general, the reaction rates depend on the temperature, the intrinsic kinetic rates, and the hydrate equilibrium conditions (temperature and pressure) expressed in terms of the distribution factor $K$. Additionally, for the dissociation and formation in porous medium the saturation or concentration of the different phases and the effective porosity are accounted for. An artefact of equation (34) (dissociation) is that if no water is present, $S_w=0$, the reaction rate is equal to zero. In reality, hydrates dissociate even though no water is present. The same holds if no gas is present, or $p_g=0$. Therefore, the determination and description of connate water and residual gas saturations is crucial for a realistic description of gas hydrate dissociation and formation.

\[
\frac{dc_h}{dt} = r_{k1} e^{-\frac{E}{RT}} \left( \phi_e \rho_w S_w (\phi_e c_h)(y, p_g) \right) \left( 1 - \frac{1}{K} \right) 
\]

\[
\frac{dc_h}{dt} = r_{k2} e^{-\frac{E}{RT}} \left( \phi_e \rho_w S_w (\phi_e c_h)(y, p_g) \right) \frac{1}{K} - 1 
\]

\[
+ r_{k3} e^{-\frac{E}{RT}} \left( \phi_e \rho_w S_w (\phi_e c_h)(y, p_g) \right) \frac{1}{K} - 1 
\]

In the phase equilibrium approach, hydrate formation and dissociation is solely described by the chemical equilibrium; the kinetics are not taken into account. The phase equilibrium approach is computationally more efficient because per grid block one equation less needs to be solved. Consequently, for large simulations, the phase equilibrium approach is favoured. A comparison of both approaches has shown that the performance is comparable on large time scales for depressurization and thermal stimulation; only short-term processes are handled better by the kinetic model. The kinetic model applied in the simulations for the comparison was a simplified model which does not account for the presence of different phases.

Reducing the size of the gridblocks has a negative effect on the numerical stability. In Figure 5.3, the CH$_4$ hydrate saturation distribution after 13 years resulting from a numerically unstable simulation with a refined grid and a maximum time step of 0.3 is shown. In the middle of the reservoir, the CH$_4$ hydrate saturation suddenly decreases sharply (see Figure 5.4). The hydrate dissociation is caused by the pressure drop in the grid block (see Figure 2.3). However, the high rate of the hydrate dissociation in only this grid block should cause a temperature drop of at least 10°C, which is not observed. This is an indication of numerical
instability. The occurrence of this kind of instability might be solved by decreasing the maximum time step.

Figure 5.3 CH₄ hydrate saturation of several gridblocks after 13 years of production for the base case with a refined grid. The arrow indicates a zone of low CH₄ hydrate saturation caused by a numerical instability.

Figure 5.4 CH₄ hydrate saturation, temperature and pressure as function of time in the grid block indicated in Figure 5.3.
6 Conclusion

The conclusions drawn from the results of the performed simulations are divided into two parts. First, the conclusions for the cases with no CO₂ injection and then the conclusions with CO₂ injection are given.

6.1 Reservoir Behaviour without Injection

The dissociation rate of the CH₄ gas hydrates is strongly dependent on the temperature and the pressure. The BHP of the production well determines the hydrate equilibrium temperature. Hydrate dissociation is endothermic so that the temperature needs to be high enough or the pressure low enough to compensate the cooling caused by hydrate dissociation and to ensure further dissociation. When the reservoir reaches the equilibrium temperature at the given pressure, the dissociation rate is greatly reduced because the driving force has been reduced. Only heat influx from the over and underburden layers is supplying heat to the gas hydrate bearing layer for dissociation. In the base case, the reservoir temperature has dropped to equilibrium temperature after only 35% of the GIIP has been produced. Until this point is reached, the low effective permeability is the limiting factor. After this point, the heat influx from the under and overburden is controlling the production rate.

When porosity is low, there is less space for hydrates to form, and more of the space is filled with the real rock. Because the physical properties of the rock are such that heat is transported more efficiently, more energy (heat) is available in the rock to support the CH₄ hydrate dissociation. Consequently, a larger percentage of the GIIP can be produced before the reservoir reaches equilibrium conditions.

6.2 Reservoir Behaviour with CO₂ Injection

Simulations have shown that CO₂ injection in a Class 2 hydrate accumulation does increase the cumulative CH₄ production with 58%, compared to production by only depressurization. At the same time, CO₂ can be efficiently sequestrated in the form of hydrates. Only 2 mol% of CO₂ is produced together with CH₄.

When CO₂ is injected in the free water zone in a Class 2 hydrate accumulation, it rises up into the reservoir due to the density difference with water. It forms secondary CO₂ hydrates directly below the CH₄ hydrates, where the temperature has dropped sufficiently due to CH₄ gas hydrate dissociation in the layers above. The heat released from the CO₂ hydrate formation enhances further dissociation of CH₄ gas hydrates.
From the simulations, it is observed that CO₂ injection maintains the CH₄ production rates even though the whole reservoir has cooled down to the hydrate equilibrium temperature at minimum reservoir pressure. There is no effect seen on the CH₄ production when the temperature has not yet reached equilibrium conditions. This indicates that CO₂ injection is only interesting when CH₄ gas production from gas hydrate bearing layers is hindered due to low temperatures. For low saturation, low porosity reservoirs where the heat capacity of the reservoir rock and other fluids is high enough to supply all CH₄ gas hydrates with heat from the adjacent layers for dissociation, CO₂ injection has no beneficial effect on the gas production.

