APPLICATION OF NUMERICAL, EXPERIMENTAL AND LIFE CYCLE ASSESSMENT METHODS TO THE INVESTIGATION OF NATURAL GAS PRODUCTION FROM METHANE HYDRATE DEPOSITS USING CARBON DIOXIDE CLATHRATE SEQUESTRATION

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Abstract

Natural gas hydrates, commonly called methane (CH₄) hydrates, are ice-like materials belonging to the family of clathrates that form at low temperature and high pressure. They can be found in permafrost and oceanic environments. The amount of natural gas trapped into worldwide hydrate deposits has been estimated at 18000 trillion m³ of methane [1] and it surpasses the world natural gas proven reserves (180 trillion m³ [2]) by two orders of magnitude. Fossil fuel based energy is still a major source of carbon dioxide (CO₂) emissions. Hence, it contributes greatly to the issues of global warming and climate change. Geological sequestration of carbon dioxide appears as the safest and most stable way to reduce such emissions for it involves CO₂ entrapment into hydrocarbon reservoirs and aquifers. Indeed, CO₂ can also be sequestered as hydrates while assisting in the dissociation of in-situ methane hydrates. This approach could help mitigate the emissions of CO₂ in the atmosphere and improve the economics of carbon dioxide sequestration and natural gas production from hydrate deposits. The proposed research focused on investigating the feasibility of the CO₂-CH₄ exchange in hydrates as a gas hydrate mining method through experimental studies and numerical modeling of the exchange, as well as the application of a life-cycle assessment (LCA) approach to the evaluation of CO₂ emissions resulting from the use of the replacement technique. Under the limitations of our numerical model and experiments, we were able to establish the influence of initial reservoir temperature and pressure on the performance of the exchange. We also noticed the influence of the presence of excess water during the exchange. These observations have been confirmed in the relevant literature. The application of the life cycle assessment method to the process of gas production from a hypothetical hydrate reservoir allowed us to highlight conditions where the use of the exchange technique could lead to emission-neutral gas extraction from methane hydrate deposits.
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Nomenclature

A : Surface area (m$^2$)
$A_{\text{dec}}$ : Area of decomposition per unit volume (m$^{-1}$)
$A_{\text{HS}}$ : Specific surface area of hydrate particles (m$^{-1}$)
$c_p$ : Heat capacity of the hydrate layer (J/kg.K)
$C_{pr}$ : Heat capacity of the base rock (J/kg.K)
Capacity : Plant capacity (MW)
CF : Capacity factor (fraction)
CH4$^\text{hydfrac}$ : Fraction of CH$_4$ remaining in the hydrate phase (dimensionless)
CO2$^\text{hydfrac}$ : Fraction of CO$_2$ in the hydrate phase (dimensionless)
CO2cumultrapped : Cumulative amount of CO$_2$ trapped in the exchange at time t (mol)
CO2trappedcumul$^{n+1}$ : Cumulative amount of CO$_2$ trapped in the exchange at time t+$\Delta$t (mol)
Cor : Correction factor (dimensionless)
D : Wellbore diameter or pipe diameter (m)
$-\frac{\text{dm}_{\text{CH4(H)}}}{\text{dt}}$ : Rate of CH$_4$ hydrate dissociation (kg.s$^{-1}$)
$\frac{\text{dm}_{\text{CO2(H)}}}{\text{dt}}$ : Rate of CO$_2$ hydrate formation (kg.s$^{-1}$)
$-\frac{\text{dn}_{\text{CO2(g)}}}{\text{dt}}$ : Amount of CO$_2$(g) consumed with time (mol.s$^{-1}$)
$\frac{\text{dn}_{\text{CO2(H)}}}{\text{dt}}$ : Amount of CO$_2$ hydrate produced with time (mol.s$^{-1}$)
EF : Emission factor (gCO$_2$/MJ)
Efficiency : Plant efficiency (fraction)
Energy : Amount of energy generated (MJ)
f$^G_{\text{CH4}}$ : Fugacity of CH$_4$ in the gas phase (kPa)
f$^H_{\text{CH4}}$ : Fugacity of CH$_4$ in the hydrate phase (kPa)
f$^G_{\text{CO2}}$ : Fugacity of CO$_2$ in the gas phase (kPa)
f$^H_{\text{CO2}}$ : Fugacity of CO$_2$ in the hydrate phase (kPa)
f$_{f}$ : Fanning friction factor (dimensionless)
g : Acceleration of gravity (m.s$^{-2}$)
h : Well depth (m)
H : Hydrate block thickness (m)
Heating value : Heating value of the raw materials used (MJ/kg of coal or kJ/m$^3$ of natural gas)
k : Permeability (md)
k$^0_d$ : Intrinsic methane hydrate dissociation kinetic constant (kmol/m$^2$.kPa.s)
k$^d$ : Overall dissociation rate constant (kmol/m$^2$.Pa.s)
k$^f$ : Hydrate formation rate constant (kmol/ m$^2$.Pa.s)
k$_r$ : Rock thermal conductivity (W/m.K)
L: Well depth or pipe length (m)

\( m_{\text{CH}_4} \): Mass of methane contained in the gas layer (Mt)

\( m_{\text{CH}_4, \text{after exchange}} \): Mass of \( \text{CH}_4 \) in the gas layer at the end of the exchange (Mt)

\( m_{\text{CH}_4, \text{after production}} \): Mass of \( \text{CH}_4 \) in the gas layer at the end of recovery (Mt)

\( m_{\text{CH}_4, \text{recoverable}} \): Mass of \( \text{CH}_4 \) that can be recovered without dissociating the hydrate structure (Mt)

\( m_{\text{CO}_2} \): Mass of \( \text{CO}_2 \) needed to fill the gas layer (Mt)

\( m_{\text{CO}_2, \text{after exchange}} \): Mass of \( \text{CO}_2 \) in the gas layer at the end of the exchange (Mt)

\( m_{\text{CO}_2, \text{after production}} \): Mass of \( \text{CO}_2 \) in the gas layer at the end of recovery (Mt)

\( m_{\text{CO}_2, \text{recoverable}} \): Mass of \( \text{CO}_2 \) that can be recovered without dissociating the hydrate structure (Mt)

\( M_{\text{CH}_4} \): Molecular weight of methane gas (g/mol)

\( M_{\text{CH}_4(H)} \): Molecular weight of methane hydrate (kg/kmol)

\( M_{\text{CO}_2(H)} \): Molecular weight of carbon dioxide hydrate (kg/kmol)

\( \text{moleCH}_4\text{released} \): Cumulative amount of \( \text{CH}_4 \) released from the exchange at time \( t \) (mol)

\( \text{moleCH}_4\text{released}^n \): Cumulative amount of \( \text{CH}_4 \) released from the exchange at time \( t \) (mol)

\( \text{moleCH}_4\text{released}^{n+1} \): Cumulative amount of \( \text{CH}_4 \) released from the exchange at time \( t+\Delta t \) (mol)

\( \text{molefreegas} \): Amount of gas in the gas phase at time \( t \) (mol)

\( \text{molegasinitial} \): Initial amount of gas in the gas phase (mol)

\( n_{\text{CH}_4(t)} \): Amount of free methane (without hydrate) (mol)

\( n_{\text{CH}_4(t) \text{ associated with CH}_4\text{hyd}} \): Amount of free methane associated with methane hydrate (mol)

\( n_{\text{G free}} \): Amount of gas in the reaction cell headspace (mol)

\( n_{\text{G ideal type II hydrate sample}} \): Amount of gas trapped by an ideal type II gas hydrate (mol)

\( n_{\text{G in hydrate}} \): Amount of gas trapped in the hydrate structure (mol)

\( n_{\text{G total in sample cell}} \): Total amount of gas introduced in the sample cell (mol)

\( n_{\text{H}} \): Hydrate number (dimensionless)

\( n_{\text{H}_2\text{O}} \): Amount of water inserted inside the sample cell (mol)

\( N_{\text{Re}} \): Reynolds number (dimensionless)

\( P_{\text{avg}} \): Average pressure (psia)

\( P_{\text{eqCH}_4\text{hyd}} \): Methane hydrate equilibrium pressure (kPa)

\( P_{\text{eqCO}_2\text{hyd}} \): Carbon dioxide hydrate equilibrium pressure (kPa)

\( P_{\text{i}} \): Methane hydrate equilibrium pressure at the initial reservoir temperature (kPa)

\( P_{\text{inj}} \): Bottom hole injection pressure (psia)

\( P_{\text{inlet}} \): Pipe inlet pressure (psia, atm or MPa)

\( P_{\text{o}} \): Operating pressure (kPa)

\( P_{\text{outlet}} \): Pipe outlet pressure (psia, atm or MPa)

\( P_{\text{res}} \): Reservoir pressure (psia)
\( P_{\text{surf}} \): Surface injection pressure (psia, atm or MPa)
\( q \): Volumetric flowrate (m\(^3\)/s)
\( q_{\text{inj}} \): Injection rate (resbbl/D)
\( Q \): Mass flowrate (kg/s)
\( r_c \): Drainage radius (ft)
\( r_w \): Wellbore radius (ft)
\( R \): Real gas constant (J.mol\(^{-1}\).K\(^{-1}\))
\( RH \): Hydrate recovery (fraction)
\( S_H \): Hydrate saturation (dimensionless)
\( \text{Ste,Ste} \): Ratio of the sensible heat of the hydrate cap or cap-rock to heat of decomposition (dimensionless);
\( t \): Time (s)
\( T \): Temperature (K)
\( T_{\text{avg}} \): Average temperature (K)
\( T_{\text{CH}_4(g)} \): Temperature of free methane (without hydrates) (K)
\( T_{\text{CH}_4(g)} \) associated with \( CH_4 \) hydrate: Temperature of free methane associated with methane hydrates (K)
\( T_{\text{hyd}} \): Temperature of the hydrate layer (K)
\( T_i \): Initial temperature (K)
\( T_{\text{inj}} \): Bottom hole injection temperature (K)
\( T^e \): Methane hydrate equilibrium temperature at the operating pressure (K)
\( T_{\text{rock}} \): Temperature of the base cap rock (K)
\( T_{\text{rockavg}} \): Average base cap rock temperature (K)
\( T_{\text{sample cell}} \): Sample cell temperature (K)
\( T_{\text{surf}} \): Surface injection temperature (K)
\( V_{\text{CH}_4(g)} \): Volume of free methane (without hydrate) (m\(^3\))
\( V_{\text{CH}_4(g)} \) associated with \( CH_4 \) hydrate: Volume of free methane associated with \( CH_4 \) hydrate (m\(^3\))
\( V_{\text{CH}_4,sc} \): Volume of methane in the gas layer at standard conditions (scm or std m\(^3\))
\( V_{\text{CH}_4,\text{res}} \): Volume of methane in the gas layer at reservoir conditions (m\(^3\))
\( V_{\text{CO}_2,sc} \): Volume of CO\(_2\) needed to fill the gas layer at standard conditions (scm or std m\(^3\))
\( V_G \) free space: Volume of the reaction cell headspace (m\(^3\))
\( V_{\text{internal sample cell}} \): Internal volume of the reaction cell (m\(^3\))
\( V_{\text{occupied by ice}} \): Volume occupied by the ice seeds inside the reaction cell (m\(^3\))
\( y_{\text{CH}_4} \): Fraction of CH\(_4\) in the gas phase (dimensionless)
\( y_{\text{CO}_2} \): Fraction of CO\(_2\) remaining in the gas phase (dimensionless)
\( Z \): Gas compressibility factor (dimensionless)
\( \alpha_r \): Rock thermal diffusivity (m\(^2/s\))

\[ \gamma = \frac{H_{\text{CH}_4(\text{H})_{\text{diss}}}}{\alpha_r / H} \]

\( \Delta H_{\text{CH}_4(\text{H})_{\text{diss}}} \): Enthalpy of CH\(_4\) hydrate dissociation (J/kg)

\( \Delta H_{\text{CO}_2(\text{H})_{\text{form}}} \): Enthalpy of CO\(_2\) hydrate formation (J/kg)

\( \Delta H_{\text{reaction}} \): Enthalpy of the exchange (J/kg)

\( \Delta P_{\text{friction}} \): Pressure drop due to friction (psia, atm or MPa)

\( \Delta P_{\text{hydrostatic}} \): Pressure drop due to the weight of the column of fluid (psia, atm or MPa)

\( \Delta T \): Duration of energy supply (hours)

\( \varepsilon \): Pipe roughness (dimensionless)

\( \mu, \mu_{\text{avg}} \): Average carbon dioxide viscosity (cp)

\( \rho \): Density of the hydrate layer (kg/m\(^3\))

\( \rho_{\text{avg}} \): Average fluid density (kg/m\(^3\))

\( \rho_{\text{CH}_4,sc} \): Methane density at standard conditions (kg/m\(^3\))

\( \rho_{\text{CO}_2,sc} \): Carbon dioxide density at standard conditions (kg/m\(^3\))

\( \rho_r \): Rock density (kg/m\(^3\))

\( \rho_{\text{H}} \): Density of methane hydrate (kg/m\(^3\))

\( \Phi \): Porosity (dimensionless)

\( \omega \): Group parameter (dimensionless); \( \omega = \frac{\gamma}{\text{Ste}} \)
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Chapter 1. Introduction

Since initially discovered by Sir Davy Humphrey in 1810, natural gas hydrates have been converted from a laboratory oddity to a hydrocarbon production nuisance as seen forming inside the chamber bell used to cap the spill in the Deep Water Horizon oil well, before being considered a potential energy resource for the future. For many decades, countries such as the United States, Canada, Japan, India, and China have funded major research projects to get a better understanding and knowledge of natural gas hydrates [3]. Resource assessment studies have demonstrated the huge potential of gas hydrate accumulations as a future energy resource [4]. Indeed, the amount of natural gas trapped into worldwide hydrate deposits has been estimated at 18000 trillion m$^3$ of methane [1] and it surpasses the world natural gas proven reserves (180 trillion m$^3$ [2]) by two orders of magnitude.

World energy demand is steadily rising due to global population and economic growth. World energy consumption is expected to increase from 472 quadrillion Btu to 678 quadrillion Btu in 2030; thus a total increase of 44% from 2006 to 2030 [5]. Most recent estimates state that the world energy demand is expected to grow from 505 quadrillion Btu in 2008 to 770 quadrillion Btu in 2035, thus an increase of 53% [6]. China and India are currently the fastest growing non-OECD (Organization for Economic Co-operation and Development) economies and their combined energy consumption is expected to represent 28% of the world energy consumption in 2030 [2]. The Energy Information Administration’s (EIA) 2011 International Energy Outlook report [6] predicts an 85% increase in energy consumption for all non-OECD nations. Despite recent progress in obtaining energy from non-fossil fuels, nearly 80% of the world energy supply will still be generated from oil, natural gas and coal. The combustion of these fuels is a major source of carbon dioxide emissions. Unfortunately, changes in the global climate have been attributed to the increasing concentration of Green House Gases such as CO$_2$ and CH$_4$ in the atmosphere. Geological sequestration of CO$_2$ is a potential solution to this problem. Typical geological sequestration consists in capturing and storing gas in geological settings such as active and depleted oil and gas
reservoirs, deep brine formations, deep coal seams and coal-bed methane formations [7]. Sequestration of CO$_2$ in marine and arctic hydrates has been considered as an advanced geological sequestration concept, which needs further investigation [8].

Gas hydrates can be naturally found in permafrost and marine environments. They contain mixtures of gases such as methane and ethane, with carbon dioxide and hydrogen sulfide as trace components. Methane is the predominant component of natural gas hydrates, which is the reason they are simply called methane hydrates. Gas hydrates form under specific conditions: (1) the right combination of pressure and temperature (high pressure and low temperature), (2) the presence of hydrate forming gas in sufficient amounts and (3) the presence of water. CO$_2$ and CH$_4$ hydrates are of interest for CO$_2$ is a preferential hydrate guest former when compared to CH$_4$. In addition, CO$_2$ hydrates are more stable than CH$_4$ hydrates and the exposure of CH$_4$ hydrates to carbon dioxide has resulted in the release of methane, while carbon dioxide remained trapped. Thus, the use of carbon dioxide to recover natural gas from hydrate deposits has gained more and more relevance in the industry. Other techniques are being explored in the area of production from hydrate deposits. However, the resource is still not commercially viable due to technical, environmental and economic issues. Any further investigation of the mixed CO$_2$-CH$_4$ gas hydrate properties could lead to major breakthroughs in the fields of unconventional resource production and carbon sequestration.

This project will focus on evaluating natural gas extraction from hydrate deposits using CO$_2$ clathrate sequestration and has been organized as follows: chapters 2 and 3 will respectively present a review of the relevant literature and describe our problem statement; results from the investigation of the technique via numerical modeling will be presented in chapter 4; chapter 5 will be centered on the experimental evaluation of the technique while chapter 6 will display results from the application of an LCA approach; finally, conclusions and recommendations will be covered in chapter 7.
Chapter 2. Literature Review

Methane clathrates have extensively been researched in the scientific and engineering literature for several decades. The understanding of the driving mechanisms, thermodynamics, kinetics and conditions involved in the formation and dissociation processes of methane hydrates is necessary to their appropriate use for energy recovery. Selected studies giving a general description of natural gas hydrates and their production techniques are included in this chapter. Emphasis is placed on the molecular exchange between CO$_2$ and CH$_4$ that occurs when methane hydrates are exposed to CO$_2$, thus generating the release of natural gas and trapping of carbon dioxide as gas clathrate. The presented projects include laboratory studies on the synthesis, thermodynamics, phase equilibrium, kinetics, cage occupancy and the methane recovery potential of the mixed CO$_2$-CH$_4$ hydrate. Field and mathematical modeling studies investigating the production potential of gas hydrate deposits are also mentioned.

Methane recovery from gas hydrate deposits with carbon dioxide clathrate sequestration could offer the additional advantage of helping to curb atmospheric CO$_2$ emissions, hence resulting in emission-neutral energy production. Life-cycle analysis has been applied to projects related to energy generation, fossil fuel extraction and carbon dioxide utilization for the evaluation of their environmental impact in terms of CO$_2$ emissions. Results from such studies are presented.

2.1. Methane Hydrates: a possible source of energy

Numerous authors have focused on discussing hydrates’ resource accumulations, their types of reservoirs, their stability conditions and their region of occurrences, in order to help better understand this material. In 1991, E. Dendy Sloan [9] published a general review of natural gas hydrates and their applications in the petroleum industry. He emphasized how gas clathrates were first considered as hindrances by the petroleum industry, for they were causing transmission line blockage and damaging deepwater platforms and pipelines. As such, the formation of hydrates needed to be prevented through:
(1) the removal of one of the components necessary to the formation process, (2) heating of the system beyond the formation temperature at a certain pressure (thermal stimulation), (3) the decrease of the system’s pressure below the hydrate stability pressure at a certain temperature (depressurization) and (4) the injection of an inhibitor like methanol or glycol to displace the hydrate stability conditions to higher pressures and lower temperatures. Yet, there was growing interest in the potential of hydrates as an energy resource due to their enormous gas storage capacity and the size of their reserves. The prevention techniques (depressurization, thermal stimulation and inhibitor injection) began to be investigated for resource recovery. Sloan also listed improvements such as cooling of the drilling fluid to avoid hydrate dissociation during drilling of hydrate deposits. Finally, Sloan highlighted possible applications of gas hydrate technology for separation processes and gas transportation and storage. Sloan’s paper offers an overview of the different implications of gas hydrates in the oil industry. It is interesting to see how the search for techniques to prevent the formation of hydrates in production facilities later translated into possible resource recovery and applications in oil and gas processing.