To obtain an increased production due to CO₂ injection, the injection pressure has to be carefully monitored. The formation of secondary CO₂ gas hydrates and the dissociation of primary CH₄ gas hydrates is only achieved when the pressure is high enough for CO₂ hydrates to form, but low enough for CH₄ hydrates to dissociate. The injection pressure should therefore not exceed 6 MPa. The injection temperature does not influence the recovery of CH₄ hydrates significantly.

If possible, the CO₂ should be injected as gas into the reservoir. Gaseous CO₂ has higher mobility than liquid CO₂. It flows more quickly into the CH₄ gas hydrate zone; the subsequent CO₂ hydrate formation is simultaneously with the dissociating of CH₄ gas hydrates. The heat released from hydrate formation compensates for the heat consumption necessary for CH₄ hydrate dissociation. Liquid CO₂ has a lower mobility, among others because of its smaller density difference with water. As a result a thick saturated CO₂ hydrate layer is formed directly under the CH₄ hydrate zone. This provides the heat for CH₄ hydrate dissociation but also slows down the further mass transfer of CO₂ into the upper layers. The CO₂ hydrate formation from liquid CO₂ is slower than from gaseous CO₂. Even though CO₂ is injected as gas, a liquid CO₂ component will always form in the given situation. Therefore, it is very important to incorporate liquid CO₂ into the model.

The kinetic rate for CO₂ hydrate formation has a very big influence on the increase of CH₄ production. When the rate is too low, not enough CO₂ hydrates are formed to supply the necessary heat for CH₄ hydrate dissociation. If the rate is too high, a thick impermeable CO₂ hydrate layer forms under the CH₄ hydrate layer, blocking further mass transfer of CO₂ into the upper layers. A large portion of CO₂ can be sequestered when injected below a CH₄ hydrate zone. CO₂ production is limited due to CO₂ hydrate formation in the reservoir but also around the production well, effectively blocking CO₂ production.

Care must be taken when formulating the equations to be incorporated in the simulations. The temperature-pressure window in which the suggested process is run, is close to the quadruple point of the CO₂ + H₂O system. This results in instabilities of the simulations. Very small time steps might resolve this problem. However, more research needs to be done on this subject.

---

**MSc Thesis Petroleum Engineering – R. Huneker**

Natural Gas Production and CO₂ Sequestration in a Class 2 Hydrate Accumulation

82
7 Recommendations

The simulations have shown that the kinetic formation rate for CO2 hydrate has a significant impact on the feasibility of the process. The literature disagrees strongly on this subject and an attempt should be made to simulate a coreflooding experiment with STARS and compare the results to actual coreflooding experiments. In this way, the CO2 hydrate formation rate could be validated in STARS.

The relative permeability behaviour of liquid CO2 and the formation rate of liquid CO2 is not documented in the literature. Although it is only a minor influence on the cumulative production, the effect is not negligible. The formation rate for liquid and gaseous CO2 should be compared to quantify the difference.

STARS is only capable of using kinetic equations and is not able to incorporate the equilibrium line shifts for mixed CO2-CH4 hydrates. The effect of not modelling these shifts is unknown and could be investigated. The STOMP-HYD software package is capable of simulating mixed hydrates and it can simulate hydrate formation and dissociation with either the kinetic method or the less computer intensive phase equilibrium method. It is advised to use this software package for the following studies on CO2 hydrates. The STOMP-HYD package was developed by the Pacific Northwest National Laboratory in the U.S. and a licence is available for $500 for Non-American universities.

The model presented in this work has not achieved optimal numerical stability when CO2 hydrates are introduced into the reservoir. Simulation runtimes can become very large in trying to obtain numerical stability and a method other than lowering the maximum timestep could be investigated to optimise simulation runtimes. Additionally, it needs to be investigated how the grid needs to be refined to obtain realistic and accurate results.
8 Acknowledgements

This study has been performed as part of the Master of Science program in Petroleum Engineering at Delft University of Technology. The study has been part of the hydrate research group under Prof. P.L.J. Zitha. I would like to thank Susanne Rudolph, Pacelli Zitha and Yuanyuan He for their input and support during this project, as well as my fellow students for their input and advice. I especially would like to thank Susanne Rudolph for her very thorough revision of this report. Last, but not least, I would like to thank my parents for funding my study in Delft.
9 References

34. Rudolph, E.S.J., He, Y.Y., 2010. Personal Communication
36. Diamond L. and Akinfiev N., 2003 Solubility of CO2 in water from -1.5 to 100 ºC and from 0.1 to 100 MPa: Evaluation of literature data and thermodynamic modelling. Fluid Phase Equilibria 208:265-290.


41. STOMP-HYD. http://stomp.pnl.gov/index.stm

Appendix

A. Known Gas Hydrate Locations

<table>
<thead>
<tr>
<th>Designation</th>
<th>Location</th>
<th>Evidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceanic:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Pacific Ocean off Panama</td>
<td>BSR</td>
</tr>
<tr>
<td>2</td>
<td>Middle America Trench off Costa Rica</td>
<td>BSR</td>
</tr>
<tr>
<td>3</td>
<td>Middle America Trench off Nicaragua</td>
<td>BSR</td>
</tr>
<tr>
<td>4</td>
<td>Middle America Trench off Guatemala</td>
<td>BSR</td>
</tr>
<tr>
<td>5</td>
<td>Middle America Trench off Mexico</td>
<td>BSR</td>
</tr>
<tr>
<td>6</td>
<td>Bel River Basin off California</td>
<td>BSR</td>
</tr>
<tr>
<td>7</td>
<td>Eastern Aleutian Trench off Alaska</td>
<td>BSR</td>
</tr>
<tr>
<td>8</td>
<td>Beringian Margin off Alaska</td>
<td>BSR</td>
</tr>
<tr>
<td>9</td>
<td>Middle Aleutian Trench off Alaska</td>
<td>BSR</td>
</tr>
<tr>
<td>10</td>
<td>Nankai Trough off Japan</td>
<td>BSR</td>
</tr>
<tr>
<td>11</td>
<td>Timor Trough off Australia</td>
<td>gas</td>
</tr>
<tr>
<td>12</td>
<td>Hikurangi Trough off New Zealand</td>
<td>BSR</td>
</tr>
<tr>
<td>13</td>
<td>Wilkes Land Margin off Antarctica</td>
<td>BSR</td>
</tr>
<tr>
<td>14</td>
<td>Western Ross Sea off Antarctica</td>
<td>gas</td>
</tr>
<tr>
<td>15</td>
<td>Peru-Chili Trench off Peru</td>
<td>BSR</td>
</tr>
<tr>
<td>16</td>
<td>Barbados Ridge Complex off Barbados</td>
<td>BSR</td>
</tr>
<tr>
<td>17</td>
<td>Colombia Basin off Panama and Colombia</td>
<td>BSR</td>
</tr>
<tr>
<td>18</td>
<td>Western Gulf of Mexico off Mexico</td>
<td>BSR</td>
</tr>
<tr>
<td>19</td>
<td>Gulf of Mexico off southern U.S.A.</td>
<td>samples</td>
</tr>
<tr>
<td>20</td>
<td>Blake Outer Ridge off southeastern U.S.A.</td>
<td>BSR</td>
</tr>
<tr>
<td>21</td>
<td>Continental rise off eastern U.S.A.</td>
<td>BSR</td>
</tr>
<tr>
<td>22</td>
<td>Labrador Shelf off Newfoundland</td>
<td>BSR</td>
</tr>
<tr>
<td>23</td>
<td>Beaufort Sea off Alaska</td>
<td>BSR</td>
</tr>
<tr>
<td>24</td>
<td>Beaufort Sea off Canada</td>
<td>logs</td>
</tr>
<tr>
<td>25</td>
<td>Sverdrup Basin off Canada</td>
<td>logs</td>
</tr>
<tr>
<td>26</td>
<td>Continental slope off western Norway</td>
<td>BSR</td>
</tr>
<tr>
<td>27</td>
<td>Continental slope off Southwest Africa</td>
<td>slides, shaps</td>
</tr>
<tr>
<td>28</td>
<td>Makran Margin, Gulf of Oman</td>
<td>BSR</td>
</tr>
<tr>
<td>29</td>
<td>Black Sea, U.S.S.R.</td>
<td>samples</td>
</tr>
<tr>
<td>30</td>
<td>Caspian Sea, U.S.S.R.</td>
<td>samples</td>
</tr>
<tr>
<td>Continental</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>North Slope, Alaska</td>
<td>logs</td>
</tr>
<tr>
<td>B</td>
<td>Mackenzie Delta, Canada</td>
<td>logs</td>
</tr>
<tr>
<td>C</td>
<td>Arctic Islands, Canada</td>
<td>logs</td>
</tr>
<tr>
<td>D</td>
<td>Timan-Pechora Province, U.S.S.R.</td>
<td>gas</td>
</tr>
<tr>
<td>E</td>
<td>Mesoyakhta Field, U.S.S.R.</td>
<td>samples</td>
</tr>
<tr>
<td>F</td>
<td>East Siberian Craton, U.S.S.R.</td>
<td>gas</td>
</tr>
<tr>
<td>G</td>
<td>Northeast Siberia, U.S.S.R.</td>
<td>gas</td>
</tr>
<tr>
<td>H</td>
<td>Kamchatka, U.S.S.R.</td>
<td>gas</td>
</tr>
</tbody>
</table>

BSR = bottom-simulating reflector

Figure A.1 Locations of gas hydrates from Figure 1.1.
B. Kinetic Equation Derivation

According to Kim et al., 1987, hydrate dissociation can be described by two processes:

1) Destruction of the clathrate lattice at the hydrate surface
2) Desorption of the guest molecules.