In the years following Sloan’s publication, methane hydrate research began to be more focused on assessing hydrate production capacity. In 2001, Thomas [10] released a study examining the potential of methane hydrates as a major source of energy. In comparison to Sloan’s paper, his study presented additional details on methane hydrate characteristics, regions of occurrences and assessment methods. At the time, methane hydrate accumulations were estimated to be twice the total carbon amount contained in coal, oil and conventional gas worldwide. Natural gas hydrates were portrayed as a subset of gas clathrates, occurring naturally in sedimentary deposits of permafrost and oceanic regions. Thomas listed bottom simulating reflectors, pore water salinity measurements, well-logging and direct observation from core samples as gas hydrate assessment methods. Thomas’ paper ends by highlighting that key technology improvements should be made in the following areas: (1) assessment of hydrate accumulations, (2) core sampling, and core sample transportation and analyses without alteration of the
cores and (3) proving the possibility of gas production from hydrate accumulations at sufficient sustained rates and low enough operating costs to be economically viable.

In 2009, Moridis et al. [11] released an exhaustive review discussing the distribution of gas hydrate accumulations, the status of international and national R&D programs, the remaining science and technological challenges facing the commercialization of gas hydrate as an energy resource and the progress made in the numerical simulation of hydrate production. It is noticeable that as of 2009, several actions had been taken to make gas hydrates a viable resource. There was an increased level of international awareness with major hydrate R&D programs being undertaken worldwide. Some attempts had been made to recover gas from hydrate deposits, but challenges still remained due to the hostile environments in which hydrates naturally occurred. In his review, Moridis underlines the importance of numerical simulation in the effort to assess the production potential of hydrate accumulations as it offers the advantages of being powerful, flexible and low-cost.

Boswell (2009) goes one step further in his paper and suggests that hydrates formed in sandy reservoirs should be the first targets of any hydrate production project as they present considerable advantages for gas extraction [12]. He stresses on the fact that the permeability of sand reservoirs allows gas hydrate to be contained within such formations at very high concentrations (60 % to 90 % of the pore space) and is key to the use of existing drilling and production technologies for gas extraction from such deposits. He adds that dissociation and CO$_2$ exchange seems to offer promising results for hydrates contained in sandy reservoirs. However, the extent of these types of hydrates in marine sediments should be better estimated and these estimates should be confirmed with drilling.

Overall, the potential of gas hydrates as a major energy source has been widely demonstrated over the past two decades and has raised national and international awareness. However, the production challenges still exist and call for a fundamental understanding of clathrate hydrates along with their
formation and dissociation processes. Attempts have been made to accomplish these goals through experimental and simulation studies and the results acquired will be presented in the following sections.

### 2.2. Laboratory studies of Gas Hydrates

Laboratory studies of gas hydrates are essential to the fundamental understanding of the processes and mechanisms involved in their formation and dissociation. Sloan (1998) reviewed in his book different experimental investigations that have been conducted in the area of gas hydrate research [13]. He classified hydrate experimental studies into three categories: (1) macroscopic, (2) mesoscopic and (3) molecular-level. The methods of hydrate formation that have been used since the discovery of gas hydrates are usually macroscopic methods. The procedure to obtain phase equilibrium data requires observing the hydrate phase by indirect means such as an associated pressure decrease or temperature increase in the fluid phase. In these cases, visual observation is typically the only direct evidence of hydrate phase. Due to the need for more direct measurements methods of hydrate properties, there has been an increase in the use of mesoscopic tools such as laser scattering, X-ray computed tomography (CT) and electron microscopy to examine the morphology and distribution of the hydrate phase. Molecular-level tools such as Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and X-ray and neutron diffraction can also be applied to determine the structure and relative guest cage occupancy of hydrates.

Winters et al. (2000) released an article describing the Gas Hydrate and Sediment Test Laboratory Instrument (GHASTLI) project [14]. GHASTLI was developed at the USGS Woods Hole Field center. Its purpose is to simulate natural conditions within the gas hydrate stability region so that gas hydrates could be formed in reconstituted sediments. GHASTLI can be used to measure physical properties such as acoustic velocity, shear strength, permeability and electrical sensitivity at different times during testing to ascertain the effect of gas hydrates on the bulk physical properties. These data are essential to
the estimation of the amount of in-situ gas hydrates and to the evaluation of seafloor and well stability. They also play an important role in the comparison to well log data. Likewise, Stern et al. (2000) accomplished major progress in the measurement of hydrate thermal and physical properties in the laboratory [15]. Stern et al. proposed a new method for synthesis of pure, polycrystalline methane hydrate and hydrate sediment aggregates based on a materials-science approach. The method involves the exposure of pre-formed ice seeds to an increase in gas hydrate former (molecular guest) pressure and an increase in temperature. The method yields highly reproducible gas hydrate samples in terms of purity, composition, stoichiometry, porosity, grain size and grain orientation that are perfect for physical measurements like thermal conductivity, acoustic wave speed and strength. Since, ice-seed based hydrate formation has been widely applied and led to successful results ([16] and [17]).

The paper published by Carolyn Koh in 2002 [18] offers an exhaustive summary of techniques to obtain gas hydrate properties. Indeed, Koh presented the application of various physico-chemical methods for the understanding of natural gas hydrate formation, decomposition and inhibition. She described the use of macroscopic time independent measurements and thermodynamic models for the determination of equilibrium properties of gas hydrates. Koh mentioned the existence of mechanistic models for the understanding of the nucleation and crystal growth processes involved in hydrate formation. In situ spectroscopic and diffraction studies could be utilized to determine the lattice constant, the ratio of occupation of large to small cavities by guest molecules. She listed the use of molecular simulation studies for the description of the structural evolution of methane hydrates. Gas consumption data as a function of time, Raman spectroscopy and energy dispersive X-ray diffraction could be applied to examine the effect of polymer inhibitors on gas hydrate formation. More importantly, Koh’s paper highlights the need for further thermodynamic and hydrate phase equilibrium studies, coupled with structural phase equilibrium measurements through the use of Raman and NMR spectroscopy, as well as X-ray and neutron diffraction and thus joins the observations made by Sloan in his book. Kinetic studies
should continue to be implemented for data collection on hydrate formation, decomposition and inhibition, which are important for the safe and efficient exploration of gas hydrate from marine deposits and for the control of gas hydrate occurrences in oil and gas pipelines.

Parallel to the numerous studies aiming at obtaining gas hydrate properties, some researchers ventured in the field of experimental, numerical and field scale-investigation to help solve gas hydrate production-related issues. These will be covered in the following section.

### 2.3. Gas hydrate production: laboratory and field studies of the production potential of hydrate deposits

Three major gas hydrate production techniques have so far been suggested: (1) thermal stimulation, (2) depressurization and (3) chemical inhibitor injection. Laboratory and field studies have been undertaken in order to evaluate the feasibility of these production techniques as well as the production capacity of gas hydrate deposits in permafrost zones and oceanic environments.

The Messoyakha field in Northern Russia is a permafrost natural gas hydrate accumulation containing both free gas and hydrate-bearing formations that is often cited as an example of a hydrate deposit from which gas has already been produced. As a matter of fact, production data and other pertinent geologic information have been used to deduce the presence of gas hydrates within the upper part of the Messoyakha field [19]. It has been suggested that the production history of the Messoyakha field demonstrates how gas hydrates can be a producible source of natural gas and how production can be started and maintained by conventional methods such as simple depressurization. The presence of hydrates was inferred from the evolution of pressure over time. Production from the lower free-gas portion of the Messoyakha field started in 1969. The measured reservoir pressures initially followed predicted decline relationships, but began to deviate from expected values in 1971. This deviation has been attributed to the release of gas from adjacent dissociating gas hydrates. In 1991, Yousif and Sloan
experimentally examined depressurization as a gas extraction technique. They accomplished the first uniform formation of synthetic natural gas hydrates in consolidated porous media by use of a flow-through system. They measured the hydrates’ dissociation rate at constant pressure and temperature in an attempt to simulate gas production by depressurization. They determined that rapid hydrate production near the freezing point could cause enough temperature reduction to stop the dissociation process. They also determined that continuous water production should be expected.

In 1994, Judge et al. [21] published a study that suggested the existence of gas hydrate accumulations in the Mackenzie Delta. The information came from data collected during the past three decades of conventional hydrocarbon exploration in the area. The Mallik gas hydrate accumulation, a permafrost deposit located in the Canadian Mackenzie Delta, can be considered as one of the best-characterized gas hydrate deposits in the world. The assessments of Judge et al. (1994) [21] have since been refined with data from scientific drilling programs that included the collection of gas-hydrate-bearing core samples and especially the 1998 Mallik 2L-38 gas hydrate research program ([22], [23] and [24]). Majorowicz and Osadetz (2001) [25] and Osadetz and Chen (2005) [26] estimated the amount of gas in the hydrate accumulations to be around $2.8 \times 10^{10} - 2.8 \times 10^{11}$ m$^3$ STP, making the Mallik field one of the most concentrated gas hydrate deposits in the world. Two additional gas hydrate production research programs were conducted at the Mallik field: The 2002 Mallik Gas Hydrate Production Research Well Program [24] and the 2006-2008 JOGMEC/NRCan/Aurora Mallik Gas Hydrate Production Research Program [27]. These programs included field studies and production tests from hydrates. They yielded geological, geochemical, geotechnical and microbiological data on gas hydrate bearing sediments in that area [28]. Short-term depressurization experiments investigated the feasibility of depressurization induced gas production from hydrates and indicated a higher effective permeability of hydrate bearing media. A longer (5-day) experiment of gas production by thermal stimulation involved the circulation of warm water in a 17m-thick section of highly concentrated hydrates and resulted in continuous gas
production at varying rates that peaked at 1500 m$^3$/day. These results confirmed earlier predictions which claimed the technical feasibility of gas production from hydrates at the Mallik site by means of thermally induced dissociation [29]. In 2005, Tang et al. [30] experimentally inquired hot brine injection as a gas hydrate production technique. Their study suggested that lower inlet brine temperatures and injection rates as well as higher hydrate contents yielded higher energy ratios (ratio of combustion heat from the produced gas over the inlet heat). However, these high energy efficiency ratios were paired with low production rates.

Gas hydrates can also be found in the Alaskan Northern Slope and more precisely in the Eileen gas hydrate accumulation. The first direct confirmation of gas hydrate on the North Slope was provided by data from a single well in the Prudhoe Bay field [31]. The volume of gas within the Eileen gas hydrate accumulation was estimated at about twice the volume of known conventional gas in the Prudhoe Bay Field [31]. It ranges between 1.0x10$^{12}$ and 1.2x10$^{12}$ m$^3$ STP [28]. A project funded by the Methane Hydrates Research and Development (MHR&D) Act and involving the collaboration of BP Exploration (Alaska - BPXA) Inc., DOE and USGS led to the recovery of core samples and the gathering of useful data describing the pore water geochemistry, microbiology, gas chemistry, as well as petrophysical, thermal and physical properties of gas hydrate bearing sediments at the Mount Elbert site. In addition to these hydrate accumulations, some oceanic deposits in the Nankai Trough (offshore Japan) and in the Gulf of Mexico, were the subject of intense production testing. Exploratory wells were drilled that led to a better characterization of hydrate bearing formations located in these areas.

The use of chemical inhibition as a production technology has also drawn some attention. In 2007, Li et al. [32] examined the behavior of gas production from hydrate bearing porous sediment by injecting ethylene glycol solutions of different concentrations at various injection rates. They used a one dimensional experimental apparatus. The results from their work suggested that production involved four stages: the initial injection, the dilution of ethylene glycol, the hydrate dissociation and the gas
output. The efficiency of this production methodology was affected by both the injection rate and concentration of the ethylene glycol solution.

Extensive work has been carried out on characterizing gas hydrate formations and examining the feasibility of depressurization, thermal stimulation and chemical inhibition as field-scale methane hydrate production strategies. Depressurization appears to be the most promising technique, as it is more economical for it can be applied through conventional hydrocarbon production facilities. However, depressurization can typically be used with Class 1 deposits and still present the issues of seafloor stability. A fourth production methodology has been suggested and is based on the chemical substitution of methane by carbon dioxide within the hydrates. This is covered in more details in section 2.4.

2.4. CO₂-CH₄ guest molecule exchange in Methane Hydrates

In 1996, Ohgaki et al. [33] examined the possible interactions between carbon dioxide hydrates and methane hydrates by injecting carbon dioxide (gas) into an aqueous-gas hydrate system containing methane. CO₂ displays a higher chemical affinity than CH₄ in the hydrate structure since it has a higher heat of formation and equilibrium temperature i.e., at 1000 psi, the equilibrium temperature of CH₄ hydrate is approximately 283.15 K while the equilibrium temperature of CO₂ hydrate is around 286.15 K. Ohgaki et al.’s experiments resulted in the synthesis of a mixed CO₂-CH₄ hydrate. The equilibrium concentrations obtained for CO₂ were greater in the hydrate phase than those of CH₄ and less than the concentrations of CH₄ in the gas phase. Nakano et al. (1998) [34] performed a similar study using carbon dioxide and ethane and obtained comparable results. Smith et al. (2001) [35] inquired the feasibility of exchanging carbon dioxide with methane in geologic accumulations of natural gas hydrates. They numerically investigated the effect of the pore size distribution on the conversion of CH₄ hydrate to CO₂ hydrate. It was demonstrated that the guest molecule exchange between CO₂ and CH₄, in
porous media, was less thermodynamically favored, as the pore size decreased. They recommended these numerical results be validated by laboratory experiments. Seo and Lee (2001) [36] experimentally examined hydrate phase equilibrium processes for mixtures of CO₂ and CH₄. They determined the existing conditions of quadruple points (H-L_w-L_CO₂-V) in order to evaluate the hydrate stability. It was noted that the equilibrium curves of the mixed hydrates lied between those of pure carbon dioxide and methane hydrates. For a given mixture, the concentration of CO₂ in the hydrate phase decreased as the pressure was lowered.

In 2003, Lee et al. [37] published the results of their study on the thermodynamics and kinetics of the conversion of CH₄ hydrate to CO₂ hydrate. They analyzed the distribution of guest molecules over different cavities for pure methane hydrates and different mixtures of CO₂-CH₄ hydrates, using solid state nuclear magnetic resonance (NMR) methods. It was observed that the cage occupancy ratio of CH₄ in pure methane hydrates decreases as the concentration of CO₂ in the mixture increases. This is explained by the fact that CO₂ preferentially occupied large 5₁²₆₂ (tetracaidecahedron) cages in the mixed hydrate. In terms of kinetics, it was noticed that the conversion of CH₄ hydrate to CO₂ hydrate happened much more quickly than the formations of pure CO₂ and CH₄ hydrates. The amount of CH₄ that could be recovered from the gas hydrate of composition CH₄•6.05H₂O is limited to 64% of the original entrapped gas, even with a CO₂ concentration of 100 mol%. Ota et al. (2004) [38] focused on the gas exchange process with liquid CO₂. They performed laboratory measurements using Raman spectroscopy and numerical simulations and they found similar results in terms of feasibility of the molecular gas exchange. Stevens (2008) [39] took the studies of this topic one step further by publishing his work on the gas exchange between CO₂ and CH₄ in hydrates formed within sandstone core samples. He used a magnetic resonance imaging (MRI) scan to analyze the samples and realized there was formation of CO₂ hydrate at the expense of the initial CH₄ hydrate. Diffusion seemed to be the main driving force behind the conversion from CH₄ hydrate to CO₂ hydrate. A considerable amount of CH₄ was released during the process, which was judged rapid and efficient. There was no free water present.
The permeability of the core was reduced during CH$_4$ hydrate formation. This reduced permeability was maintained constant during the CH$_4$-CO$_2$ exchange, and the permeability levels were considered sufficient for gas transportation.

In 2008, Park et al. [40] made a major discovery while inquiring the effect of the injection of a binary mixture of N$_2$ and CO$_2$ on methane hydrate recovery. They found out that the injection of a binary mixture of N$_2$ and CO$_2$, instead of the traditional pure CO$_2$, increased the percentage of methane recovered from 64% to 85% for type I gas hydrates. They also looked at the potential influence of structural transition by forming a type II CH$_4$-C$_2$H$_6$ hydrate and injecting CO$_2$ and a mixture of CO$_2$ with N$_2$. It was determined that the hydrate structure changed from type II to type I during the gas injection, thus increasing the gas recovery to more than 90% for CH$_4$. In 2012, Beeskow-Strauch and Schicks [41] experimentally investigated the CH$_4$-CO$_2$ exchange process in the presence of SO$_2$ and C$_2$H$_6$ using laser Raman spectroscopy. They observed the exchange between pure CH$_4$ hydrate and CO$_2$, as well as pure CH$_4$ hydrate and mixed CO$_2$-SO$_2$. They performed similar experiments with mixed CH$_4$-C$_2$H$_6$ hydrate and CO$_2$, as well as mixed CH$_4$-C$_2$H$_6$ hydrate and mixed CO$_2$-SO$_2$. The results obtained by Beeskow-Strauch and Schicks’ study confirm that more CH$_4$ recovery can be achieved when mixed CH$_4$-C$_2$H$_6$ hydrates are exposed to CO$_2$ due to a structural change during the exchange from type I to type II hydrates. Indeed, they achieved a methane release of 85% after four days of CH$_4$-C$_2$H$_6$-CO$_2$ exchange against only 50% of methane release for the CH$_4$-CO$_2$ exchange during the same time-span. Besides, the addition of SO$_2$ to the carbon dioxide stream enhanced the stability of the resulting hydrate structure in comparison with pure CO$_2$ hydrate, as well as the induction time of the exchange reaction. However, it did not influence the final recovery results. Finally, their study presents the aim for equilibrium state of the chemical potential between all phases as main driving force for the exchange. Horvat et al.(2012) [42] performed a macroscale gas hydrate experiment in order to analyze the formation of pure CO$_2$ and mixed CH$_4$-CO$_2$ hydrates in the presence of sodium dodecyl sulfate (SDS) under seafloor-mimic conditions. Gas chromatography was used to monitor the components’ compositions throughout the
experiment. They successfully created synthetic CO\textsubscript{2} and CH\textsubscript{4}-CO\textsubscript{2} hydrates using liquid water with 300 ppm of SDS. CO\textsubscript{2} hydrate yield seemed to decrease with a decrease in SDS concentration in water due to SDS precipitation in the aqueous phase under certain conditions. The exchange between CH\textsubscript{4} and CO\textsubscript{2} within the hydrates could be observed as CH\textsubscript{4} content decreased in the early stages of the experiment, and then increased again showing that CO\textsubscript{2} was replacing CH\textsubscript{4} in the hydrates. The hydrate conversion percentages that were achieved appeared to be lower than theoretical values for the given conditions probably because not enough gas was incorporated into the vessel for complete hydrate formation. It was also impossible to distinguish between pure CH\textsubscript{4} hydrate, pure CO\textsubscript{2} hydrates or pure CH\textsubscript{4}-CO\textsubscript{2} hydrates with direct visualization.

In 2012, Zhao et al. [43] published a review of several research projects on the replacement of CH\textsubscript{4} in natural gas hydrates by the use of CO\textsubscript{2}. They acknowledged that the thermodynamic feasibility and kinetic feasibility of the exchange had been proven at various conditions through the use of experiments, molecular dynamic simulations and Raman spectroscopy. They highlighted the use of CO\textsubscript{2} gas, CO\textsubscript{2} liquid and a CO\textsubscript{2} emulsion during various exchange experiments at different pressure and temperature conditions. From the results of the exchange experiments performed with CO\textsubscript{2} gas, the following can be inferred: (1) replacement consists essentially in CO\textsubscript{2} molecules occupying CH\textsubscript{4} molecules’ cages within the hydrates, (2) temperature and pressure increase seems to promote CH\textsubscript{4} hydrate decomposition and CO\textsubscript{2} hydrate formation, (3) rapid reaction rates could be achieved in the early stages of the experimental runs (up to 10 hours), but their values eventually decreased (4) low recovery efficiencies were achieved and (5) the amount of CO\textsubscript{2} hydrate formed surpassed the amount of CH\textsubscript{4} hydrate dissociated due to the presence of free water in the system. The use of CO\textsubscript{2} liquid allowed the completion of faster reaction rates and recovery efficiencies than with CO\textsubscript{2} gas. The use of CO\textsubscript{2} emulsion led to even better reaction rates and recovery efficiencies than both CO\textsubscript{2} gas and CO\textsubscript{2} liquid. This could be explained by the better conductivity and diffusivity of the emulsion. However, the performance of the emulsion in the exchange seemed to be dependent on the CO\textsubscript{2} content in the emulsion and the emulsion preparation technique is
still new and immature. Zhao et al’s review also pointed out factors influencing the performance of the exchange and its potential for application in commercial production. They emphasized that high initial pressure, high initial temperature and the addition of SDS have been proven beneficial to the recovery efficiency of the exchange by the use of gaseous CO₂. High initial temperature also favors improved replacement efficiency when using liquid CO₂. Additionally, they highlighted that the presence of free water could negatively impact the process efficiency.

Deusner et al. (2012) [44] presented experimental results for the CH₄-CO₂ exchange within hydrates using hot supercritical CO₂. They performed flow-through experiments and synthetically created hydrates inside porous sediments in the presence of excess water. They determined that continuous methane recovery could be achieved using this technique. However, they obtained low recovery efficiencies when applying the technique at cold temperatures. They also noted the influence of excess water on recovery. This confirms observations that have been made in similar studies. They explained the fact that the injected CO₂ underwent rapid cooling at cold initial reservoir temperatures leading to the formation of pure CO₂ hydrates with excess water. The hydrates thus formed blocked fluid pathways, which led to the failure of the exchange technique at cold temperatures, as it reduced the amount of methane that could be recovered. Their study’s results allowed them to differentiate between CH₄ released through the exchange and CH₄ produced which should correspond to the amount of CH₄ that is recoverable at the wellhead. Indeed, the exchange may be successful in releasing a huge amount of methane inside the reservoir, but the actual amount of methane produced could be limited by gas immobilization due to inherent reservoir and injected fluid properties. They also highlighted that although the exchange seemed feasible with the use of hot supercritical CO₂, it was difficult to differentiate between methane release due to thermal stimulation and methane release due to CH₄ hydrate conversion to CO₂ hydrate. They suggested that more research be conducted involving the injection of hot supercritical CO₂ coupled with depressurization in order to initially destabilize the hydrate deposit via depressurization and compensate for the effects of the endothermic hydrate
decomposition on the reservoir with the heat provided by the hot CO$_2$ injection. They also suggested the modification of the injection fluid composition and temperature as well as the modification of the injection strategy in order to avoid early CO$_2$ breakthrough and gas immobilization.

Besides these major thermodynamically-related numerical and laboratory investigations, several studies were conducted to evaluate the potential of this new concept as a field scale production method for methane hydrate deposits. In 2003, Rice [45] proposed a scheme for methane recovery from marine hydrate accumulations. In this scheme, the produced methane would be converted into hydrogen and carbon dioxide; then, the carbon dioxide would be re-injected into the ocean to be converted into CO$_2$ hydrates and finally the produced hydrogen would be used as fuel. Methane would be recovered from hydrates using depressurization combined with thermal stimulation. No direct molecular gas exchange between CH$_4$ and CO$_2$ was inferred in this production scheme. In 2004, McGrail et al. [46] investigated Ohgaki et al.’s method to determine the rate of CO$_2$ gas penetration in the bulk methane hydrate, using Raman spectroscopy. They discovered that the rates of CO$_2$ gas penetration were too low for this method to be useful for gas hydrate production. Then, they performed a preliminary study on a new enhanced gas hydrate recovery concept based on the injection of a micro-emulsion of CO$_2$ and water in the methane hydrate core samples. The technique was validated through laboratory experiments and numerical simulation, using a custom model based on STOMP-CO$_2$. Castaldi et al. (2006) [47] examined the technical feasibility of applying a down-hole combustion method for gas recovery from hydrate accumulations, while sequestrating CO$_2$ as hydrates. The gas molecular exchange between CH$_4$ and CO$_2$ was not directly mentioned, but they suggested there should be equality between the rates of CO$_2$ hydrate formation and CH$_4$ hydrate dissociation, during the process. In 2012, the first field scale production trial of the CH$_4$-CO$_2$ exchange within hydrates was carried out at the Ignik Sikimi well #1 [48] in the Prudhoe Bay unit of the Alaska’s North Slope. The project has been executed by Conocophillips and Japan Oil, Gas & Metals National Corporation under the sponsorship of the U.S.
Department of Energy. The main objective is to evaluate the viability of the guest molecule replacement within hydrates as a production technique and understand the implications of the process at a field scale. So far, hydrate production testing operations have successfully been completed and have involved the injection of 210,000 SCF of a gaseous mixture of CO$_2$ and N$_2$ leading to 6 weeks of sustainable flowback of gas. Large amounts of data including temperature and pressure monitoring and real time data on return gas composition and constituent volumes have been collected and are being analyzed. The project started in 2008 and is expected to end in June 2013. The final results obtained from this field trial should allow the oil industry to make tremendous progress toward the commercial implementation of methane hydrate production.

Reviews of the technique and continuous updates on the advances that have been made concerning the understanding of the exchange are also essential. In 2006, Goel [49] released a review of the status of research projects and issues related to methane hydrate production with carbon dioxide sequestration. It was concluded that although several studies had already been performed, additional experimental data was needed on the topic of CH$_4$-CO$_2$ molecular guest exchange in hydrate bearing sediments. He emphasized the importance of fully knowing the thermodynamics and kinetics of the formation and dissociation of this mixed hydrate and of the conversion process, in porous media. He also pointed out the importance of understanding the equilibrium conditions of the mixed hydrate in sediments as a function of pressure, temperature, mole fraction of CO$_2$ and CH$_4$ in the mixture, pore size, porous material and flow properties. As mentioned earlier, Zhao et al. (2012) [43] published a more recent study of the advances made on the replacement of CH$_4$ in the hydrates with the use of CO$_2$. Their review enabled to confirm the feasibility of the exchange and highlighted the difficulty of reaching a consensus concerning the exchange efficiency due to the variety of experiments that had been performed from microscale to macroscale and from batch to flow-through experiments, as well as to the variety of pressure and temperature conditions employed. However, it helped in seeing additional potential issues
for the commercial application of the technique, which were not necessarily mentioned in previous studies such as the CO₂ phases that could be utilized, the influence of pressure and temperature of the reservoir, the effect of additives and the impact of the presence of excess free water inside the reservoir. They also suggested that additional research be conducted on the exchange.

Production of methane from hydrate deposits has also been investigated through mathematical modeling and numerical simulations. Some of the major findings are presented in section 2.5.

2.5. Mathematical modeling of gas extraction from Methane Hydrate deposits

Modeling the mechanisms involved in gas production from hydrates offers the advantage of predicting in a cost-effective manner and with relative accuracy the response of hydrate formations to different production scenarios. Since depressurization has been acknowledged as the most promising and economically viable production technology for hydrate reservoirs, several studies have focused on designing mathematical models to further understand this technique. Yousif et al (1991) [50] developed one of the first mathematical models of production from hydrates with the depressurization method. They proposed a three phase (gas, water, hydrate) one-dimensional linear depressurization model for hydrates in porous medium. They assumed isothermal conditions for the dissociation. They included hydrate dissociation kinetics with the use of the Kim-Bishnoi model [51]. They also accounted for flow of gas and water through the porous medium. The mathematical model’s results were compared to experimental results of dissociation undertaken with gas hydrates in Berea sandstone cores. They obtained good matching between both procedures and demonstrated a significant release of water with the depressurization model. Goel et al. (2001) [52] designed a model predicting the performance of a naturally occurring in-situ hydrate reservoir under gas production through depressurization. Goel et al. included the kinetics of hydrate dissociation in their formulation and used an n th order rate equation instead of the traditional first order equation suggested by Kim et al. (1987) [51]. They also selected a
radial description of the reservoir and accounted for fluid flow. Their model showed that slow hydrate decomposition and low production rates would be achieved by depressurization alone. They suggested that production might be increased by the use of chemical enhancers. In 2003, Ji et al. [53] examined the production of natural gas from a hydrate reservoir with a constant well output. They also used depressurization as the production method and accounted for heat and fluid flow. They determined that pressure would need to be continuously reduced in order to maintain a constant production rate. Another depressurization model combining hydrate dissociation intrinsic kinetics, mass balance and energy balance was proposed by Hong and Pooladi-Darvish in 2003 [54]. Their purpose was to investigate the relative importance of the different mechanisms involved in gas production from hydrate reservoirs by depressurization and to inquire if that technique could lead to high enough production rates for commercial viability. Their study resulted in 50% of the total gas produced being attributed to decomposition of the hydrates. They also demonstrated that high thermal conductivities should result in an increase of the recovery from hydrates and that production was also affected by rock permeability. They suggested that a deep decomposition model be applied for hydrate reservoirs associated to a mobile phase.

Gerami and Pooladi-Darvish published their work in 2007 [55] and used the deep decomposition assumption in designing an analytical model able to predict the rate of gas generation from a hydrate reservoir by the depressurization method. They suggested in their work the existence of two stages for the dissociation of hydrate at constant pressure: (1) a non-equilibrium stage where gas generation is governed by the sensible heat from the hydrate zone and the conductive heat flux from cap and base rocks and (2) an equilibrium stage where gas generation is attributed solely to the conductive heat flux from cap and base rocks. They performed sensitivity analyses and confirmed that the operating pressure of the free gas layer has a fundamental effect on recovery. The operating pressure corresponds to the reduced pressure of the gas layer prior to depressurization. Indeed, lowering that pressure resulted in a
significant increase of the recovery ratio. They also compared the deep decomposition model to the sharp-interface model used in previous projects ([50], [53], [54] and [56]) and concluded that the deep decomposition assumption led to optimistic predictions.

Similar work was published in 2009 by Tabatabaie and Pooladi-Darvish [57]. They designed an analytical model for gas production from Class 1 hydrate deposits using the sharp-interface assumption. The model showed a decline in temperature during constant rate production and a resulting increase in heat flux and dissociation rate with time. The model also displayed a ‘near-linear’ decline in temperature. They concluded that porosity and drainage area have an impact on recovery, but not thermal conductivity, which differs from the conclusions by Hong and Pooladi-Darvish (2003) [54]. They confirmed the fact that the sharp-interface assumption might lead to pessimistic predictions while the deep decomposition assumption would lead to optimistic ones and suggested both models be used as lower and upper bounds of the production from Class 1 hydrate deposits by depressurization.

Another advantage of the replacement technique for methane recovery from natural gas hydrates is the possibility to reach emission-neutral energy extraction. Life cycle assessment is a tool allowing the evaluation of the environmental burden of a process during its lifetime. A few examples of its application in the fields of energy supply and carbon sequestration can be seen in the following section.

2.6. Life cycle assessment technique applied to energy-related projects

In 2001, Aycaguer et al. [58] conducted a life cycle assessment (LCA) to determine the benefits derived from storing carbon dioxide in active reservoirs while enhancing the extraction of oil and its potential impacts on the environment. An active reservoir located in the Permian basin in West Texas and undergoing enhanced oil recovery with CO$_2$ injection at the time was selected for the study. The injected carbon dioxide was initially supplied from a natural carbon dioxide reservoir and then recycled from the produced stream later in the field’s life. It was possible to evaluate the storage capacity of the reservoir,
the emissions generated by the process, and the amount of CO₂ needed to maintain optimal recovery throughout the project’s lifetime. The study only focused on assessing CO₂, CH₄ and N₂O emissions from the project. The system’s boundaries included the extraction of oil and associated gas from the reservoir, gas processing, compression and recycling of the CO₂ stream and CO₂ transportation and injection into the reservoir. Aycaguer et al.’s work succeeded in showing that 5.5 kgCO₂/kg of oil produced would need to be supplied to the reservoir for optimal recovery. It also demonstrated that CO₂ recycling avoided the release into the atmosphere of 2.6 kgCO₂/kg of oil produced. The storage capacity of the reservoir was estimated to be 3 kgCO₂/kg of oil produced, out of which 2.6 kgCO₂/kg of oil produced could be stored. The remaining 0.4 kgCO₂/kg of oil produced constituted the net CO₂ emissions of the process. Aycaguer et al. also compared the amount of carbon dioxide stored inside the reservoir to the emissions resulting from the incremental oil produced from the reservoir and deduced that the system studied had almost neutral emissions with carbon dioxide storage.

Khoo and Tan (2006) [59] used the life cycle assessment technique to examine a coal-fired power plant (from coal mining, processing and transportation to power generation), four types of CO₂ recovery technologies and nine types of CO₂ sequestration options. They completed a full LCA including emission inventory and impact assessment and looked into CO₂ recovery and sequestration beyond the aspect of climate change. They published a second paper [60] in which they applied the LCA technique to two case studies of enhanced resource recovery methods for oil and natural gas with CO₂ sequestration: CO₂ enhanced oil recovery (EOR) and CO₂ enhanced coalbed methane recovery (ECBMR). The use of LCA helped predict their potential impacts on the environment and compare those to the environmental burdens of conventional oil and natural gas recovery. They were able to demonstrate the environmental advantage of EOR and ECBMR coupled with CO₂ sequestration through their work. They encouraged for similar studies to be performed for other CO₂ emission mitigation solutions.
Suebsiri et al. (2006) [61] utilized the life cycle assessment framework for the case of CO$_2$ sequestration at the Weyburn unit. They analyzed the process of CO$_2$ storage from delivery to the oil field through production, transportation and oil refining and usage. They tried to identify opportunities to optimize the process. The Weyburn unit was selected for their case study due to the public availability of large amounts of data from previous research projects. They assessed it would be possible to store a third of the total amount of CO$_2$ emissions from the entire EOR process in the reservoir. Thus, they obtained positive net emissions for their case.

In 2009, Jaramillo et al. [62] performed the life cycle assessment of CO$_2$-EOR projects under different scenarios. They departed from similar work in the literature by including in their study emissions associated with the life cycle of power generation and downstream processing of produced crude oil. However, they did not account for emissions related to the transportation of petroleum products from the refinery to the consumer and emissions associated with the construction of the physical infrastructures needed for the project. They obtained positive net GHG emissions for the projects under all scenarios, meaning that the estimated GHG emissions were larger than the amount of CO$_2$ injected and stored in the reservoirs.

2.7. Summary

The topic of methane hydrates has been largely covered in the literature. Natural gas hydrates’ potential as a major energy source has been demonstrated and has raised national and international awareness. Much progress has been made on the understanding of the mechanisms involved in the formation and dissociation of methane clathrates and several techniques now exist to help measure gas hydrate properties. Some major field scale projects have been executed and have resulted in a better assessment of gas hydrate resources and evaluation of depressurization, thermal stimulation and chemical inhibition as viable production techniques. Depressurization seems to be the most promising method; however its
implementation presents challenges due to gas hydrate’s regions of occurrences. CH₄-CO₂ exchange within hydrates has also been suggested as an alternative production method for hydrate formations and has produced interesting recovery ratios. Several studies have been published on the topic, and although most of them agree on the feasibility of the exchange and the mechanisms involved, it seems difficult to reach a consensus concerning the recovery efficiencies of the method and the optimal performance conditions of the method. The very first CH₄-CO₂ exchange within hydrates production field trial was executed in 2012 and should lead to a better evaluation of the commercial viability of the technique. Depressurization has been evaluated through modeling, yet not many models have been focused on the feasibility and production potential of the CH₄-CO₂ exchange technique within hydrates. The potential advantage of the process in terms of CO₂ emission mitigation has also been mentioned and an assessment of the environmental impact from the use of the technique could help verify these assumptions. Thus, more information on the recovery potential of this process and its environmental effects in terms of carbon dioxide emissions would be useful.
Chapter 3. Problem Statement

Global energy sources can be classified into renewable and non-renewable categories. Non-renewable energy sources include coal, oil, gas, gas hydrates, shale gas, tar sands and fissile materials (nuclear energy) while renewable energy sources correspond to biomass, hydro, geothermal, solar and wind energy. Among the non-renewable sources of energy, fossil fuels (oil, gas and coal) supply over 80% of the global demand for energy. They have been the prime sources of energy for the purpose of transportation, power generation and agriculture as well as commercial, domestic and industrial activity for more than a century [63].

Unfortunately, about 98% of carbon emissions result from the combustion of fossil fuels. The rise of CO$_2$ content in the atmosphere is one of the main causes of global warming and climate change. Renewable energy sources offer the advantage of providing cleaner energy than fossil fuels, however the amount of energy supplied from these sources is still very limited (about 14% of the world’s energy supply [64]). Natural gas combustion emits less CO$_2$ than coal and all other petroleum-derivative fuels. As of 2008, 21% of the global energy demand was supplied by natural gas [64]. Thus, many countries have started to transition from coal and oil as main source of energy to natural gas. Natural gas is currently used across all sectors including industrial and residential energy generation, commercial sectors and transportation sectors in varying amounts. Furthermore, world energy demand is expected to suffer an increase of 53% by 2035 [6]. Natural gas consumption should nearly double from 2001 to 2025. Conversely, there is a decline in the production from conventional energy sources that will potentially lead to a lack of energy in the years to come.

Meanwhile, the most conservative estimates state the world reserves of methane hydrates at 18000 trillion m$^3$ [1], which are two orders of magnitudes higher than the world’s natural gas proven reserves. Methane gas hydrates could approximately meet global energy demands for one thousand years and thus
compensate for the predicted gap in energy supply. Three production techniques have so far been suggested for the production of natural gas from methane hydrates and are based upon the dissociation or melting of in-situ hydrates: (1) depressurization, (2) thermal stimulation and (3) chemical inhibitor injection. Yet, the following issues need to be resolved for production of methane hydrates to become commercially viable [65]:

- Drilling through formations containing methane hydrates could become unsafe as hydrate removal could possibly impact ocean floor stability and lead to an uncontrolled release of methane
- This sudden and uncontrolled release of the methane trapped in gas hydrate formations could potentially influence and worsen global warming and climate change as methane is a greenhouse gas and every cubic meter of hydrate block can contain up to 180 cubic meters of gas
- Large amounts of water should be expected to be released and would need to be properly removed from the reservoir
- Economic evaluations of the thermal stimulation and chemical inhibitor injection techniques have revealed that their implementation would be too costly. Depressurization appears to be the most promising production method; however it can only be applied to hydrate formations associated with a free gas layer.
- Long-term field scale studies have to be undertaken to verify more accurately the potential of gas hydrates as a relevant energy source.

Recently, a fourth technique has been getting the interest of the scientific community. It appears that the injection of CO₂ into methane hydrate formations leads to a molecular guest exchange between CO₂ molecules and CH₄ molecules; CH₄ is released and CO₂ is trapped as clathrate. This technique offers several advantages:

- It provides an option for CO₂ sequestration and should help reduce the CO₂ content in the atmosphere.
- It reduces or eliminates water release from gas hydrate production.
- It enhances reservoir geo-mechanical stability and could possibly be extended to other classes of hydrate deposits besides sand-dominated reservoirs.

As mentioned in section 2.5, various studies have been carried out on the exchange. The thermodynamic and kinetic feasibility of the guest molecule replacement technique within hydrates have been proven through different types of experiments (batch, flow-through, macroscale, microscale) performed at various pressure and temperature conditions. Experimental work has involved pure or mixed hydrates in bulk or embedded into porous sediments. The first field trial of the technique has just been completed in 2012. Yet, it is still difficult to reach a consensus concerning the performance of the exchange technique in terms of recovery since various recovery percentages can be found in the literature. Few factors which could influence the performance of the exchange have been highlighted. Many simulation and numerical studies have been specifically designed to mimic the reservoir’s response to depressurization, thermal stimulation and chemical inhibition. However, not many models have focused solely on the exchange. Finally, the potential of the CO₂-CH₄ molecular guest exchange within hydrate to aid in curbing atmospheric CO₂ emissions has been mentioned, but not evaluated in details.