Above processes only take place at the interface between the clathrate and the liquid phase. Therefore, the rate of dissociation is a function of the size of the hydrate surface exposed to the liquid phase. The driving force is described by the difference in fugacity of the guest component in the hydrate and in the liquid phase. The rate of hydrate dissociation is then:

\[ -\frac{dc_h}{dt} = k_d A_s (f_e - f) \]  

(36)

\[ \frac{dc_h}{dt} \]  
Rate of dissociation (mol/(m^3.s))

\[ k_d \]  
Dissociation rate constant (mol/(m^2 Pa s))

\[ A_s \]  
Hydrate surface per volume hydrate exposed to liquid phase. (m^2/m^3)

\[ (f_e - f) \]  
Guest component fugacity difference between the bulk phase (equilibrium state) and the hydrate surface. (Pa)

The term \( k_d \) has an Arrhenius-type temperature dependency and can be described as:

\[ k_d = k_d^0 e^{\frac{-E}{RT}} \]  

(37)

The hydrate surface per volume hydrate exposed to liquid phase for dissociation is described by equation (38) and the surface for formation is described by (39):

\[ A_s = \phi_e^2 S_w S_i A_s \]  
(dissociation)  

(38)

\[ A_s = \phi_e S_w A_s + \phi_e^2 S_i S_w A_s \]  
(formation)  

(39)

For hydrate dissociation, combining equations (36), (37) and (38) yields equation (40), which can be written as equation (41).

\[ -\frac{dc_h}{dt} = k_d^0 \phi_e^2 S_w S_i e^{\frac{-E}{RT}} (f_e - f) \]  

(40)
\[
\frac{dc_h}{dt} = k_f^o e^{\frac{-E}{RT}} (\phi_e S_{W} \rho_H) (\phi_e S_{W} \rho_W) (f_e - f) \quad (41)
\]

For hydrate formation, combining equations (36), (37) and (39) yields equation (42), which can be written as equation (43).

\[
\frac{dc_h}{dt} = k_f^o e^{\frac{-E}{RT}} (\phi_e S_{W} A_{si} + \phi_e^2 S_{W} A_{si}) (f - f_e) \quad (42)
\]

\[
\frac{dc_h}{dt} = \frac{A_w k_f^o}{\rho_W} e^{\frac{-E}{RT}} (\phi_e S_{W} \rho_W) (f - f_e) + \frac{A_w k_f^o}{\rho_H \rho_W} e^{\frac{-E}{RT}} (\phi_e S_{H} \rho_H) (\phi_e S_{W} \rho_W) (f - f_e) \quad (43)
\]

The fugacity difference \((f - f_e)\) can be converted into the partial gas pressure and the equilibrium pressure. This transforms equations (41) into equation (44) and equation (43) into equation (45).

\[
\frac{dc_h}{dt} = \frac{k_f^o A_{si}}{r_{H \rho_W}} e^{\frac{E}{RT}} (\phi_e S_{H} \rho_H) (\phi_e S_{W} \rho_W) p_e (1 - \frac{p_g}{p_e}) \quad (44)
\]

and

\[
\frac{dc_h}{dt} = \frac{A_w k_f^o}{\rho_W} e^{\frac{-E}{RT}} (\phi_e S_{W} \rho_W) p_e (\frac{p_g}{p_e} - 1) + \frac{A_w k_f^o}{\rho_H \rho_W} e^{\frac{-E}{RT}} (\phi_e S_{H} \rho_H) (\phi_e S_{W} \rho_W) p_e (\frac{p_g}{p_e} - 1) \quad (45)
\]

Raoult’s Law states that:

\[
p_e x_i = y_i p_g \quad (46)
\]

The hydrate equilibrium is modelled by equation (47):

\[
\frac{p_e x_i}{p_g y_i} \equiv K_{Equilibrium\ Hydrate} \quad (47)
\]

Combining equation (44), (46) and (47) yields equation (48):
\[-\frac{dc_h}{dt} = \frac{k_d^\circ A_{Si}}{\rho_h \rho_w} e^{-\frac{E}{RT}} \left( \phi_e S_H \rho_H \right) \left( \phi_e S_W \rho_W \right) \left( \frac{y_i}{x_i} \rho_g \right) \left( 1 - \frac{1}{K} \right) \tag{48}\]

Combining equation (45), (46) and (47) yields equation (49):

\[-\frac{dc_h}{dt} = \frac{A_w k_d^\circ}{\rho_w} e^{-\frac{E}{RT}} \left( \phi_e S_W \rho_W \right) \left( \frac{y_i}{x_i} \rho_g \right) \left( 1 - \frac{1}{K} \right) \]

\[-\frac{dc_h}{dt} = \frac{A_w k_d^\circ}{\rho_h \rho_w} e^{-\frac{E}{RT}} \left( \phi_e S_H \rho_H \right) \left( \phi_e S_W \rho_W \right) \left( \frac{y_i}{x_i} \rho_g \right) \left( 1 - \frac{1}{K} \right) \tag{49}\]