This research has been centered on experimentally and numerically investigating the molecular guest exchange as a natural gas production method, as well as applying a life cycle assessment approach to the replacement technique in order to evaluate its environmental load in terms of carbon dioxide emissions. These three methods were selected in an attempt to compensate the missing notions highlighted from our analysis of the relevant literature, as well as to present an evaluation of the exchange technique from macroscale to field scale. An experimental apparatus has been designed and built in order to help examine through experiments the feasibility of the chemical substitution method as a methane recovery method from hydrates. Mostly methane and carbon dioxide were used to synthesize hydrates in the laboratory and mimic the exchange. A numerical model has been developed and has served for comparison with some experimental results. Sensitivity analyses were also performed, allowing the
investigation of scenarios that would be too complex to reproduce in the laboratory. A case study was designed for the application of life-cycle analysis and the assessment of the exchange environmental load in terms of carbon dioxide emissions.

The goals of this study are:

1. Numerical modeling of the CO$_2$-CH$_4$ molecular guest exchange for a gas hydrate formation with the estimation of CO$_2$ consumption rates, CH$_4$ yield rates, and CH$_4$ recovery efficiencies with time
2. Laboratory synthesis of pure hydrates and reproduction of the CO$_2$-CH$_4$ exchange within hydrates
3. Experimental and numerical investigation of selected factors which could influence the performance of the exchange
4. Life-cycle assessment of the exchange process applied to a hypothetical hydrate reservoir
Chapter 4. Modeling CO$_2$-CH$_4$ molecular guest exchange in methane hydrates

In this chapter, the methodology, assumptions and mathematical equations used to model the CO$_2$-CH$_4$ molecular guest exchange in methane hydrates are described. First, the methodology is explained, then a non-isothermal model is presented. In addition, a sensitivity analysis is performed with the model and enables to improve the understanding of the gas exchange. Finally, results from our mathematical model are compared to relevant similar existing models from the literature.

4.1. Theoretical study

4.1.1. Overall description of gas clathrates

Gas hydrates are crystalline compounds that belong to the family of clathrates. They are constituted of gas and water molecules. The water molecules or host molecules form a hydrogen-bonded lattice, where gas molecules or guest molecules are entrapped. The presence of guest molecules stabilizes the lattice due to the sum of the attractive or repulsive forces between molecules known as Van der Waals forces. There is no bonding between the host and the guest molecules, i.e., the gas molecules are free to rotate inside the lattice ([4], [66], [67] and [68]). Gas hydrate formation and dissociation are described by the following equations: $G+N_H \text{H}_2\text{O} \rightarrow G\cdot N_H \text{H}_2\text{O}$ and $G\cdot N_H \text{H}_2\text{O} \rightarrow G+N_H \text{H}_2\text{O}$ where $N_H$ is the hydration number and $G$ is the guest molecule. Gas hydrate formation is an exothermic process while gas hydrate dissociation is endothermic.

Gas hydrates appear under three distinguishable structures: type I, type II and type H. All structures involve a network of interconnected cages. Structure I (sI) hydrates display unit cells that are constituted of 46 water molecules organized into 2 small cavities and 6 large cavities. The small cavities are dodecahedral cages with 12 pentagonal faces. They are usually denoted as $5^{12}$ cages. The large cavities are 14-sided polyhedra (tetrakaidecahedron), which are usually denoted as $5^{12}6^2$. The unit cells of Type II hydrates (sII) contain 136 water molecules. They are organized into 16 small cavities and 8 large
cavities. The small cavities are of the same kind as the small cavities in sI hydrates. However, the large cavities are hexacaidecahedra ($5^{12}6^4$) with 12 pentagonal faces and 4 hexagonal faces [68]. In 1987, a new hydrate structure was discovered and called structure H (sH). This structure contains 34 water molecules in its unit cell, forming a hexagonal lattice. Type H hydrates display three types of cavities: three $5^{12}$ cages, two $4^35^66^3$ cages and one large $5^{12}6^8$ cage ([68] and [69]). The description of the different hydrate structures is summarized in table 4-1.

Table 4-1: Structures of hydrates ([68] and [69])

<table>
<thead>
<tr>
<th></th>
<th>Type I</th>
<th>Type II</th>
<th>Type H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of water</td>
<td>46</td>
<td>136</td>
<td>34</td>
</tr>
<tr>
<td>molecules per unit cell</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Types of cavities per</td>
<td>2 small cavities ($5^{12}$)</td>
<td>16 small cavities ($5^{12}$)</td>
<td>3 small cavities ($5^{12}$)</td>
</tr>
<tr>
<td>unit cell</td>
<td>6 large cavities ($5^{12}6^2$)</td>
<td>8 large cavities ($5^{12}6^4$)</td>
<td>2 medium cavities ($4^35^66^3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 large cavity ($5^{12}6^8$)</td>
</tr>
</tbody>
</table>

Because of the size difference between the cages, the three types of hydrate tend to trap different kinds of molecules. Type I hydrates are usually formed with smaller molecules such as ethane, hydrogen sulfide etc. Type II clathrates are formed by larger molecules such as propane and isobutane. Type H hydrates require the presence of a small molecule such as methane and a type H gas former like 2-methylbutane or cycloheptane, to be created. They are less common in nature than the other types of gas hydrates ([68] and [69]). Figure 4-1 illustrates the different sorts of hydrate structures and some of their gas forming molecules. These structures have been observed with X-ray diffraction.

Figure 4-1: Different types of clathrate hydrates ([68 and [69])
The types of hydrates that can be found in nature are natural gas hydrates. They are formed with natural gas which is a mixture of methane, ethane, and propane with carbon dioxide and hydrogen sulfide as trace components. These gas mixtures contain close to 90% of methane. As a result, natural gas hydrates are commonly called methane hydrates. Methane hydrates occur in permafrost areas and subsea environments. The temperature and pressure gradients which are at play underneath the Earth help define specific hydrate occurring zones, when associated to the thermodynamic hydrate equilibrium conditions. These zones are called hydrate stability zones [67]. Figure 4-2 displays the hydrate stability zones in permafrost and marine environments. The dashed lines representing the temperature gradients in figure 4-2, mark the boundary of the lowest temperatures found at the pressures present in permafrost and marine environments.
Assessment methods for gas hydrates include seismic studies (bottom simulating reflectors), pore water salinity measurements, well-logging and direct observations from core samples [11]. So far, 89 hydrate locations have been discovered worldwide [70]. These locations are presented in figure 4-3.
4.1.2. Methane hydrates versus Carbon dioxide hydrates

Methane and carbon dioxide both form type I hydrates. The comparison of their hydrate phase equilibrium conditions suggests the occurrence of a transition zone between both hydrate equilibrium curves where CO$_2$ hydrates can exist while CH$_4$ hydrates dissociate into methane gas and water. Indeed, CO$_2$ hydrates are more stable than CH$_4$ hydrates for temperatures below 283.15 K. The hydrate phase diagrams of both compounds were obtained using the CSMHYD software [72] and are presented in figure 4-4. In addition, the heat of dissociation of carbon dioxide hydrate (57.98 kJ/mol) is greater than the heat of dissociation of methane hydrate (54.49 kJ/mol). Thus, it is more difficult to dissociate CO$_2$ hydrates in comparison to methane hydrates. This also shows that CO$_2$ has a larger affinity than methane in the hydrate form. Thirdly, it has been experimentally proven that carbon dioxide is preferentially trapped over methane in the hydrate phase [33]. The heat released from the formation of carbon dioxide hydrate in the presence of methane hydrate should be sufficient to dissociate the methane hydrate and recover methane gas [49]. These observations fuel the growing interest in the use of carbon dioxide for natural gas recovery from gas hydrate deposits.
4.1.3. General assumptions

The following general assumptions have been applied to the mathematical modeling of the CO\textsubscript{2}-CH\textsubscript{4} exchange within hydrates:

4.1.3.1. Class 1 type of reservoir

We consider a reservoir with a hydrate layer topped by a free gas phase. The gas phase is initially filled with CO\textsubscript{2}. Moridis and Collett (2003) [73] established a classification of geologic deposits of gas hydrates based on their production strategy and behavior which can be found in table 4-2. According to their classification, the reservoirs we will be examining in this study can be associated to the Class 1 type of hydrate reservoirs.
Table 4-2: Classification of gas hydrate deposits [73]

<table>
<thead>
<tr>
<th>Types of hydrate deposits</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1</td>
<td>Permeable hydrate layer associated with a hydrate-free, unsaturated interval with a mobile aqueous and gas phases beneath</td>
</tr>
<tr>
<td>Class 2</td>
<td>Permeable hydrate layer associated with a hydrate-free saturated interval with a mobile aqueous phase beneath (no gas phase in the hydrate-free interval)</td>
</tr>
<tr>
<td>Class 3</td>
<td>No hydrate-free zone beneath the hydrate-layer</td>
</tr>
<tr>
<td>Class 4</td>
<td>Disperse, low-saturation accumulations in marine geologic media</td>
</tr>
</tbody>
</table>

During the exchange, the composition of the gas phase will evolve as CO\textsubscript{2} gets trapped into the hydrate layer and CH\textsubscript{4} is simultaneously released. A schematic representation of the reservoir is shown in figure 4-5. It is important to highlight that figure 4-5 is not an accurate depiction of class 1 hydrate reservoirs; however this drawing is a good representation of the gas hydrate formation and exchange conditions used in our experimental vessel which will be described in chapter 5.

![Schematic representation of the reservoir](image)

**Figure 4-5: Schematic representation of the reservoir**

### 4.1.3.2. Reservoir geometry

The reservoir is treated as an idealized container. The gas phase, hydrate phase and rock formation are represented as blocks or containers of volume corresponding to the saturation volumes for the fluids and
bulk volume for the cap rock. We do not incorporate any volume change for any of the three layers displayed in figure 4-5. In the formulation, the reservoir is described in Cartesian system coordinates. There is no discretization of the reservoir properties in the x and y directions, but changes in the z-direction are included for certain reservoir properties. The thermo-physical properties of the reservoir (thermal diffusivity, thermal conductivity) are taken constant with time.

4.1.3.3. Closed system

The hydrate-filled formation is considered as a closed system. There is no exchange of matter with the surroundings. All the components initially present in the reservoir will be found at the end of the production process, possibly in different phases. Heat exchange is allowed in-between layers.

4.1.3.4. Fluid flow

We do not account for any fluid flow in the reservoir. Although, pressure gradients between the layers may result from the exchange process, we are only focusing on understanding the mechanisms of the exchange and obtaining an overall estimate of the amount of methane that can be released from the reservoir. In addition, the model’s performance is purposed to be compared to experimental results obtained with our experimental set-up which does not include gas flow during the exchange process. Instead, the gas phase is collected at the end of the experiment for gas chromatography analysis.

4.1.3.5. Energy balance

No convective flux or radiation has been considered in developing the energy balance equations. We are accounting for the contributions from the kinetic energy, potential energy and internal energy of the layers, as well as heat transfers and work transfers if any. The exchange reaction is expected to change the temperature of the hydrate layer and adjacent base cap rock and gas phase. However, since we are not including any fluid flow in this study and convection is usually the dominant form of heat in flowing liquids and gases, we will assume that the temperature of the gas phase remains constant throughout the exchange process. We will only take into account the heat transfer between the base rock and the hydrate layer. Table 4-3 displays thermal conductivity values for CO$_2$ (g), CH$_4$ (g), hydrate and rock:
Table 4-3: Thermal conductivity values

<table>
<thead>
<tr>
<th></th>
<th>Thermal conductivity (W/m.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2) (g)</td>
<td>0.0146</td>
</tr>
<tr>
<td>CH(_4) (g)</td>
<td>0.03</td>
</tr>
<tr>
<td>Hydrate</td>
<td>0.393</td>
</tr>
<tr>
<td>Rock</td>
<td>1.5</td>
</tr>
</tbody>
</table>

4.1.3.6. CO\(_2\)-CH\(_4\) exchange reaction

We assume that the hydrates have a perfect stoichiometry and that all cages are filled. The exchange reaction is considered to occur in all hydrate cages. Thus, the reaction can be described by the simultaneous dissociation of CH\(_4\) hydrates and formation of CO\(_2\) hydrates, as shown in figure 4-6. The intrinsic kinetics of hydrate formation and decomposition are taken into account.

(1) \(8\text{CH}_4\cdot46\text{H}_2\text{O} \rightarrow 8\text{CH}_4 + 46\text{H}_2\text{O}\)

(2) \(8\text{CO}_2 + 46\text{H}_2\text{O} \rightarrow 8\text{CO}_2\cdot46\text{H}_2\text{O}\)

(1)+(2) \(8\text{CO}_2 + 8\text{CH}_4\cdot46\text{H}_2\text{O} \rightarrow 8\text{CH}_4 + 8\text{CO}_2\cdot46\text{H}_2\text{O}\)

Figure 4-6: Hydrate guest exchange reaction

4.1.4. Fundamental Equations

4.1.4.1. Gas hydrate formation and dissociation kinetics

Gas hydrate formation is a crystallization process. It involves two steps: nucleation and growth. Nucleation is the process of forming critical sized, stable hydrate nuclei. Hydrate growth is the process of growth of these nuclei. Nucleation kinetics are not well understood. However, several studies have succeeded in explaining the kinetics of hydrate growth. The kinetic equations for the formation and decomposition of gas hydrates are based on results by Kim et al. (1987) [51] and Englezos et al. (1987) [74].
In their model, the driving force for the transition between fluid phase and hydrate phase is the fugacity difference between the fluid phase and the hydrate phase $\Delta f = f - f_{eq}$ where $f$ is the fugacity of the gas former in the fluid phase and $f_{eq}$ is the fugacity of the gas former at the water-hydrate-gas three phase equilibrium. Hydrates tend to form when $f - f_{eq}$ is positive and they tend to dissociate when $f - f_{eq}$ is negative. Equilibrium is reached when $f - f_{eq} = 0$. Figure 4-7 displays typical gas consumption during hydrate formation. Nucleation takes place during the induction time. At the end of the induction time, steady hydrate growth begins.

![Figure 4-7: Gas consumption plot during hydrate formation](image)

Kim et al.’s kinetics model [51] states that gas consumption rate during hydrate formation is proportional to the driving force. The equation of CO$_2$ hydrate formation reaction can be written as

$$\text{CO}_2 + n_{H_2} \text{O} \rightarrow \text{CO}_2.n_{H_2} \text{O}.$$  

The rate of this equation is by definition: $R = \frac{d\text{CO}_2(H)}{dt} = -\frac{d\text{CO}_2(g)}{dt}$. It defines the amount of reactant consumed and the amount of product formed with respect to time. $R$ is usually expressed in mol/s. Applying Kim et al.’s model [51] to the calculation of $R$, we obtain:

$$\frac{d\text{m}\text{CO}_2(H)}{dt} = k_f M_{\text{CO}_2(H)}A_{de} \Delta H (f_G^{\text{CO}_2} - f_H^{\text{CO}_2})$$  

(Eq 4-1)
\( \frac{\text{dm}_{\text{CO}_2(H)}}{\text{dt}} \) is the rate of CO\(_2\) hydrate formed (kg.s\(^{-1}\)); \( k_f \) is the formation rate constant (kmol/m\(^2\).kPa.s);

\( M_{\text{CO}_2(H)} \) is the molecular weight of carbon dioxide hydrate (kg/kmol); \( A_{\text{dec}} \) is the area of decomposition per unit volume (m\(^{-1}\)); \( A \) is the surface area (m\(^2\)); \( H \) is the hydrate block thickness (m); \( f_H^{\text{CO}_2} \) is the fugacity of CO\(_2\) in the hydrate phase (kPa) and \( f_G^{\text{CO}_2} \) is the fugacity of CO\(_2\) in the gas phase (kPa). Here, the reaction rate is calculated in kg.s\(^{-1}\). Kim et al.’s equation is modified in consequence to obtain the rate in the adequate set of units.

Similarly, CH\(_4\) hydrate dissociation reaction is described by the following equation:

\[ \text{CH}_4.n_{\text{H}}.\text{H}_2\text{O} \rightarrow \text{CH}_4 + n_{\text{H}}.\text{H}_2\text{O}. \]

The reaction rate \( R = -\frac{\text{dn}_{\text{CH}_4(H)}}{\text{dt}} = \frac{\text{dn}_{\text{CH}_4(g)}}{\text{dt}} \) can be calculated using Kim et al.’s kinetic model [51] and the equation is modified to express R in kg.s\(^{-1}\):

\[ -\frac{\text{dm}_{\text{CH}_4(H)}}{\text{dt}} = k_d M_{\text{CH}_4(H)} A_{\text{dec}} A H (f_H^{\text{CH}_4} - f_G^{\text{CH}_4}) \]  

(Eq 4-2)

\( -\frac{\text{dm}_{\text{CH}_4(H)}}{\text{dt}} \) is the rate of methane hydrate dissociated (kg.s\(^{-1}\)); \( k_d \) is the overall dissociation rate constant (kmol/m\(^2\).kPa.s); \( M_{\text{CH}_4(H)} \) is the molecular weight of methane hydrate (kg/kmol); \( A_{\text{dec}} \) is the area of decomposition per unit volume (m\(^{-1}\)); \( A \) is the surface area (m\(^2\)); \( H \) is the hydrate block thickness (m);

\( f_H^{\text{CH}_4} \) is the fugacity of CH\(_4\) in the hydrate phase (kPa) and \( f_G^{\text{CH}_4} \) is the fugacity of CH\(_4\) in the gas phase (kPa).

\[ 4.1.4.2. \text{ Energy balance equations} \]

Considering a control volume \( V \), the principle of conservation of energy states that:

\[
\left\{ \begin{array}{c}
\text{Rate of accumulation} \\
\text{of energy}
\end{array} \right\}_{\text{in control volume V}} = \left\{ \begin{array}{c}
\text{Rate of energy} \\
\text{entering V}
\end{array} \right\}_{\text{by inflow}} - \left\{ \begin{array}{c}
\text{Rate of energy} \\
\text{leaving V}
\end{array} \right\}_{\text{by outflow}} + Q + \dot{W}_f + \dot{W}_s + \dot{W}_b
\]  

(Eq 4-3)
where $Q$ is the rate of heat added to the control volume by conduction ($W$); $W$ is the rate of work done by the flow stream ($W$); $\dot{W}_s$ is the rate of shaft work ($W$); $\dot{W}_b$ is the rate of work done by moving boundary forces ($W$).

![Diagram of Control Volume](image)

**Figure 4-8: Control Volume**

This principle is applied to the base cap rock; assuming no fluid flow, no heat transfer by radiation or convection, no displacement of the base cap rock and no shaft work. Thus:

$$\text{Rate of accumulation of energy in control volume } V = \frac{dU}{dt} + \frac{d(KE)}{dt} + \frac{d(PE)}{dt} = \frac{dU}{dt} \quad \text{where } U \text{ is the internal energy of the control volume (J)}$$  

$KE$ is the kinetic energy of the control volume (J) and $PE$ is the potential energy of the control volume (J).

$$\begin{align*}
\text{Rate of energy entering } V & = 0; \quad W_f = W_s = 0
\end{align*}$$
Equation 4-3 becomes: \( \frac{dU}{dt} = Q + \dot{W}_b \). There is a relationship between the change in internal energy and the change in temperature, which can be written as \( dU = \rho V C_v dT \). \( C_v \) is the specific heat capacity at constant volume (J/kg.K). For solids, \( C_v = C_p \), which is the specific heat capacity at constant pressure. 

\( Q \) can be expressed using Fourier’s law which relates the heat transfer rate and the temperature gradient.

![Figure 4-9: Schematic representation of the reservoir and assumptions used for the energy balance](image)

Figure 4-9 presents a schematic representation of the reservoir as well as some of the assumptions used in the energy balance calculation. Similar to the work by Gerami and Pooladi-Darvish (2007) [55], the base cap rock is represented by a semi-infinite medium (\( z=0 \) to \( \infty \)) with a variable temperature at the interface, which is the temperature of the hydrate block. The gas layer is assumed to remain at the initial reservoir temperature throughout the exchange process, as explained in section 4.1.3. The volume of the base cap rock remains constant, thus \( \dot{W}_b = 0 \).
The following equation is obtained for the energy balance of the base cap rock:

\[
\frac{\partial T}{\partial t} = \frac{k_r}{\rho_r C_{pr}} \frac{\partial^2 T}{\partial z^2} = \alpha_r \frac{\partial^2 T}{\partial z^2}
\]

(Eq 4-4)

where \(k_r\) is the rock thermal conductivity (W/mK); \(\rho_r\) is the rock density (kg/m\(^3\)); \(C_{pr}\) is the heat capacity of the base rock (J/kg.K) and \(\alpha_r\) is the rock thermal diffusivity (m\(^2\)/s). The initial and boundary conditions can be written as:

1. \(T = T_i\) at \(t = 0; z \geq 0\)
2. \(T = T_{hyd}(t)\) at \(z = 0; t > 0\)
3. \(T = T_i\) at \(z \to \infty; t > 0\)

We apply the conservation of energy to the hydrate block. The change in internal energy of the hydrate layer is associated to the release of energy during the exchange reaction and the heat transfer with the cap rock. We have: \(\dot{W}_b = -P \frac{dV}{dt}\); \(Q\) is expressed with Fourier’s first law of heat conduction. The enthalpy change due to the exchange reaction is also taken into account and can be written as:

\[
\Delta H_{\text{reaction}} = \Delta H_{\text{CH}_4(\text{H})\text{diss}} + \Delta H_{\text{CO}_2(\text{H})\text{form}}
\]

\[
\frac{dT}{dz_{z=0}} = \frac{\rho_{C_{pr}} dT}{k_r dt} + \frac{\Delta H_{\text{reaction}} dm_{hyd}}{k_r A dt}
\]

(Eq 4-5)

### 4.1.4.3. Thermodynamic calculations

The Soave Redlich and Kwong equation of state (SRK EOS) serves to calculate the fugacity of methane and carbon dioxide in the hydrate and gas phases, as well as the compressibility factor of the gas phase throughout the exchange process. The SRK EOS is a cubic equation of state which is an analytical expression relating the pressure, temperature and volume of a system. Coats (1985) [75] developed a Z-factor form of the generalized EOS that can be written as:
$$Z^3 + [(m_1 + m_2 - 1)B - 1]Z^2 + [A + m_1m_2B^2 - (m_1 + m_2)B(B + 1)]Z - [AB + m_1m_2B^2(B + 1)] = 0$$

(Eq 4-6)

The formulas needed to calculate the different components of the above equation are contained in table 4-4.

**Table 4-4: SRK EOS components' formulas**

<table>
<thead>
<tr>
<th>SRK EOS components</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_1 = 0; m_2 = 1; m_1 = 0.48 + 1.574\omega_i - 0.176\omega_i^2$</td>
</tr>
<tr>
<td>$\Omega_{ai} = 0.4274802; \Omega_{bi} = 0.08664035; P_n = \frac{P}{P_{ci}}; T_n = \frac{T}{T_{ci}}$</td>
</tr>
<tr>
<td>$A = \sum_{i} \sum_{j} c_i c_j A_{ij}; A_{ij} = (1-\delta_{ij})(A_i A_j)^{0.5}; A_i = \Omega_{ai}^* [1 + m_i (1 - T_n^{0.5})^2] \frac{P_n}{T_n^2}$</td>
</tr>
<tr>
<td>$B = \sum_{i} c_i B_i; B_i = \Omega_{bi}^* \frac{P_n}{T_n}$</td>
</tr>
</tbody>
</table>

The composition of the gas phase will change during the molecular guest exchange as CO$_2$ is consumed by the hydrate and CH$_4$ is released. The gas phase is treated as a mixture of real gases. Thus, we will need to calculate the compressibility factor of the gas phase or $Z_{mix}$ while the exchange takes place. We have assumed that there is no volume change due to the exchange. Thus, we can write the following equations to describe the state of the gas phase initially and at a certain time $t$, after the beginning of the exchange:

Initially, $P_{initial} V_{freegas} = n_{initial} Z_{initial} RT_{initial}$

At time $t$, $PV_{freegas} = nZ_{mix} RT$

Thus, $P = \frac{nZ_{mix} T}{n_{initial} Z_{initial} T_{initial}} P_{initial}$

After replacing $P$ by the above expression in the calculation of the components of the SRK equations and assuming that the binary interaction coefficients are all equal to zero, we have:
\[ A_i = A_{i(n,T)} Z_{\text{mix}} \] with \[ A_{i(n,T)} = \Omega_i^{\ast} \left[ 1 + m_i (1 - \left( \frac{T}{T_{\text{ci}}} \right)^{0.5} )^2 \right] \frac{n}{n_{\text{initial}}} \frac{1}{T_{\text{initial}}} \frac{1}{P_{\text{initial}}} \frac{T_{\text{ci}}^2}{P_{\text{ci}} T} \]

\[ B_i = B_{i(n,T)} Z_{\text{mix}} \] with \[ B_{i(n,T)} = \Omega_{bi}^{\ast} \frac{n}{n_{\text{initial}}} \frac{T_{\text{ci}}}{T_{\text{initial}}} \frac{P_{\text{initial}}}{P_{\text{ci}}} \frac{1}{Z_{\text{initial}}} \]

Solving Eq 4-6 for \( Z_{\text{mix}} \) becomes equivalent to solving the following equation:

\[ F(Z_{\text{mix}}) = 0 \iff Z_{\text{mix}}^3 - Z_{\text{mix}}^2 + (A - B^2 - B)Z_{\text{mix}} - AB = 0 \iff (DZ_{\text{mix}} - E)Z_{\text{mix}}^2 = 0 \]
with

\[ E = 1 - (c_1 \sqrt{A_{i(n,T)}} + c_2 \sqrt{A_{2(n,T)}})^2 + (c_1 \sqrt{A_{i(n,T)}} + c_2 \sqrt{A_{2(n,T)}})^2 (c_1 B_{i(n,T)} + c_2 B_{2(n,T)}) + (c_1 B_{i(n,T)} + c_2 B_{2(n,T)}) \]

and \( D = 1 - (c_1 B_{i(n,T)} + c_2 B_{2(n,T)})^2 \) for a 2-component mixture.

\[ Z_{\text{mix}} = \frac{E}{D} \]

The CH\(_4\) and CO\(_2\) fugacities are calculated at \( P_g \) and \( T_g \) for the gas phase and at \( P_{\text{eqhyd}} \) and \( T_{\text{hyd}} \) for the hydrate phase. In the case of the hydrate phase, we are able to estimate the hydrate guest fugacity, because at equilibrium conditions: \( f_{\text{gas former, hydrate}} = f_{\text{gas former, gas phase}} \). Below are the formulations used to calculate the fugacities of CH\(_4\) and CO\(_2\) with SRK EOS:

Pure component:

\[ \ln \Phi = Z - 1 - \ln(Z - B) - \frac{A}{B} \ln(1 + \frac{B}{Z}) \]  

(Eq 4-7)

Eq 4-7 serves to estimate the fugacity of CO\(_2\) in the gas phase at the beginning of the exchange process.

Mixture:
\[
\ln \Phi_i = -(\ln Z - B) + \frac{A}{(m_1 - m_2)B} \left( 2 \sum_{i=1}^{n_c} A_i c_i - B_i \right) \ln \left( \frac{2 + m_2 B}{2 + m_1 B} \right) + \frac{B_i}{B} (Z - 1)
\]  
(Eq 4-8)

where \( \Phi = f/P \) is the fugacity coefficient; \( Z \) is the compressibility factor calculated with Eq 4-6; \( A \) and \( B \) are coefficients related to the EOS.

At time \( t \), during the exchange, it is possible to calculate the pressure in the gas phase using:

\[
P_{\text{freesg}} = \frac{\text{molefreesg} Z_{\text{max}} T_{\text{freesg}}}{V_{\text{freesg}}}
\]  
(Eq 4-9)

### 4.2. Model for the CO\(_2\)-CH\(_4\) exchange in hydrates

A model was developed under MATLAB environment to simulate the CO\(_2\)-CH\(_4\) molecular guest exchange within CH\(_4\) hydrates. This model can be qualified as non-isothermal as we are allowing the temperature of the hydrate block to change during the exchange process. Reservoir and hydrate properties are fed into the program. Initial reservoir conditions are chosen so that the fugacity difference between the fluid phase and the hydrate phase is positive for CO\(_2\) and negative for CH\(_4\) and the exchange can start immediately. In order to simplify the calculation of the methane hydrate dissociation and CO\(_2\) hydrate formation rates, as the exchange evolves in time, we chose to discretize the experiment duration into small equal intervals \( \Delta t \). The fugacities of CH\(_4\) and CO\(_2\) in the gas phase and hydrate phase are updated for every time step using Eq 4-8. Then, the amounts of CH\(_4\) released and CO\(_2\) hydrate formed are estimated using the following:

\[
-\frac{dm_{\text{CH}_4(H)}}{dt} = -\frac{m_{\text{CH}_4(H)}^{n+1} - m_{\text{CH}_4(H)}^n}{\Delta t} \rightarrow m_{\text{CH}_4(H)}^{n+1} = m_{\text{CH}_4(H)}^n + \frac{dm_{\text{CH}_4(H)}}{dt} \Delta t
\]  
(Eq 4-10)

\[
\frac{dm_{\text{CO}_2(H)}}{dt} = \frac{m_{\text{CO}_2(H)}^{n+1} - m_{\text{CO}_2(H)}^n}{\Delta t} \rightarrow m_{\text{CO}_2(H)}^{n+1} = m_{\text{CO}_2(H)}^n + \frac{dm_{\text{CO}_2(H)}}{dt} \Delta t
\]  
(Eq 4-11)

\( \frac{dm_{\text{CH}_4(H)}}{dt} \) and \( \frac{dm_{\text{CO}_2(H)}}{dt} \) are estimated with a first order Taylor series expansion.
Then, the cumulative amounts of CH$_4$ released and CO$_2$ consumed in moles for every time step are given by:

\[
mole_{\text{CH}_4\text{released}}^{n+1} = mole_{\text{CH}_4\text{released}}^n + 0.1481\left(-\frac{dm_{\text{CH}_4(\text{H})}}{dt}\right) \frac{\Delta t}{M_{\text{CH}_4(\text{H})}}
\]

(Eq 4-12)

\[
\text{CO}_2\text{trappedcumul}^{n+1} = \frac{0.1481mole_{\text{CO}_2(\text{H})}^{n+1}}{\text{Cor}}
\]

(Eq 4-13)

with \(\text{Cor} = \frac{M_{\text{CH}_4(\text{H})}}{M_{\text{CO}_2(\text{H})}} \sum_{i}^{\text{ntimesteps}} \frac{dm_{\text{CO}_2(\text{H})}}{dt} \cdot i \)

Because the rates of formation and dissociation of CO$_2$ hydrates and CH$_4$ hydrates are different, a correction factor “Cor” was introduced in the equations in order to allow the amounts of CO$_2$ consumed and CH$_4$ released during the exchange to be equal at every time step. This technique justifies the assumption of an ideal molecular exchange where all methane molecules within the hydrate are replaced by carbon dioxide molecules.

Material balance is verified at every time step during the exchange. The amount of gas in the gas phase is given by:

\[
mole_{\text{free gas}} = mole_{\text{gas initial}} - \text{CO}_2\text{cumultrapped} + mole_{\text{CH}_4\text{released}}
\]

(Eq 4-14)

The composition of the gas phase and the hydrate phase at every time step can also be determined:

\[
y_{\text{CH}_4} = \frac{mole_{\text{CH}_4\text{released}}}{mole_{\text{free gas}}}
\]

(Eq 4-15)

\[
y_{\text{CO}_2} = \frac{mole_{\text{CO}_2\text{initial}} - \text{CO}_2\text{trappedcumul}}{mole_{\text{free gas}}}
\]

(Eq 4-16)

\[
\text{CH}_4\text{hydfrac} = \frac{mole_{\text{CH}_4\text{initial}} - mole_{\text{CH}_4\text{released}}}{mole_{\text{CH}_4\text{initial}}}
\]

(Eq 4-17)
CO2hydfrac = \frac{\text{CO2}\text{trappedcumul}}{\text{moleCH4initial}} \quad \text{(Eq 4-18)}

Successful exchange leads to \( \text{CH4hydfrac} + \text{CO2hydfrac} = 1 \). The temperature of the hydrate block and the pressure of the gas phase are also updated, as the exchange process evolves with time. Laplace transforms serve in the calculation of the temperature of the base cap rock with time. For simplification purposes when converting the solution from the Laplace domain to the real domain, the hydrate block temperature is taken constant. We obtain:

\[
T_{\text{rock}}(z, t) = T_{\text{hyd}} \text{erfc} \left( \frac{z}{2\sqrt{\alpha_t t}} \right) + T_i (1 - \text{erfc} \left( \frac{z}{2\sqrt{\alpha_t t}} \right)) \quad \text{(Eq 4-19)}
\]

with the following initial and boundary conditions

1. \( T = T_i \) at \( t = 0; \ z \geq 0 \)
2. \( T = T_{\text{hyd}}(t) \) at \( z = 0; \ t > 0 \)
3. \( T = T_i \) at \( z \rightarrow \infty; \ t > 0 \)

We would like to apply the same type of solution to the calculation of the temperature of the base cap rock over an interval \([t_n, t_{n+1}]\). On such interval, we neglect the difference between \( T_{\text{hyd}}^n \) and \( T_{\text{hyd}}^{n+1} \), so that \( T_{\text{hyd}} \) can be considered constant when using the Laplace transforms technique. We also use the average base cap rock temperature instead of the initial temperature for initial and boundary conditions (see (1) and (3)). Applying the above assumptions, the base cap rock temperatures can be given as:

\[
T_{\text{rock}}^{n+1}(z) = T_{\text{hyd}}^{n+1} \text{erfc} \left( \frac{z}{2\sqrt{\alpha_t \Delta t}} \right) + T_{\text{rockavg}}^n (1 - \text{erfc} \left( \frac{z}{2\sqrt{\alpha_t \Delta t}} \right)) \quad \text{(Eq 4-20)}
\]

\[
T_{\text{rockavg}}^{n+1} = (T_{\text{hyd}}^{n+1} - T_{\text{rockavg}}^n) \frac{2\sqrt{\alpha_t \Delta t}}{h_{\text{rock}}} \left( \frac{h_{\text{rock}}}{2\sqrt{\alpha_t \Delta t}} \text{erfc} \left( \frac{h_{\text{rock}}}{2\sqrt{\alpha_t \Delta t}} \right) - \frac{\frac{h^2}{4M_0}}{\sqrt{\pi}} + \frac{1}{\sqrt{\pi}} + T_{\text{rockavg}}^n \right) \quad \text{(Eq 4-21)}
\]
In the case of the hydrate block temperature, the difference between $T_{\text{hyd}}^n$ and $T_{\text{hyd}}^{n+1}$ is not neglected.

Applying the Laplace transform technique to Eq 4-5, the hydrate block temperature can be written as:

$$T_{\text{hyd}}^{n+1} = \frac{K_1'}{1 + K_1'} T_{\text{hyd}}^n - \frac{K_2'}{1 + K_1'} \left( - \frac{dm_{\text{CH}_4(H)}}{dt} \right) + \frac{T_{\text{rockavg}}^n}{1 + K_1'}$$

(Eq 4-22)

with

$$K_1' = \frac{\rho_{c,H}}{k_r} \sqrt{\frac{\alpha_r \pi}{t}}$$

$$K_2' = \frac{\Delta H_{\text{reaction}}}{k_r A} \sqrt{\frac{\alpha_r \pi}{\Delta t}}$$

Finally, Eq 4-6 and 4-9 serve to estimate the Z-factor of the gas phase and the new pressure after the exchange. The entire procedure is repeated for subsequent time intervals until it is no more possible to extract methane from the hydrate block. A flow chart displaying the different steps involved in modeling the exchange for the chosen reservoir geometry and conditions is presented in figure 4-10.
4.3. Sensitivity analysis

4.3.1. Presentation of the base case scenario

We have studied a hypothetical hydrate reservoir constituted of a hydrate layer with a top gas layer and a base cap rock. No flow was considered for this study. The gas layer was initially filled with carbon dioxide. The reservoir conditions (pressure, temperature) determine the types of production techniques that can be applied for methane recovery.
Figure 4-11: Methane and Carbon dioxide stability regions in permafrost environments

Figure 4-11 displays the phase diagrams of methane and carbon dioxide hydrates. The pressure and temperature conditions in permafrost environments as well as the carbon dioxide vapor pressure curve are also represented on the above chart. The information used to evaluate the pressure and temperature conditions in permafrost regions are contained in table 4-5.

Table 4-5: Data used in the calculation of (P,T) conditions in permafrost environments

| Pore pressure gradient (MPa/m) | 0.01 |
| Temperature at the permafrost surface (°C) | -10 |
| Temperature equation for depths below 600 m | -10(°C)+Depth(m)x0.017 (°C/m) |
| Temperature equation for depth above 600 m | -15(°C)+Depth(m)x0.025 (°C/m) |

Zones A, B, C and D are of interest in this study. In zone A, both methane hydrates and carbon dioxide hydrates can be found. The CO_{2}-CH_{4} exchange method can be used to recover methane from the hydrate deposits. However, since zone A is above the carbon dioxide vapor pressure curve, CO_{2} will be liquid at
those conditions. Thus, it will be necessary to inject CO$_2$ liquid instead of CO$_2$ gas into the hydrate formation for recovery purposes.

Similar observations can be made for the pressure and temperature conditions at stake in zone B. The major difference is that CO$_2$ gas should be used for methane recovery purposes, as zone B falls below the CO$_2$ vapor pressure curve. On the other hand the CO$_2$-CH$_4$ exchange method might not be applicable to reservoir conditions within zones C and D as these zones are outside the methane hydrate stability region. Zone E represents (P,T) conditions where CH$_4$ hydrates are stable while CO$_2$ hydrates should not form. Therefore, the exchange method might not be successful when applied to deposits with such reservoir conditions.

Figure 4-12: Methane and Carbon dioxide hydrate stability regions in marine environments
Figure 4-12 shows the phase diagrams of methane hydrate and carbon dioxide hydrates. The pressure and temperature conditions in marine environments as well as the carbon dioxide vapor pressure curve are also represented on the above chart. The information used to evaluate the pressure and temperature conditions in marine regions are contained in table 4-6.

Table 4-6: Data used in the calculation of (P,T) conditions in oceanic environments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore pressure gradient (MPa/m)</td>
<td>0.01</td>
</tr>
<tr>
<td>Temperature at the ocean floor (°C)</td>
<td>4</td>
</tr>
<tr>
<td>Temperature equation for depths below 1200 m</td>
<td>-32(°C)+Depth(m)x0.03 (°C/m)</td>
</tr>
</tbody>
</table>

Zones A1, B1, C1 and D1 are of interest for this study for they fall within the boundary of (P,T) conditions in marine environments. No methane hydrates can be found for (P,T) conditions belonging to zones C1 and D1 because they are outside the methane hydrate stability region. Methane hydrate can be found in formations with (P,T) conditions inside zone A1. However, the CH$_4$-CO$_2$ exchange technique might not be effective as carbon dioxide hydrate cannot be formed in that region.