In Raoult’s law, the $x_i$ represents the mole fraction of the gas in the liquid phase, in this case the hydrate phase. The CH$_4$ mole fraction in the hydrate phase is always the same, so $x_i = 1$. This simplifies equation (48) into (50) and equation (49) into equation (51).

\[-\frac{dc_h}{dt} = \frac{k_d^\circ A_{Si}}{\rho_h \rho_w} e^{-\frac{E}{RT}} \left( \phi_e S_H \rho_H \right) \left( \phi_e S_W \rho_W \right) \left( \frac{1}{x_i} \rho_g \right) \left( 1 - \frac{1}{K} \right) \tag{50}\]

And

\[-\frac{dc_h}{dt} = \frac{A_w k_d^\circ}{\rho_w} e^{-\frac{E}{RT}} \left( \phi_e S_W \rho_W \right) \left( \frac{1}{x_i} \rho_g \right) \left( 1 - \frac{1}{K} \right) \]

\[-\frac{dc_h}{dt} = \frac{A_w k_d^\circ}{\rho_h \rho_w} e^{-\frac{E}{RT}} \left( \phi_e S_H \rho_H \right) \left( \phi_e S_W \rho_W \right) \left( \frac{1}{x_i} \rho_g \right) \left( 1 - \frac{1}{K} \right) \tag{51}\]

The 1st terms on the RHS of (50) and (51) simplifies into the kinetic rate constant in equation (52):

\[\frac{k_d^\circ A_{Si}}{\rho_h \rho_w} = r_{k1} \tag{52}\]

\[\frac{k_d^\circ A_{Si}}{\rho_w} = r_{k2}\]

\[\frac{k_d^\circ A_{Si}}{\rho_w \rho_H} = r_{k3}\]

Combining equation (50) and (52) results in equation (53) for hydrate dissociation.

\[-\frac{dc_h}{dt} = r_{k1} e^{-\frac{E}{RT}} \left( \phi_e \rho_h S_H \right) \left( \phi_e S_W \rho_W \right) \left( y_i \rho_g \right) \left( 1 - \frac{1}{K} \right) \tag{53}\]
Combining equation (51) and (52) results in equation (54) for hydrate formation.

\[
\frac{dc_h}{dt} = r_{k2}e^{-\frac{-E}{RT}} \left( \phi_e \rho_w S_w \left( y_i p_g \right) \left( \frac{1}{K} - 1 \right) \right) \\
+ r_{k3}e^{-\frac{-E}{RT}} \left( \phi_e \rho_w S_w \left( y_i p_g \right) \left( \frac{1}{K} - 1 \right) \right)
\]

\[(54)\]

We have assumed that the formation rate of CO₂ hydrates is fifty times faster than CH₄ hydrates. For this purpose, the rate of formation of CH₄ hydrate at 5 MPa and 5 °C with \( \phi=0.2; S_h=0.5; S_w=0.35 \) and \( S_g=0.15 \) has been calculated. The rate has been multiplied by fifty and converted into an intrinsic kinetic rate for CO₂ hydrate formation of \( 3.37 \cdot 10^7 \) mol/(day.kPa.m²).
C. Simulation Scenario