In the case of marine environments, the CO$_2$-CH$_4$ exchange technique can be applied to reservoirs whose conditions fall into zone B1 to recover methane without decomposition of the hydrate accumulations. CO$_2$ liquid should be injected into such reservoirs as the pressure and temperature conditions of zone B1 are above the CO$_2$ vapor pressure curve. Pressure limitations at certain temperatures for reservoirs within the zones A and B in permafrost environments and B1 in oceanic environments are presented in table 4-7:
Table 4-7: Pressure limitations at selected temperatures for zones A, B and B1 of permafrost and oceanic environments

<table>
<thead>
<tr>
<th>Stability region</th>
<th>Temperature (K)</th>
<th>CO₂ hydrate equilibrium pressure (atm)</th>
<th>CH₄ hydrate equilibrium pressure (atm)</th>
<th>CO₂ liquid – vapor equilibrium pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone B in permafrost regions (CH₄ hydrate can be produced with injection of gaseous CO₂)</td>
<td>268.15</td>
<td>9.39</td>
<td>22.1</td>
<td>29.92</td>
</tr>
<tr>
<td></td>
<td>269.15</td>
<td>9.72</td>
<td>22.8</td>
<td>30.71</td>
</tr>
<tr>
<td></td>
<td>270.15</td>
<td>10.06</td>
<td>23.4</td>
<td>31.52</td>
</tr>
<tr>
<td></td>
<td>271.15</td>
<td>10.42</td>
<td>24.1</td>
<td>32.34</td>
</tr>
<tr>
<td></td>
<td>272.15</td>
<td>10.78</td>
<td>24.9</td>
<td>33.19</td>
</tr>
<tr>
<td></td>
<td>273.15</td>
<td>12.26</td>
<td>25.2</td>
<td>34.05</td>
</tr>
<tr>
<td></td>
<td>274.15</td>
<td>13.96</td>
<td>28.6</td>
<td>34.93</td>
</tr>
<tr>
<td></td>
<td>275.15</td>
<td>15.59</td>
<td>31.4</td>
<td>35.83</td>
</tr>
<tr>
<td></td>
<td>276.15</td>
<td>17.45</td>
<td>34.5</td>
<td>36.75</td>
</tr>
<tr>
<td>Zone A in permafrost regions and zone B1 in oceanic regions (CH₄ hydrate can be produced with injection of liquid CO₂)</td>
<td>278.15</td>
<td>21.98</td>
<td>41.8</td>
<td>38.66</td>
</tr>
<tr>
<td></td>
<td>279.15</td>
<td>24.78</td>
<td>46.1</td>
<td>39.64</td>
</tr>
<tr>
<td></td>
<td>280.15</td>
<td>28.03</td>
<td>50.8</td>
<td>40.65</td>
</tr>
<tr>
<td></td>
<td>281.15</td>
<td>31.91</td>
<td>56.1</td>
<td>41.67</td>
</tr>
<tr>
<td></td>
<td>282.15</td>
<td>36.56</td>
<td>62</td>
<td>42.72</td>
</tr>
<tr>
<td></td>
<td>283.15</td>
<td>42.36</td>
<td>68.6</td>
<td>43.79</td>
</tr>
</tbody>
</table>

For the purpose of this study, we have mainly focused on hydrate deposits in the permafrost regions. The base case scenario has been designed in order to examine the performance of the CO₂-CH₄ molecular guest exchange process for reservoir conditions placed in zone B, thus requesting the injection of gaseous CO₂ into the reservoir. We restrain our study to these types of reservoirs for the pressures at stakes are low (≈2-3 MPa; 290-435 psia) and the temperatures are moderate (≈ 267K-277 K). These conditions are easier to reproduce in the laboratory and less costly, which can enable the comparison of simulation results to experimental outcomes. The hydrate containing formation conditions, physical properties and parameters are tabulated in tables 4-8, 4-9 and 4-10.
### Table 4-8: Reservoir conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir Area (m²)</td>
<td>40468.56</td>
</tr>
<tr>
<td>Hydrate zone (m)</td>
<td>10</td>
</tr>
<tr>
<td>Gas zone (m)</td>
<td>10</td>
</tr>
<tr>
<td>Cap rock thickness (m)</td>
<td>10</td>
</tr>
<tr>
<td>Hydrate saturation (Hydrate zone)</td>
<td>0.8</td>
</tr>
<tr>
<td>Gas saturation (Gas zone)</td>
<td>1</td>
</tr>
<tr>
<td>Porosity (Hydrate zone)</td>
<td>0.3</td>
</tr>
<tr>
<td>Porosity (Gas zone)</td>
<td>0.9</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>268.15</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>28</td>
</tr>
<tr>
<td>Initial gas in place (SCM)</td>
<td>1.95x10⁶</td>
</tr>
</tbody>
</table>

### Table 4-9: Physical properties of rock, hydrate and water

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rock</strong></td>
<td></td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>2650</td>
</tr>
<tr>
<td>Heat capacity (J/kg.K)</td>
<td>800</td>
</tr>
<tr>
<td>Thermal conductivity (W/m.K)</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Hydrate</strong></td>
<td></td>
</tr>
<tr>
<td>Molecular weight (kg/kmol)</td>
<td>17.74</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>913</td>
</tr>
<tr>
<td>Heat capacity (J/kg.K)</td>
<td>1600</td>
</tr>
<tr>
<td>Thermal conductivity (W/m.K)</td>
<td>0.393</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td></td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>1000</td>
</tr>
<tr>
<td>Heat capacity (J/kg.K)</td>
<td>4180</td>
</tr>
<tr>
<td>Thermal conductivity (W/m.K)</td>
<td>0.6</td>
</tr>
</tbody>
</table>

### Table 4-10: Hydrate parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_d^0$ (kmol/m².kPa.s) (Kim et al., 1987) [51]</td>
<td>3.6x10⁴</td>
</tr>
<tr>
<td>$A_{HS}$ (m⁻¹)</td>
<td>3.00x10⁵</td>
</tr>
<tr>
<td>$E/R$ (K)</td>
<td>9400</td>
</tr>
<tr>
<td>$A_{dec}$ (m⁻¹) (Hong and Pooladi-Darvish, 2005) [76]</td>
<td>$\Phi_{HS}A_{HS}$</td>
</tr>
<tr>
<td>$k_d$ (kmol/m².kPa.s) (Kim et al., 1987) [51]</td>
<td>$k_d^0\exp(\frac{E}{RT})$</td>
</tr>
<tr>
<td>$P_{eqCH4hyd}$ (kPa) (T≤273.15 K) (Sloan and Koh, 2008) [4]</td>
<td>$\exp(14.717 - \frac{1886.79}{T})$</td>
</tr>
<tr>
<td>$P_{eqCH4hyd}$ (kPa) (T&gt;273.15 K) (Sloan and Koh, 2008) [4]</td>
<td>$\exp(38.980 - \frac{8533.80}{T})$</td>
</tr>
<tr>
<td>$\Delta H_{CH4(H)disss}$ (J/kg) (Gerami and Pooladi-Darvish, 2007)</td>
<td>477000</td>
</tr>
<tr>
<td>$k_f$ (kmol/m².kPa.s) (Malegaonkar et al., 1997) [77]</td>
<td>0.35x10⁻¹⁰</td>
</tr>
<tr>
<td>$P_{eqCO2hyd}$ (kPa) (T≤283.17 K) (Sloan and Koh, 2008) [4]</td>
<td>$\exp(44.580 - \frac{10246.28}{T})$</td>
</tr>
<tr>
<td>$P_{eqCO2hyd}$ (MPa) (T&gt;283.17 K) (Jung et al., 2010) [78]</td>
<td>$3.34x10^{-4}\left(\frac{T}{273.15}\right)^{264.4}$</td>
</tr>
</tbody>
</table>
4.3.2. Model results for the base case scenario

The CO$_2$-CH$_4$ exchange model was run using the properties contained in tables 4-8 through 4-10. The hydrate block temperature, hydrate phase composition and recovery are presented in the following figures.

Figure 4-13: Fractions of CO$_2$ and CH$_4$ in the hydrates during the exchange

Figure 4-13 presents the evolution of the composition of the hydrate phase during the exchange. The curves displayed on the plot represent the ratios of the amount of CO$_2$ trapped and CH$_4$ remaining relative to the initial amount of CH$_4$ contained in the hydrates. As time evolves, we can see that the methane fraction in the hydrate decreases while the carbon dioxide fraction simultaneously increases, thus displaying the success of the CO$_2$-CH$_4$ molecular guest exchange. It is noticeable that for these reservoir conditions, the amount of methane initially trapped in the hydrates is not completely replaced.
by the injected gaseous CO$_2$. The exchange process takes place in 15420 seconds (4.28 hours) and 57.42% of the initial methane content is recovered.

Figure 4-14: Rates of methane hydrate dissociation and carbon dioxide hydrate formation during the exchange

Figure 4-14 shows the calculated rates of methane hydrate dissociation and carbon dioxide hydrate formation during the exchange. The dissociation rate of CH$_4$ hydrate decreases during the exchange. Indeed, as more methane is extracted, $f^G_{\text{CH}_4}$ approaches $f^H_{\text{CH}_4}$. The fugacity difference for CH$_4$ reaches zero at $t=15420$ seconds (4.28 hours). Beyond that time, $f^G_{\text{CH}_4}$ becomes greater than $f^H_{\text{CH}_4}$ and the newly dissociated CH$_4$ hydrate should form again, which is why the exchange is stopped. Similarly, we can observe a decrease in the rate of CO$_2$ hydrate formation, which is significant of the decrease in the fugacity difference between the fluid phase and the hydrate phase for that component. At $t=15420$ s, the formation rate of CO$_2$ hydrate is still higher than zero, which is an indication that equilibrium has not yet been reached. In this case, the exchange is limited by the dissociation of methane hydrates.
Figure 4-15: Temperature of the hydrate block and its time derivative throughout the exchange

Figure 4-15 displays the evolution of the hydrate block temperature and of its time derivative throughout the exchange. We can notice that the exchange reaction causes a slight elevation of the hydrate block temperature over the duration of the experiment. $T_{\text{hyd}}$ goes from 268.15 K to 269.2 K by the end of the exchange. This is in agreement with the exothermic exchange assumption, considering that the CO$_2$ hydrate formation equation is exothermic and its enthalpy is larger than the enthalpy of dissociation of CH$_4$ hydrate. We also assumed for the calculation of the new base rock temperature after the exchange that the difference between $T_{\text{hyd}}^n$ and $T_{\text{hyd}}^{n+1}$ would be small enough to be neglected. As can be seen in Figure 4-15, the values of the hydrate block temperature time derivative stay below $6 \times 10^{-4}$ K/s throughout the exchange process.
Figure 4-16: Percentage of initial methane recovered during exchange

Figure 4-16 displays the percentage of the initial volume of methane that gets recovered during the exchange. After 15420 seconds (4.28 hours), 57.42% of the methane initially in place have been replaced by carbon dioxide in the hydrate. For this case scenario, the recovery percentage is lower than the 64% reported by Lee et al. (2003) [37], but still close. The final hydrate is a mixed CO$_2$-CH$_4$ hydrate with the following formula: $4.58\text{CO}_2\bullet 3.42\text{CH}_4\bullet 46\text{H}_2\text{O}$.

4.3.3. Model results for a reservoir in marine conditions

The CO$_2$-CH$_4$ exchange program was run for a reservoir at $T_{res}=277.15$ K and $P_{res}=88.8$ atm (1305 psia). All the other parameters of table 4-8, 4-9 and 4-10 were kept constants. CO$_2$ (L) was injected into the reservoir instead of CO$_2$ (G) because of the reservoir conditions. The obtained results can be seen in figures 4-17 through 4-20.
Figure 4-17: Fractions of CH₄ and CO₂ in the hydrate phase during the exchange

Similar to the results obtained in section 4.3.2, the fraction of methane in the hydrate phase decreases while the fraction of carbon dioxide in the hydrate phase increases during the exchange. The experiment duration is shorter in this case (t=850s; 14.17 min) and 100% of the initial methane is recovered from the reservoir. Indeed, we have higher fugacity values for methane and especially for carbon dioxide in the fluid and hydrate phases, which is in agreement with the fact that hydrates formed with liquid CO₂ have higher equilibrium pressures than hydrates formed with gaseous CO₂. Thus, we have higher magnitudes for the driving forces of the exchange allowing the entire initial methane content to be extracted after 850 seconds.
Figure 4-18: Calculated rates of dissociation of CH₄ hydrate and CO₂ hydrate during the exchange

As can be seen in figure 4-18, the rates of dissociation of CH₄ hydrate and formation of CO₂ hydrate follow the same evolution trend as in section 4.3.3. CH₄ hydrate dissociates at an increasingly slower rate as CH₄ molecules are replaced by CO₂ molecules in the hydrate lattice and CO₂ hydrate gets formed. The same can be observed for the formation of CO₂ hydrates. We can also notice that faster reaction rates and shorter reaction times are achieved, which is in agreement with observations by Zhao et al. (2012) [43] about the use of liquid CO₂ for the exchange. At the end of the exchange, both rates are still higher than zero, thus indicating that the exchange is stopped before any of the involved reactions can reach equilibrium. In this case, we can say that the amount of reactant (CH₄ hydrates) limits the exchange process.
Figure 4-19: Temperature of the hydrate block and its time derivative during the exchange

Figure 4-19 displays how the temperature of the hydrate block evolves during the exchange. It can be seen that $T_{\text{hyd}}$ rises from 277.15 K to 279.1 K. The hydrate block temperature time derivative values stay below $3 \times 10^{-3}$ K/s throughout the exchange, as it can be observed from figure 4-20.
Figure 4-20: Percentage of methane recovery during the exchange

As it is shown in figure 4-21, 100% of the methane initially in place can be recovered for these reservoir conditions by the end of the experiment. This percentage is higher than the previously calculated methane recovery with CO$_2$ (g). It is also above the 64% recovery stated by Lee et al. (2003) [37]. The results are in accordance with the observations reported in recent publications [43]. Yet, it might not be practically possible to extract 100% of the hydrate deposits’ initial methane content, even if higher CO$_2$ pressures in the gas layer should lead to better recoveries. Indeed, this result is closely related to the assumptions of deep decomposition, perfect stoichiometry and exchange within all hydrates’ cages.

4.3.4. Sensitivity analysis for reservoirs in permafrost conditions

In this section, we will be looking at the effects of the initial temperature, initial pressure, CH$_4$ hydrate dissociation kinetics, rock thermal conductivity, hydrate layer thickness, hydrate layer porosity and cap
rock thickness over the performance of the CO$_2$-CH$_4$ exchange within hydrate as a production technique for reservoirs in permafrost environments.

4.3.4.1. Effect of the initial reservoir pressure on methane recovery from hydrates

In an effort to evaluate the effect of the initial reservoir temperature on the exchange, the CO$_2$-CH$_4$ MATLAB replacement model within hydrates was run at T=270.15 K for the following pressures: P=25 atm (367 psia), P=30 atm (441 psia), P=35 atm (514 psia) and P=40 atm (588 psia). It is important to notice that at T=270.15 K, the CO$_2$ liquid-vapor equilibrium pressure is 31.5 atm (463 psia). Thus, the two last pressures investigated in this case scenario will require the injection of liquid CO$_2$ into the formation.

![Figure 4-21: Effect of reservoir initial pressure on recovery (T=270.15 K)](image-url)
Figure 4-21 displays the model results at T=270.15 K. It can be seen that the cumulative recovery percentage of methane at the end of the exchange process, increases with higher initial pressures. This is in agreement with the effect of initial reservoir pressure on recovery that has been described in the literature ([43] and [44]). The duration of the exchange process also increases. It can be explained by the fact that more CO$_2$ is injected into the formation with higher pressures, thus the CO$_2$ fugacity difference between the fluid phase and the hydrate phase becomes larger. This allows more CH$_4$ to be replaced within the hydrates, since it results in greater CH$_4$ hydrate dissociation rates (see Figure 4-24). It also takes longer for the CH$_4$ hydrate formation reaction to reach equilibrium as it can be seen in figure 4-22.

![Effect of Reservoir Initial Pressure on CO$_2$ Hydrate Formation Rate](image1)

![Effect of Reservoir Initial Pressure on CH$_4$ Hydrate Dissociation Rate](image2)

Figure 4-22: Effect of the initial reservoir pressure on the CO$_2$ hydrate formation rate and CH$_4$ hydrate dissociation reaction rate (T=270.15 K)
4.3.4.2. Effect of initial reservoir temperature on methane recovery from hydrates

The CO$_2$-CH$_4$ MATLAB replacement model within hydrates was run at P=29 atm (426 psia) for temperatures ranging from 268.15 K to 274.15 K. The results are presented in the figures below.

Figure 4-23: Effect of initial reservoir temperature on recovery (P=29 atm)

Figure 4-23 displays the effect of changing the initial reservoir temperature on recovery. It is noticeable that higher temperatures lead to higher recovery ratios. The slopes of the recovery curves at T=272.15 K and T=274.15 K indicate the maximum recovery ratios for those temperatures should be greater than the ones obtained at T=268.15 K and T=270.15 K. This observation is in agreement with the effect of initial reservoir temperature that has been reported in the literature ([43] and [44]). However, increasing the initial reservoir temperature moves reservoir conditions closer to the CO$_2$ hydrate phase equilibrium curve. Thus, the difference between f$_{CO2}^H$ and f$_{CO2}^G$ is further reduced, leading to shorter reaction
durations. The reaction is stopped before the maximum recovery ratios can be reached. This fact is illustrated in figure 4-24.

Figure 4-24: Effect of reservoir initial temperature on the CO$_2$ hydrate formation and CH$_4$ hydrate dissociation rates (P=29 atm)

Indeed, the rates of CO$_2$ hydrate formation decrease while you increase the initial temperature of the reservoir. On the other hand, we have higher CH$_4$ hydrate dissociation rates for higher reservoir initial temperatures. For T=268.15 K and T=270.15 K, the exchange process is limited by CH$_4$ hydrate dissociation as the rates of CH$_4$ hydrate dissociation reach zero before the rates of CO$_2$ hydrate formation. For higher initial reservoir temperatures, the exchange process becomes limited by CO$_2$ hydrate formation reaction. The lowest reaction time is $t=800$ seconds ($\approx 14$ mins) at T=274.15 K and P=29 atm (429 psia).
4.3.4.3. Effect of hydrate cap thickness on recovery from hydrates

The model was run to evaluate the effect of hydrate cap thickness on recovery at \( h=5 \text{m} \), \( h=10 \text{m} \) and \( h=20 \text{m} \). Results are presented in figure 4-25.

![Effect of hydrate cap thickness on recovery](image)

**Figure 4-25: Effect of hydrate cap thickness on recovery**

Three different thicknesses were evaluated for the reservoir conditions presented in table 4-7. The hydrate layer porosity and saturation were kept constant at \( \phi=0.3 \) and \( S_h=0.8 \). As it can be seen, recovery ratios decreases with increasing hydrate cap thicknesses. This can be attributed to the fact that increasing the hydrate layer thickness increases the volume of hydrate of the formation and its methane content. The thickness of the free gas layer is kept constant as well as the initial reservoir conditions. Thus, less CO\(_2\) is available for recovery of methane from hydrates and less methane can be released from the formation. The dissociation of CH\(_4\) reaches equilibrium \( (f_{CH4}^G = f_{CH4}^H) \) faster, which leads to
shorter reaction times for \( h = 10 \text{m} \) and \( h = 20 \text{m} \). For \( h = 5 \text{m} \), the reaction is stopped because 100% recovery has been reached.