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>No Injection</td>
</tr>
<tr>
<td>Case 1</td>
<td>Base Case with Liquid CO\textsubscript{2} injection at 5 MPa</td>
</tr>
<tr>
<td><strong>Numerical Aspects</strong></td>
<td></td>
</tr>
<tr>
<td>Case 2</td>
<td>$t_{\text{max}} = 0.05$ days</td>
</tr>
<tr>
<td>Case 3</td>
<td>Refined grid around wellbores</td>
</tr>
<tr>
<td><strong>Reaction Kinetics</strong></td>
<td></td>
</tr>
<tr>
<td>Case 4</td>
<td>CO\textsubscript{2} hydrate formation 7x faster</td>
</tr>
<tr>
<td>Case 5</td>
<td>CO\textsubscript{2} hydrate formation 20x slower</td>
</tr>
<tr>
<td>Case 6</td>
<td>CO\textsubscript{2} hydrate formation 50x slower</td>
</tr>
<tr>
<td>Case 7</td>
<td>CO\textsubscript{2} hydrate formation 100x slower</td>
</tr>
<tr>
<td>Case 8</td>
<td>CO\textsubscript{2} hydrate formation with published values</td>
</tr>
<tr>
<td>Case 9</td>
<td>CO\textsubscript{2} hydrate formation with equal mass transfer rate for gas/liquid CO\textsubscript{2}</td>
</tr>
<tr>
<td><strong>Injection Pressure</strong></td>
<td></td>
</tr>
<tr>
<td>Case 10</td>
<td>Injecting Gaseous CO\textsubscript{2} at 4 MPa</td>
</tr>
<tr>
<td>Case 11</td>
<td>Injecting Liquid CO\textsubscript{2} at 5.5 MPa</td>
</tr>
<tr>
<td>Case 12</td>
<td>Injecting Liquid CO\textsubscript{2} at 6 MPa</td>
</tr>
<tr>
<td>Case 13</td>
<td>Injecting Liquid CO\textsubscript{2} at 7 MPa</td>
</tr>
<tr>
<td>Case 14</td>
<td>Injecting Liquid CO\textsubscript{2} at 8 MPa</td>
</tr>
<tr>
<td><strong>Injection Temperature</strong></td>
<td></td>
</tr>
<tr>
<td>Case 15</td>
<td>Injecting Liquid CO\textsubscript{2} with $T = 8 \degree$ C</td>
</tr>
<tr>
<td>Case 16</td>
<td>Injecting Liquid CO\textsubscript{2} with $T = 10 \degree$ C</td>
</tr>
<tr>
<td>Case 17</td>
<td>Injecting Liquid CO\textsubscript{2} with $T = 15 \degree$ C</td>
</tr>
<tr>
<td>Case 18</td>
<td>Injecting Water with $T = 13 \degree$ C</td>
</tr>
<tr>
<td>Case 19</td>
<td>Injecting Water with $T = 18 \degree$ C</td>
</tr>
<tr>
<td>Case 20</td>
<td>Injecting Water with $T = 25 \degree$ C</td>
</tr>
<tr>
<td>Case 21</td>
<td>Injecting Water with $T = 30 \degree$ C</td>
</tr>
<tr>
<td><strong>Permeability</strong></td>
<td></td>
</tr>
<tr>
<td>Case 22</td>
<td>$k_h = 1$ D with CO\textsubscript{2} injection</td>
</tr>
<tr>
<td>Case 23</td>
<td>$k_h = 1$ D</td>
</tr>
<tr>
<td>Case 24</td>
<td>$k_h = 2$ D with CO\textsubscript{2} injection</td>
</tr>
<tr>
<td>Case 25</td>
<td>$k_h = 2$ D</td>
</tr>
<tr>
<td>Case 26</td>
<td>$k_v/k_h = 1$ with CO\textsubscript{2} injection</td>
</tr>
<tr>
<td>Case 27</td>
<td>$k_v/k_h = 1$</td>
</tr>
<tr>
<td>Case 28</td>
<td>$k_v/k_h = 0.01$ with CO\textsubscript{2} injection</td>
</tr>
<tr>
<td>Case 29</td>
<td>$k_v/k_h = 0.01$</td>
</tr>
<tr>
<td><strong>Hydrate Blockage</strong></td>
<td></td>
</tr>
<tr>
<td>Case 30</td>
<td>Hydrate Blockage with $n = 3$ with CO\textsubscript{2} injection</td>
</tr>
<tr>
<td>Case 31</td>
<td>Hydrate Blockage with $n = 3$</td>
</tr>
<tr>
<td>Case 32</td>
<td>Hydrate Blockage with $n = 8$ with CO\textsubscript{2} injection</td>
</tr>
<tr>
<td>Case 33</td>
<td>Hydrate Blockage with $n = 8$</td>
</tr>
<tr>
<td>Case 34</td>
<td>Hydrate Blockage with $n = 10$ with CO\textsubscript{2} injection</td>
</tr>
<tr>
<td>Case 35</td>
<td>Hydrate Blockage with $n = 10$</td>
</tr>
<tr>
<td><strong>Porosity</strong></td>
<td></td>
</tr>
<tr>
<td>Case 36</td>
<td>$\Phi = 0.2$ with CO\textsubscript{2} injection</td>
</tr>
<tr>
<td>Case 37</td>
<td>$\Phi = 0.2$</td>
</tr>
<tr>
<td>Case 38</td>
<td>$\Phi = 0.3$ with CO\textsubscript{2} injection</td>
</tr>
</tbody>
</table>
Table C.1 Name and description of the simulation scenarios used to investigate several aspects of CO₂ injection combined with natural gas production.

<table>
<thead>
<tr>
<th>Case</th>
<th>Grid Block Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>$\Phi = 0.3$</td>
</tr>
<tr>
<td>40</td>
<td>Gridblock Size 10 x 10 x 5 m with CO₂ injection</td>
</tr>
<tr>
<td>41</td>
<td>Gridblock Size 10 x 10 x 5 m</td>
</tr>
<tr>
<td>42</td>
<td>Gridblock Size 20 x 20 x 5 m with CO₂ injection</td>
</tr>
<tr>
<td>43</td>
<td>Gridblock Size 20 x 20 x 5 m</td>
</tr>
<tr>
<td>44</td>
<td>Gridblock Size 40 x 40 x 5 m with CO₂ injection</td>
</tr>
<tr>
<td>45</td>
<td>Gridblock Size 40 x 40 x 5 m</td>
</tr>
<tr>
<td>46</td>
<td>Gridblock Size 50 x 50 x 5 m with CO₂ injection</td>
</tr>
<tr>
<td>47</td>
<td>Gridblock Size 50 x 50 x 5 m</td>
</tr>
</tbody>
</table>
D. Nomenclature

\[ A_s = \text{surface area per unit volume (m}^2/\text{m}^3) \]
\[ A_{si} = \text{surface area per unit volume of the hydrates (m}^2/\text{m}^3) \]
\[ C = \text{concentration factor (units vary)} \]
\[ c = \text{concentration (mole/m}^3\text{)} \]
\[ c_p = \text{gas heat capacity (J/(mole K))} \]
\[ E = \text{activation energy (J/mole)} \]
\[ H_l = \text{liquid enthalpy (J/mole)} \]
\[ H_g = \text{gas enthalpy (J/mole)} \]
\[ H_{vap} = \text{vaporization enthalpy (J/mole)} \]
\[ k = \text{permeability (D)} \]
\[ k = \text{thermal conductivity (J/(m day K))} \]
\[ K = \text{distribution factors (-)} \]
\[ k_o = \text{absolute permeability (D)} \]
\[ k_d = \text{dissociation rate constant (mol/(m}^2\text{Pa.s})} \]
\[ k_f = \text{formation rate constant (mol/(m}^2\text{Pa.s})} \]
\[ P = \text{pressure (Pa)} \]
\[ r_{rk} = \text{kinetic rate constant, units vary} \]
\[ R = \text{universal gas constant (J/mole K)} \]
\[ S = \text{saturation (-)} \]
\[ t = \text{time (day)} \]
\[ T = \text{temperature (°C or K)} \]
\[ z = \text{depth (m)} \]
\[ \phi = \text{porosity (-)} \]
\[ \mu = \text{viscosity (cp)} \]
\[ \rho = \text{density (mole/m}^3\text{)} \]

Subscripts

\[ h = \text{hydrate} \]
\[ w = \text{water} \]
\[ g = \text{gas} \]
\[ o = \text{liquid CO}_2 \]
\[ v = \text{void} \]
\[ e = \text{effective} \]
\[ crit = \text{critical saturation} \]
\[ ir = \text{irreducible} \]
E. Correlations

Viscosity correlation:

The gas viscosity is taken as a constant, since no suitable correlation could be found. Values are in Table . The liquid viscosity is using equation (55) with values from Table E.2.

\[
\mu_i (\text{cp}) = A_{\text{visc}} \exp\left( B_{\text{visc}} / T \right)
\]

(55)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$H_2O$</th>
<th>$CO_2$</th>
<th>$CH_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{visc}}$</td>
<td>0.0047352</td>
<td>0.000757</td>
<td></td>
</tr>
<tr>
<td>$B_{\text{visc}}$</td>
<td>1515.7</td>
<td>1331.1</td>
<td></td>
</tr>
</tbody>
</table>

Table E.2 Parameters for the liquid viscosity.

Heat capacity correlation:

The heat capacity of a component can be described by equation (56) and Table . The component phase enthalpy is the integral of the heat capacity $C_p$ (equation (56)) from the reference temperature to the component phase temperature. The phase enthalpy of the gas $H_g$ minus the liquid $H_l$ is equal to the vaporization enthalpy (see equation (57)). The vaporization enthalpy is not constant, as $H_l$ and $H_g$ have different gradients, as is shown in Figure . At the critical point (31.1 °C for CO2), the liquid and gas enthalpy are equal, resulting in a vaporization enthalpy of zero for CO2 at 31.1 °C.

\[
C_p(T) = c_1 + c_2 T + c_3 T^2 + c_4 T^3
\]

(56)

<table>
<thead>
<tr>
<th>Phase Constant</th>
<th>$H_2O$</th>
<th>$CO_2$</th>
<th>$CH_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas $c_1$</td>
<td>32.2</td>
<td>29.3</td>
<td>1.93E+01</td>
</tr>
<tr>
<td>$c_2$</td>
<td>$1.92 \times 10^{-3}$</td>
<td>$-2.24 \times 10^{-2}$</td>
<td>$5.21 \times 10^{-2}$</td>
</tr>
<tr>
<td>$c_3$</td>
<td>$1.06 \times 10^{-5}$</td>
<td>$2.65 \times 10^{-4}$</td>
<td>$1.20 \times 10^{-5}$</td>
</tr>
<tr>
<td>$c_4$</td>
<td>$-3.60 \times 10^{-9}$</td>
<td>$-4.15 \times 10^{-7}$</td>
<td>$-1.13 \times 10^{-8}$</td>
</tr>
<tr>
<td>Liquid $c_1$</td>
<td>$50.81069$</td>
<td>$-3553.844$</td>
<td>-</td>
</tr>
<tr>
<td>$c_2$</td>
<td>$0.2129361$</td>
<td>$46.88128$</td>
<td>-</td>
</tr>
<tr>
<td>$c_3$</td>
<td>$-6.31 \times 10^{-4}$</td>
<td>$-0.201722$</td>
<td>-</td>
</tr>
<tr>
<td>$c_4$</td>
<td>$6.48 \times 10^{-7}$</td>
<td>$2.90 \times 10^{-4}$</td>
<td>-</td>
</tr>
<tr>
<td>Vaporization Enthalpy (25 °C)</td>
<td>44.6 (KJ/mole)</td>
<td>5172 (J/mole)</td>
<td>-</td>
</tr>
</tbody>
</table>