### 4.3.4.4. Effect of gas layer thickness on recovery from hydrates

The model was run for different values of the free gas layer thickness in order to examine its effect on recovery. Results are presented in figure 4-26.

![Figure 4-26: Effect of gas layer thickness on recovery](image)

The free gas layer thickness was increased from 5 m to 20 m for this analysis. It can be observed from the plot that the recovery increases from 28.79% to 100% (see table 4-11). Indeed, increasing the free gas layer thickness while keeping all the other reservoir properties constant implies that more \( \text{CO}_2 \) is available for recovery. As the thickness of the free gas layer is raised, the fugacity difference between the fluid phase and the hydrate phase for \( \text{CO}_2 \) becomes larger. It takes longer times for the exchange
reaction to occur because it takes longer for the driving force to reach zero (h=5m, h=10m); for the case h=20m, the reaction time is shorter because 100% recovery has been reached.

### Table 4-11: Effect of gas layer thickness on recovery and reaction times

<table>
<thead>
<tr>
<th>Gas layer thickness (m)</th>
<th>Recovery (%)</th>
<th>Reaction time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 m</td>
<td>28.79</td>
<td>7740 (2.15 hrs)</td>
</tr>
<tr>
<td>10 m</td>
<td>57.42</td>
<td>15420 (4.28 hrs)</td>
</tr>
<tr>
<td>20 m</td>
<td>99.6</td>
<td>5520 (1.53 hrs)</td>
</tr>
</tbody>
</table>

#### 4.3.4.5. Effect of CH₄ hydrate dissociation kinetic constant on recovery

The CO₂-Ch₄ MATLAB replacement model within hydrates was run at T=268.15 K and P=28 atm (411 psia) for different values of the CH₄ hydrate dissociation kinetic constant. The results are presented in the figures below.

![Figure 4-27: Effect of the CH₄ hydrate dissociation kinetic constant on recovery from hydrates](image-url)
As it can be seen in figure 4-27, the model was run for different orders of magnitude of the CH₄ hydrate dissociation kinetic constant. It can be observed that recovery ratios are not much affected by the CH₄ hydrate dissociation kinetic constant. The duration of the exchange decreases with higher kinetic constants. Indeed, for higher order of magnitudes of the CH₄ hydrate dissociation kinetic constant, it takes shorter times for the exchange to reach equilibrium.

4.3.4.6. Effect of hydrate layer porosity on recovery

The model was run for three different values of the hydrate layer porosity in order to investigate its impact on recovery from hydrate deposits. The results are shown in the figure 4-28.

![Figure 4-28: Effect of the hydrate layer porosity on recovery from hydrates](image)

The model results display that an increase in the hydrate layer porosity causes a decline of the cumulative recovery ratio from hydrates. Indeed, larger hydrate layer porosities are synonym of larger
volumes of hydrates and volumes of trapped gas. Thus the available carbon dioxide becomes insufficient to recover the entire volume of trapped gas.

![Diagram](image.png)

Figure 4-29: Effect of hydrate layer porosity on the CO₂ hydrate formation and CH₄ hydrate dissociation rates during the exchange

Figure 4-29 portrays the effect of the hydrate layer porosity on the CO₂ hydrate formation and CH₄ hydrate dissociation rates during the exchange. It can be seen that the duration of the reaction is shortened with decreasing porosity values. Indeed, at lower hydrate volumes, more methane can be recovered from the hydrates despite the lower rates, because a large amount of carbon dioxide has been supplied for the exchange.

4.3.4.7. Effect of Rock thermal conductivity on recovery

Three different values of the rock thermal conductivity were evaluated in order to investigate their influence on recovery. Results are shown in figure 4-30.
Figure 4-30: Effect of the rock thermal conductivity on recovery from hydrates

Figure 4-30 displays that the rock thermal conductivity has little effect on the recovery from hydrates. Indeed, this property is related to the heat transfer from the hydrate layer to the cap rock. The evolution of the hydrate layer temperature is affected by the heat released from the reaction and the heat transfer between the hydrate layer and the cap rock. This result suggests the heat released from the reaction should have more effect on recovery than the heat exchange with the cap-rock. This is verified by the results plotted in figure 4-31.
Indeed, we can see that the cumulative recovery ratios are improved by raising the enthalpy of the exchange reaction. It can also be observed that we obtain higher hydrate layer temperatures at the end of exchange with higher reaction enthalpies.

### 4.3.5. Comparison with the Gerami and Pooladi-Darvish deep decomposition model

Three major production techniques have so far been suggested for the recovery of methane from hydrates: Depressurization, thermal stimulation and inhibitor injection. Among these, depressurization appears to be the most promising technique to be used for Class 1 hydrate deposits which are deposits associated with a free gas layer. The principle of this production technique is to reduce the pressure in the free gas layer by producing a certain amount of the contained gas. This pressure reduction will instigate the dissociation of neighboring hydrates and allow recovery of the trapped gas. In 2007,
Gerami and Pooladi-Darvish [55] developed a mathematical model of the depressurization production technique, assuming deep decomposition of the hydrate layer. Their solution suggests that hydrate production takes place in two stages: a non-equilibrium stage where methane release is driven by the pressure difference between the gas phase and the hydrate phase and an equilibrium stage where more methane can be released due mainly to the transfer of heat from the adjacent cap rock. Two sets of equations have been developed for both stages, which can be written as:

\[ RH(t) = \frac{Ste}{S_{hi}} \left( 1 - \exp \left( -\frac{\alpha e^\omega}{H^2} t \right) \right) \quad t \leq t_{eq} \]  \hspace{1cm} (Eq 4-23)

\[ RH(t) = \left( \frac{2}{HS_{hi}} \right) \sqrt{\frac{\alpha e^\omega}{\pi}} Ste \sqrt{t} \quad t \geq t_{eq} \]  \hspace{1cm} (Eq 4-24)

For the sake of this study, we are going to compare the results from the CO₂-CH₄ exchange modeling program to the results of the Gerami and Pooladi-Darvish’s model [55] in the non-equilibrium stage, in order to further validate the results from our numerical model. It is important to highlight that the amount of methane released calculated either with our model or with the Gerami and Pooladi-Darvish’s model [55] does not necessarily correspond to the amount of gas produced at the wellhead. In both cases, we are interested in estimating the amount of methane initially trapped in the hydrates that could become accessible for production after being released from the hydrate cages.

The model was run for pressures ranging from 20 atm (294 psia) to 36.75 atm (540 psia) and temperatures between 268.15 K and 276.15K, with \( P_o=6.5 \) atm (96 psia) and \( P_o=20 \) atm (294 psia) . The operating pressure \( P_o \) is the new reduced reservoir pressure obtained prior to depressurization-induced hydrate decomposition. The parameters of table 4-8 through 4-10 were also used. The results are presented in figure 4-32.
Figure 4-32: Comparison of recovery by depressurization and CO$_2$-CH$_4$ exchange within hydrates

Figure 4-32 displays the obtained cumulative recovery ratios of methane for the exchange model and the Gerami and Pooladi-Darvish depressurization model. It can be seen that the CO$_2$-CH$_4$ exchange technique allows the extraction of a higher amount of methane from the hydrates when compared to the depressurization technique, for a high operating pressure P$_o$ relative to the reservoir pressure. When P$_o$ is lowered enough, depressurization yields higher recovery ratios. Furthermore, it can be noticed that for most of the (P,T) conditions evaluated in this case, the exchange technique led to recovery ratios ranging mostly from 60% to 100%. These results reinforce our model’s ability to produce plausible recovery values, as well as the fact that the replacement technique could be a valid option for the extraction of methane from hydrates. However, they do not necessarily present the replacement technique as a better alternative to gas hydrate production than depressurization since the model does not result in higher recoveries by the exchange for all the conditions evaluated here.

4.4. Summary

The results from the numerical evaluation of the CO$_2$-CH$_4$ exchange within hydrates enable to draw the following conclusions:
An increase of the initial reservoir temperature and of the initial reservoir pressure should lead to higher recovery ratios for the exchange; higher methane recoveries and faster reaction rates should also be achieved with the injection of CO₂ liquid, as mentioned in Zhao et al.’s review [43].

The exchange technique may yield low recovery ratios when applied to hydrate reservoirs with a large hydrate zone thickness and porosity associated to a thin gas layer.

The cap rock thermal conductivity does not seem to have an impact on recovery which is instead more affected by the enthalpy of the exchange reaction. Higher enthalpy values result in higher recovery ratios and higher hydrate block temperatures at the end of the exchange.

The outcomes of the Gerami and Pooladi-Darvish depressurization model and of the CO₂-CH₄ exchange in hydrate model for the family of (P, T) conditions analyzed in chapter 4 suggest that the exchange could yield higher recoveries than depressurization under specific circumstances; yet this analysis does not present the replacement technique as a better alternative to gas production from hydrates than depressurization at all conditions. For the conditions investigated in chapter 4, the model produced plausible exchange recovery ratios varying from 60% to 100% in most cases. Thus, the CO₂-CH₄ exchange within hydrates seems to be a legitimate option for hydrate production, offering the double advantage of recovering natural gas while sequestrating carbon dioxide.

Nevertheless, the results obtained in chapter 4, fall under the assumptions of deep decomposition in the hydrate layer, perfect stoichiometry of hydrates and exchange within all hydrate cages, thus making them optimistic predictions. Actual recovery ratios from the field might be lower. In addition, the evolution of temperature with the thickness of the layers and the change of the thermal conductivity and of the specific heat constant with temperature were not incorporated in the model. Thus, conclusions related to the influence of thickness on recovery might be erroneous. Further investigation of the technique is still needed in order to acquire a better match between simulation results and field data.
Chapter 5. Laboratory investigation of the CO$_2$-CH$_4$ exchange within hydrates

In chapter 4, we displayed the feasibility and effectiveness of the CO$_2$-CH$_4$ exchange within hydrates as a potential production technique for the extraction of natural gas from gas hydrate deposits, using a numerical method. We compared the technique to depressurization for a hypothetical permafrost gas hydrate deposit and concluded that the chemical substitution of methane by carbon dioxide within hydrates could lead to higher recoveries under specific conditions. In addition, we would like to examine the effectiveness of the CO$_2$-CH$_4$ exchange technique in the laboratory. A gas hydrate production laboratory was designed for that purpose. In the following section, we will be describing the experimental set up, the goals and the procedures. Preliminary tests were performed, which allowed the modification and improvement of the experimental set up and procedures for a better description of the exchange. Final tests were conducted with a modified experimental equipment leading to a better understanding of the practicality of the exchange and enabling to obtain a set of conditions favorable for the use of that technique. Results from these tests are presented and discussed in this chapter.

5.1. Research goals

The overall purpose of this study is to evaluate the feasibility of the CO$_2$-CH$_4$ exchange in hydrates as a viable production technique for gas hydrates with simultaneous carbon dioxide clathrate sequestration. Hydrates naturally occur in permafrost and oceanic sediments under specific conditions as seen in figures 4-11 and 4-12. The experimental portion of this work is focused on attempting to form gas hydrates in conditions that are representative of the gas hydrate stability settings in permafrost environments. Indeed, the formation of hydrates in the permafrost require lower pressures and higher temperatures when compared to the conditions at stake in oceanic sediments (see figure 4-11 and 4-12). Such conditions, and especially the pressures at stake, are much easier and less costly to reproduce in the laboratory. Methane, carbon dioxide and a mixture of propane and methane were utilized for the
formation of synthetic hydrates in the laboratory. The use of a propane-methane gas mixture is justified since naturally occurring gas hydrates contain mixtures of hydrocarbons with methane being the major component. Formation and dissociation runs were executed in order to get a better understanding of the mechanisms involved in the formation and dissociation of hydrates and compare the obtained results to experimental outcomes presented in the literature. Carbon dioxide was injected into synthetic CH₄ hydrates in an attempt to recover methane from the bulk hydrates. The effect of initial pressures and temperatures of the synthetic hydrates on methane recovery was evaluated.

5.2. Description of the preliminary experimental set-up

A preliminary experimental set-up for the formation and dissociation of bulk gas hydrate samples, along with the investigation of the molecular guest exchange as a production technique was designed and built. Figure 5.1 presents the components of the experimental set-up. The apparatus comprises four main sections: the gas supply section, the hydrate formation, dissociation and production section, the pressure and temperature recording section and the gas recovery section.

![Figure 5-1: Experimental apparatus (gas hydrate formation, dissociation and production section)](image)

Figure 5-1 is an image of the hydrate formation, dissociation and production section. This section is contained inside a 12.8 ft³ Frigidaire commercial freezer. The reaction cell is a 316 stainless steel cylindrical pressure vessel. It was manufactured at the Penn State College of Earth and Mineral Sciences
machine shop. The pressure vessel has a volume of 254 cm$^3$ and an inside diameter of 5.96 cm. A pressure transducer (Omega Engineering, Model: PX303-1KG5V, 0-1000 psig, ± 0.25 % full scale, 1/4” NPT male) is attached to the top cap of the vessel and enables to monitor the pressure inside the cell during the experiments. A type T thermocouple (Omega Engineering, Model: TC-T-1/8NPT-U-72, 1/8” NPT male) is also connected to the top of the vessel and records the changes in temperature. A cryogenic brass pop safety valve has been added to the vessel to avoid issues of pressure overload. The reaction cell is connected to a 316 stainless steel double-ended gas sample cylinder (Swagelok, Part No.:316L-HDF4-500, ¼” NPT female, 0-1800 psig) through a ¼” stainless steel pipe. The sample cylinder has a volume of 500 cm$^3$ and serves as gas reservoir. During gas hydrate formation and production experiments, gas is released from the reservoir and delivered to the reaction cell by using a needle valve (Swagelok, Part No.: SS-4GUF4-G, ¼” NPT female, 0.20 in. (5.0 mm) Orifice). A pressure gauge (Swagelok, Model: PGI-63C-PG400-LAOX, 2 ½” diameter, 0-400 psig, ¼” NPT male, lower mount unfilled) is placed at the head of the gas cylinder in order to check the gas pressure in the cylinder throughout the process. The vessel is immersed in a 50 vol% ethylene glycol-water bath for uniform cooling and heating as needed since this mixture has a freezing point of -37ºC (236.15 K) at atmospheric pressure (instead of 0ºC (273.15 K) for water or -12ºC (261.15 K) for pure ethylene glycol) and our experiments will be performed at temperatures below the freezing point of water. Another type T thermocouple (Omega Engineering, Model: HTTC36-T-18G-6) helps to record the bath temperature.

As most hydrate-related experiments can typically last from several hours to several days, a data acquisition system was designed and incorporated into the experimental apparatus. It enables to check and record the pressure and temperature changes during the experiments. The pressure and temperature recording section of our experimental set up comprises a USB data acquisition module (Omega Engineering, Model: OMB-DAQ-54, 5 single-ended/10 differential volts channel inputs, programmable inputs from ±31 mV to ±20V Full Scale) that collects the measurements from the transducer and the two
thermocouples. A regulated power supply (Omega Engineering, Model: PST-4130, input: 115 Vac ±10%, 50 to 60 Hz, output voltage: adjustable 4 to 15 Vdc) is utilized to provide excitation to the transducer. The measurements are transferred to a computer and analyzed with the software PDAQView [79]. The pressure and temperature recording section is presented in figure 5-2.

![Image](image.png)

**Figure 5-2: Experimental apparatus (Pressure and Temperature recording section)**

Attached to the reaction cell are an inlet pipe that connects it to the gas sample cylinder and an outlet pipe that is linked to a vacuum line and to a gas collector bag. The reaction cell and the gas collector bag are separated by a needle valve. The valve is opened during the hydrate production experiment to allow the released gas to be collected and conserved for further analysis. A 30% C₃H₈- 70%CH₄ gas mixture, pure methane and pure carbon dioxide are used for the creation of synthetic hydrate samples and for the exchange experiments. The gases are supplied by GTS-WELCO and PRAXAIR. Figure 5-3 presents the complete schematic diagram of the preliminary experimental apparatus.
5.3. Preliminary experiments

5.3.1. Trial test of the formation and dissociation of mixed propane-methane hydrates

5.3.1.1. Experimental procedure

We chose to initiate our series of tests with the formation and dissociation of mixed propane-methane hydrates. Indeed, hydrates formed with a 30% C₃H₈ - 70% CH₄ gas mixture have lower stability conditions than methane and carbon dioxide hydrate, as it can be seen in figure 5-4, that are easier and less costly to reproduce in the laboratory.
Figure 5-4: CH₄ hydrate, CO₂ hydrate, and Propane-methane hydrate stability conditions in permafrost environments

The following procedure was used in this test and in subsequent ones for the formation of gas hydrates: 50 ml of water were introduced into a buret, placed above a Dewar flask filled with liquid nitrogen. The water drip was adjusted so that water could slowly fall into liquid nitrogen and form ice pellets. The pellets were collected with a strainer and crushed into snow with the use of a previously cooled coffee grinder. 30 g of snow were collected and placed inside the reaction cell. These steps are displayed in figure 5-5.
Then, the cell was placed inside the freezer and connected back to the experimental apparatus. The sample cylinder was pressurized with 58 psig of the propane-methane gas mixture. We waited a few hours for the gas to be cooled and for the temperature inside the freezer to stabilize at 248.15 K. Following this, the needle valve was opened in order to introduce some gas into the reaction cell. The pressure inside the vessel was equilibrated with the pressure of the gas reservoir at 50 psig. Thus, the needle valve was closed. We noticed a decrease in the vessel’s pressure once the supply of gas was stopped, which could be an indication of the beginning of the hydrate formation. The ice seeds remained
exposed to the gas for 66 hours. At the end of the experiment, the vessel pressure had stabilized around 10 psig.

Next, the freezer was stopped. The bath was heated and the dissociation experiment was started. The bath was heated from 248.15 K to 284.15 K in 28 hours, thus a temperature increase rate of about 1.3 K/hour. At the end of the experiment, the pressure inside the vessel had increased back to 50 psig and 30 grams of liquid water were collected.