Table E.3 Parameters and values for the calculation of the heat capacity with equation (56).
\[ H_L = \int_{T_{REF}}^{T} C_{p,\text{liquid}} dT \]
\[ H_G = \int_{T_{REF}}^{T} C_{p,\text{gas}} dT \]
\[ H_{Vap} = H_G - H_L \]  \hspace{1cm} (57)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Enthalpy for liquid and gaseous CO\textsubscript{2} with the reference temperature at 25\textdegree C. The difference between the liquid enthalpy and the gaseous enthalpy is the vaporization enthalpy.}
\end{figure}
F. Model Validation

The simulations were validated by comparing the results with the work of Uddin et al., 2006,6 and Hong and Pooladi-Darvish, 2003.40 The validation model consists of a single well, located at the center of a cylindrical reservoir with a radius of 200 m. A 10 m hydrate layer overlies a 10 m free gas zone. The well has been completed in the free gas zone. The reservoir has an initial temperature of 10 °C. For the CH4 hydrate scenarios, the initial pressure is 6913 kPa and the BHP of the well is 4500 kPa. For the CO2 hydrate scenario, the initial pressure is 4500 kPa and the BHP is 3000 kPa. The reservoir and well properties6, such as dimensions, porosities, saturations, absolute permeabilities and BHP's were taken from the literature data. Input parameters such as kinetic parameters, hydrate equilibrium values and other parameters listed in Table 3.4 were derived in this work. The existence of a liquid CO2 phase was not accounted for in the literature6 model. Therefore only gaseous CO2 was considered in the simulations for validation.

The results of our dissociation simulations match reasonably well with the simulation results from literature,6,40 as seen in Figure F.1 through Figure F.5. The small differences in the results are likely to be caused by the assumed relative permeability model and of the description of the dependence of the effective hydrate permeability on the hydrate saturation. Unfortunately, the results of the gas hydrate formation simulations did not match well with literature data. According to the results from literature6, a temperature drop occurs when small amounts of gas are injected into the water saturated reservoir. The reason for this temperature drop in the simulations described in literature is not clear, in particular because the formation of gas hydrates is an exothermic process. A possible explanation for this temperature drop is cooling due to the Joule-Thompson effect. However, this was not observed in our simulations.

In Figure F.1 and Figure F.2, the influence of the kinetic rate of dissociation (r_{rk1}) on the cumulative production of both CH4 and CO2 is depicted. The resulting cumulative CH4 production as found in this work is more sensitive to variation of the reaction rate than as found in literature. The description of the cumulative CO2 production of this work and the literature match closely (see Figure F.2).

The effect of variations in the absolute permeability on the cumulative gas production is shown in Figure F.3 and Figure F.4. The cumulative gas production for the k=200 md case from this work is slightly higher than the results from literature. This might be caused by applying a different hydrate blockage model.

The effect of changing the thermal conductivity of the rock is shown in Figure F.5. The results match nicely with results from literature. In general, it can be observed that a higher thermal conductivity rock increases the cumulative gas production. This is due to the improved heat transport from the surrounding strata so that the cooling due hydrate dissociation is compensated.
Figure F.1 Cumulative gas Production from a CH₄ hydrate deposit as a function of time – Effect of the reaction rate. On the left the model from this work, on the right the model presented by Uddin et al., 2006 (Right image from Uddin et al., 2006).

Figure F.2 Cumulative gas Production from a CO₂ hydrate deposit as a function of time – Effect of the reaction rate. On the left the model from this work, on the right the model presented by Uddin et al., 2006 (Right image from Uddin et al., 2006).
Figure F.3 Cumulative gas Production from a CH₄ hydrate deposit as a function of time – effect of Permeability. On the left are the results from this model; on the right are the results from Uddin et al., 2006 (lines) and Hong and Pooladi-Darvish, 2003 (markers). (Right image from Uddin et al., 2006).

Figure F.4 Cumulative gas production from a CO₂ hydrate Deposit as a function of time – effect of permeability. On the left the model from this work, on the right the model presented by Uddin et al., 2006 (Right image from Uddin et al., 2006).
Figure F.5 Cumulative gas production as a function of time from a CH₄ hydrate deposit - effect of rock thermal conductivity. On the left are the results from this model; on the right are the results from Uddin et al., 2006 (lines) and Hong and Pooladi-Darvish, 2003 (markers). (Right image from Uddin et al., 2006).
G. Images

Figure G.1 Copy of Figure 4.1 with a more detailed scale.

Figure G.2 Cumulative gas production and CO$_2$ injected as a function of time for the base case and case 1.
Figure G.3 Case 1: Liquid CO$_2$ Saturation after 0, 10, 20, 30, 40 and 50 years simulation times.

Figure G.4 Case 3: Reservoir pressure after 7 years. The grid around the wellbore is refined.
Figure G.5 Case 1: Reservoir pressure after 7 years.