5.3.1.2. Results and discussion

The following results were obtained during the trial run for the formation of mixed propane-methane hydrate and are displayed in figure 5-6

![Figure 5-6: Pressure and Gas uptake during formation of mixed propane-methane hydrates](image)

We notice a decrease in the vessel pressure, which could be indicating the conversion of gas into hydrates.
Assuming that all the gas introduced into the sample cell at the beginning of the experiment was consumed by the formation of propane-methane mixed hydrates, the gas uptake was estimated using the following:

\[ n_{G_{\text{total in sample cell}}} = n_{G_{\text{in hydrate}}} + n_{G_{\text{free}}} \]  

(Eq 5-1)

\[ n_{G_{\text{total in sample cell}}} \] is constant because we have a closed system (we stop supplying gas to the sample cell as soon we have reached the required pressure for the experiment).

\[ n_{G_{\text{in hydrate}}} (t) = n_{G_{\text{total in sample cell}}} - n_{G_{\text{free}}} (t) \]  

(Eq 5-2)

At \( t=0 \), \( n_{G_{\text{in hydrate}}} = 0; \ n_{G_{\text{total in sample cell}}} = n_{G_{\text{free}}} = V_{G_{\text{free space}}} \left( \frac{P_{\text{sample cell}}}{ZRT_{\text{sample cell}}} \right)_{t=0} \)

\[ V_{G_{\text{free space}}} = V_{\text{internal sample cell}} - V_{\text{occupied by ice}} \]  

(Eq 5-3)

Table 5-1: Dimensions of the sample cell and the space occupied by ice

<table>
<thead>
<tr>
<th>Sample cell</th>
<th>Height (inches)</th>
<th>Diameter (inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>1.75</td>
<td>2.3125</td>
</tr>
<tr>
<td>Sample cell</td>
<td>3.5</td>
<td>2.3125</td>
</tr>
</tbody>
</table>

Table 5-1 contains the dimensions of the sample cell and of the space occupied by the crushed ice within the cell. These dimensions are used in the evaluation of the free space occupied by the gas mixture.

\[ V_{G_{\text{free space}}} = 1.75 \times \pi \times \frac{2.3125^2}{4} = 7.35 \text{ in}^3 \approx 120.5 \text{ cc} \]

Thus:

\[ n_{G_{\text{in hydrate}}} (t)(\text{cum}) = V_{G_{\text{free space}}} \left( \frac{P_{\text{sample cell}}}{ZRT_{\text{sample cell}}} \right)_0 \left( \frac{P_{\text{sample cell}}}{ZRT_{\text{sample cell}}} \right)_t \]  

(Eq 5-4)

Z-factor was calculated for every time step with the Soave Redlich and Kwong (SRK) equation of state.
As it can be seen in figure 5-6, the total number of moles in the hydrate at the end of the experiment is 16 millimoles. The selected mixture of propane and methane forms type II gas hydrates following the equation [69]: \( G + n_H H_2O \rightarrow G.n_H H_2O \) with \( n_H = 17 \)

The hydrate conversion percent can be estimated as follows:

Amount of water inserted:

\[ n_{H_2O} = \frac{30 \text{ g}}{18 \text{ g/mol}} = 1.67 \text{ mol} \]

\[ n_{G \text{ ideal type II hydrate sample}} = \frac{n_{H_2O}}{17} = 98 \text{ mmol} \]

Percent hydrate conversion:

\[ \frac{n_{G \text{ hydrate } (t_{\text{final}})(cum)}}{n_{G \text{ ideal type II hydrate sample}}} \times 100 = \frac{16}{98} \times 100 = 16.3\% \]

It can be inferred that this trial resulted in a conversion percent of 16.3%. The results obtained during the dissociation experiment can be seen in figure 5-7.
Figure 5-7: Pressure and temperature changes during the dissociation of mixed propane-methane hydrate

We can notice there is an increase in pressure when the hydrate sample temperature is raised via isochoric heating. The final dissociation pressure and temperature are respectively 50 psig and 284 K. Our results were compared with similar work by Prado (2009) [80]. It can be seen in figure 5-8 that the curve we obtained during this trial validates the presence of hydrates as the curve shows the typical trend for a gas hydrate dissociation curve.
Figure 5-8: Comparison of our dissociation results with similar work by Prado (2009) [80]

The real gas law served to estimate the amount of gas present at the end of the decomposition experiment, using the final dissociation conditions. Once again, the Z-factor was calculated with the SRK equation of state. We obtained that 23.2 mmol of gas were present in the sample cell at the end of the experiment corresponding to a hydrate conversion percent of 23.6%. There is a 7% error between the results obtained before and after dissociation that could be coming from an accumulation of measurement and calculation errors. However, both calculations gave results that are in the same order of magnitude and add additional confirmation to the successful formation of synthetic hydrates during the test.

These outcomes are encouraging as they demonstrate that the experimental apparatus is capable of producing hydrates, still they remain low compared to results of 68% conversion obtained by similar studies in the literature [80]. This might be due to experimental errors that occurred during the procedure. In the future, it is essential to try and increase the hydrate conversion percent and obtain better quality samples.
5.3.2. Trial test of the formation and dissociation of pure methane hydrate

5.3.2.1. Experimental procedure

As the chemical substitution within hydrates mainly occurs between CO\textsubscript{2} and CH\textsubscript{4} hydrates, our next step was to create pure hydrate samples. The experimental set-up proposed above was modified in an attempt to optimize the synthesis of gas hydrate samples in the laboratory. The gas reservoir was removed and the sample cell is now directly connected to the gas cylinder in order to reduce potential leaks within the system. The temperature bath volume was also reduced in an effort to decrease heating and cooling periods during experiments. The following procedures were followed for the formation of pure CH\textsubscript{4} hydrates. 40.8 g of ice seed were created with a method similar to the one described in section 5.3.1. The ice seeds were then placed into the sample cell which had previously been cooled to 246.15 K. After the sample cell was sealed, it was pressurized with methane gas at 300 psig. The ice seed remained exposed to the gas for about 144 hours. Pressure and temperature were monitored using the PDAQView data acquisition system. At the end of the experiment, the pressure had stabilized around 140 psig.

Next, the freezer was stopped and the sample cell was warmed from 246.15K to 293.15K in 42 hours, hence a temperature increase rate of 1.12 K/hour. The pressure of the sample cell reached a final value of 163 psig.

5.3.2.2. Results and discussion

The evolution of pressure in the sample cell during the formation of pure methane hydrate can be seen at the top of figure 5-9.
Figure 5-9: Pressure inside the reaction cell during the formation of pure methane hydrate (top) and comparison between experimental conditions and hydrate deposit conditions in permafrost regions (bottom)

Similarly to what occurred with the methane-propane gas mixture, we can notice a decrease in the pressure of the sample cell over time until it stabilizes around 140 psig. This is close to the methane hydrate equilibrium pressure at 246.15 K that has been estimated at 161.5 psia (146.8 psig) with the
CSMHYD software [72]. This pressure trend could be related to (1) gas cooling from room temperature to experiment temperature and (2) the presence of methane gas hydrate inside the vessel. The experimental conditions for this trial run were placed on the plot presented at the bottom of figure 5-9. As it can be observed, the selected pressure conditions are well within the methane hydrate stability region. It can also be noticed that the selected conditions are quite different from the conditions selected for the base case scenario described in chapter 4 or from typical P-T conditions encountered in the permafrost. This is related to the limitations of the experimental set-up. Indeed, experimental temperatures of 268.15 K and above would require the use of much higher pressures for efficient hydrate formation, which would be more complex to handle. Furthermore, the pop-off valve used to avoid pressure overload has a threshold pressure value of 350 psig. The results from the dissociation experiment are presented in figure 5-10.

![Graph showing pressure and temperature changes during dissociation of pure CH₄ hydrate](image)

Figure 5-10: Pressure and temperature changes during the dissociation of pure CH₄ hydrate
Figure 5-10 displays the pressure and temperature data recorded during the hydrate decomposition via isochoric heating. It can be seen that pressure is linearly increasing with temperature between 244 K and 272 K and between 279 K and 290 K. The P-T curve displays a different trend between 272 K and 279 K, which could be attributed to the decomposition of gas hydrate present in the sample cell. In order to validate this observation, we estimated the increase in pressure due to isochoric heating for a closed system with the same constant volume as the free gas space inside the pressure vessel. We used the real gas law to evaluate the number of moles of gas present at the beginning of the dissociation experiment. Assuming that this amount of gas would stay constant in the system, we used the following equation to determine $P/Z$ for different values of temperatures and compared it to $P/Z$ values obtained from the dissociation experiment’s pressure and temperature measurements:

$$\frac{P}{Z} = \frac{nRT}{V}$$  \hspace{1cm} (Eq 5-5)

The results of that comparison are presented in figure 5-11.
Figure 5-11: P/Z values during methane hydrate formation and P/Z values calculated with the real gas law

It can be observed from the results presented in figure 5-11 that the real gas law predicts $\frac{P}{Z}$ evolves linearly with temperature during isochoric heating of a constant amount of CH$_4$ (gas). The deviation between the $\frac{P}{Z}$ values calculated for the heating of CH$_4$ (gas) at constant volume and the $\frac{P}{Z}$ values estimated from the dissociation data of the methane hydrate sample are an indication that an additional amount of gas was progressively released in the pressure vessel, as temperature increased from 244 K to 290 K.

Indeed,
\[
\left(\frac{P}{Z}\right)_{\text{CH}_4(g)\ associated\ with\ CH_{4(g)\ bound}} = \frac{n_{\text{CH}_4(g)\ associated\ with\ CH_{4(g)\ bound}} \cdot RT_{\text{CH}_4(g)\ associated\ with\ CH_{4(g)\ bound}}}{V_{\text{CH}_4(g)\ associated\ with\ CH_{4(g)\ bound}}}
\]

and:

\[
\left(\frac{P}{Z}\right)_{\text{CH}_4(g)} = \frac{n_{\text{CH}_4(g)} \cdot RT_{\text{CH}_4(g)}}{V_{\text{CH}_4(g)}}
\]

with:

\[
V_{\text{CH}_4(g)\ associated\ with\ CH_{4(g)\ bound}} = V_{\text{CH}_4(g)} = V_{\text{G\ free\ space}}
\]

\[
T_{\text{CH}_4(g)\ associated\ with\ CH_{4(g)\ bound}} = T_{\text{CH}_4(g)} = T_{\text{sample\ cell}}
\]

thus:

\[
\left(\frac{P}{Z}\right)_{\text{CH}_4(g)\ associated\ with\ CH_{4(g)\ bound}} - \left(\frac{P}{Z}\right)_{\text{CH}_4(g)} = \frac{RT_{\text{sample\ cell}}}{V_{\text{G\ free\ space}}} \left(n_{\text{CH}_4(g),\ associated\ with\ CH_{4(g)\ bound}} - n_{\text{CH}_4(g)}\right)
\]

Pressure stalls around 157 psig between 275 K and 280 K, which should indicate the end of hydrate dissociation. The additional pressure increase beyond that point is solely due to the fact that the temperature of the sample continues to increase at constant volume. There should be no additional amount of CH\textsubscript{4} that is being released from hydrate dissociation. Figure 5-12 allows the validation of this explanation.
Figure 5-12: Calculated amount of CH₄ in the sample cell during the dissociation of pure methane hydrate

The red curve represents the evolution of the amount of CH₄ in the reaction cell containing CH₄ hydrate during the dissociation experiment. The blue curve corresponds to the evolution of the sample cell pressure with respect to temperature during the dissociation experiment. The black dashed line describes the amount of CH₄ present in a hypothetical sample cell with the same free gas space and containing no hydrates, during an isochoric heating experiment. The amount of CH₄ in the sample cell with no hydrates is kept constant throughout the experiment since no gas is being added to or removed from the system in that case. This is based on the assumption that the effects of leaks within the system are minimized. The amount of CH₄ in the sample cell containing hydrates is slowly increasing as temperature rises, which confirms the presence of gas trapped in the hydrate form that is progressively being released. It can be noticed that the rate of increase of the amount of CH₄ in the sample cell containing hydrates shows an abrupt change around 272 K and the number of moles of methane gas
increases more rapidly until it reaches a maximum at 275 K, which is the same temperature where the pressure in the sample cell begins to stall indicating the end of the dissociation process. The red curve indicates a decrease in the amount of CH$_4$ that can be associated to the existence of leaks within the experimental system. Despite this observation, the data gathered allowed to verify the formation of methane hydrates during the experiment. Still, the experimental set up might need to be further modified to curb the effects of gas leaks and obtain better quality samples.

5.3.3. Trial tests of CO$_2$-CH$_4$ exchange within hydrates

5.3.3.1. Experimental procedure

Three trial tests of the CO$_2$-CH$_4$ exchange within hydrates were completed. First, CH$_4$ hydrate was prepared using the method described in section 5.3.2. Ice seeds were obtained by introducing small drops of distilled water into liquid nitrogen. The drops were collected with a strain and crushed into snow using the pre-cooled coffee grinder. 20.1 g of ice seeds were introduced into the pre-cooled reaction cell for the first test. 21 g of ice seeds were utilized for the two subsequent tests. The sample vessel was then pressurized with CH$_4$ at 330 psig for the first two tests and at 340 psig for the third one. The respective temperatures were 245.15 K and 253.15 K. The ice seeds were exposed to methane during 75 hours for the first test and 73 hours for the third test. They were exposed to methane for 61 hours during the second test. The sample cell headspace was then evacuated and the vessel was pressurized for a second time with CO$_2$. The sample was exposed to carbon dioxide for 59.6 hours, 47 hours and 38.5 hours respectively during the first, second and third tests. The experimental conditions of these three tests are summarized in table 5-2.
Table 5-2: Experimental conditions during the CO$_2$-CH$_4$ exchange in hydrate trial tests

<table>
<thead>
<tr>
<th></th>
<th>$P_{\text{CH}_4}$ (psig)</th>
<th>$P_{\text{CO}_2}$ (psig)</th>
<th>$T$ (K)</th>
<th>$t_{\text{injCO}_2}$ (hrs)</th>
<th>$t_{\text{finalCO}_2}$ (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>330</td>
<td>300</td>
<td>245.15</td>
<td>75</td>
<td>59.6</td>
</tr>
<tr>
<td>Test 2</td>
<td>330</td>
<td>200</td>
<td>245.15</td>
<td>61</td>
<td>47</td>
</tr>
<tr>
<td>Test 3</td>
<td>340</td>
<td>330</td>
<td>253.15</td>
<td>73</td>
<td>38.5</td>
</tr>
</tbody>
</table>

After leaving the sample exposed to carbon dioxide, the vessel was depressurized by extracting the gas phase at the top of the vessel. A gas sample was taken to perform a gas chromatography analysis and determine the composition of the gas phase. The supposedly mixed hydrate sample thus formed was dissociated by raising its temperature back to the room temperature of about 293.15 K. At the end of the decomposition experiment, the pressure vessel was once more depressurized by evacuating the reaction cell headspace. Another gas sample was extracted for chromatography analysis purposes. The dissociation conditions observed in the three tests presented here are summarized in Table 5-3.

Table 5-3: Dissociation conditions during the CO$_2$-CH$_4$ exchange in hydrate trial tests

<table>
<thead>
<tr>
<th></th>
<th>$T_{\text{initial}}$ (K)</th>
<th>$T_{\text{final}}$ (K)</th>
<th>$P_{\text{final}}$ (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>243</td>
<td>292.15</td>
<td>330</td>
</tr>
<tr>
<td>Test 2</td>
<td>245</td>
<td>293.15</td>
<td>84</td>
</tr>
<tr>
<td>Test 3</td>
<td>253</td>
<td>293.15</td>
<td>93</td>
</tr>
</tbody>
</table>

5.3.3.2. Results and discussion

5.3.3.2.1. Test 1 of the CO$_2$-CH$_4$ exchange within hydrates

The evolution of pressure with temperature obtained during test 1 of the CO$_2$-CH$_4$ exchange within hydrates is presented in figure 5-13.
Figure 5-13: Pressure inside the reaction cell during test 1 of the CO₂-CH₄ exchange in hydrates

Three different segments are shown on the plot corresponding to: (1) the injection of CH₄ and formation of CH₄ hydrate, (2) the injection of CO₂ and exchange within hydrates and (3) the dissociation of mixed CO₂-CH₄ hydrates. It can be observed from the figure that the pressure in the vessel is decreasing with time after the ice seeds have been exposed to methane for 75 hours, which could be attributed to the effect of: (1) gas cooling from room temperature (293.15 K) to experiment temperature (245.15 K) and (2) formation of pure CH₄ hydrates. This explanation takes into account the fact that the sample vessel has a constant volume and it also relies on the assumption that the effects of leaks within the experimental set-up are minimized. The pressure reaches a final value of 250 psig after 75 hours. Once carbon dioxide has been introduced into the vessel, it can be seen that there is an initial decrease from 300 psig to 220 psig. Then, the pressure in the vessel seems to stabilize around 220 psig. The initial decrease could be attributed to the combined effect of (1) gas cooling from room temperature to
experiment temperature (245.15 K), and (2) conversion of CO$_2$ into hydrates through the chemical substitution with CH$_4$ in the hydrate cages; assuming that any amount of gas leaking out of the experimental set up can be neglected. The fact that the pressure inside the vessel stabilizes around 220 psig could be an indication of the occurrence of the exchange. Indeed, assuming that any leak within the system could be minimized during the CO$_2$-CH$_4$ exchange within hydrates, every molecule of methane released by the hydrates should be replaced by a molecule of carbon dioxide, thus allowing the maintenance of the system’s pressure.

The final segment of the plot displays the evolution of pressure in the sample vessel during the dissociation of hydrates through thermal stimulation. This segment is presented in figure 5-14.

![Pressure in the sample cell during the dissociation of mixed CO$_2$-CH$_4$ hydrate](image)

**Figure 5-14:** Pressure inside the reaction cell during the dissociation cycle of test 1
It can be noticed that pressure is rising as the temperature of the sample cell is being increased. The trend is similar to that of the propane hydrate dissociation curve displayed in section 5.3.1.2. There is an initial fast increase in pressure between 243 K and 248 K. Pressure rises from 0 psig to about 220 psig. Then, the pressure slowly increases from 220 psig to 250 psig between 248 K and 278 K. There is another fast pressure increase from 250 psig to about 320 psig between 278 K and 282 K. Finally, the pressure stabilizes again around 320 psig between 282 K and 293 K.

The dissociation experiment P-T conditions where plotted against the methane and carbon dioxide hydrate phase diagrams in order to help interpret the trend of the curve.

![CH4 Hydrate and CO2 Hydrate Stability Regions in Permafrost Environments](image_url)

**Figure 5-15:** Comparison between the dissociation data of test 1 and the stability conditions of methane and carbon dioxide hydrates in permafrost regions

The initial fast rise in pressure between 243 K and 248 K could be associated to gas initially released from the mixed hydrates due to the evacuation of the reaction cell headspace prior to the beginning of
the dissociation experiment. Indeed, at the beginning of the dissociation experiment, the P-T conditions (243.15 K, 18 psig) are outside of both the CO₂ hydrate stability region and the CH₄ hydrate stability region. Some amount of gas could have been released, which caused the pressure to increase with temperature since we have a constant volume system. Between 248 K and 258 K, the P-T conditions are within both the CO₂ hydrate stability region and the CH₄ hydrate stability region. The pressure is stabilizing around 220 psig, indicated that there is no significant amount of additional gas being released from the hydrates. Beyond 258 K, the P-T conditions are outside the CH₄ hydrate stability region, but still inside the CO₂ hydrate stability region. The pressure slowly increases as temperature increases from 258 K to 276 K, which could indicate the release of some amount of gas from the hydrate. Once 276 K has been reached, we are outside the CO₂ hydrate stability zone. Pressure displays a fast increase from 250 psig to 320 psig between 278 K and 282 K, which should correspond to the completion of the hydrates’ dissociation. It seems most of the gas is being released during that time.

In order to confirm the occurrence of the exchange and the presence of mixed CO₂-CH₄ hydrates, some gas samples were taken to be analyzed by gas chromatography. The Shimadzu GC 17-A gas chromatograph was utilized in order to determine the composition of the gaseous mixtures involved during our experiments. The gas chromatograph was calibrated with mixtures of carbon dioxide and methane of known composition and SUPELCO standard mixtures containing known amounts of nitrogen, oxygen, methane and carbon dioxide. 200 μL gas samples were used for the analysis. As mentioned earlier, gas samples were taken before and after dissociation of the hydrates. Results are presented below.
Figure 5-16: Chromatogram obtained before dissociation during test 1 of the CO$_2$-CH$_4$ exchange in hydrates

The gas chromatography analysis performed before dissociation shows the presence of methane and carbon dioxide in the mixture before dissociation; with carbon dioxide being the main component of the mixture. Indeed, the sample is taken after the hydrate has been exposed to carbon dioxide for about 59 hours. The small quantity of methane present (2.32 mol %) seems to indicate the success of the exchange. We can also notice the presence of oxygen and nitrogen which shows that air was introduced either in the experimental set-up during the experimental process or in the gas sampling bag during the extraction of the gas mixture.
Figure 5-17: Chromatogram obtained after dissociation during test 1 of the CO$_2$-CH$_4$ exchange in hydrates

The gas chromatography analysis of the gas mixture obtained after dissociation of the hydrates shows the presence of methane and carbon dioxide as expected. This confirms that these two gases were trapped into the hydrate form during the experiment. However, carbon dioxide is still the main component of the mixture with a concentration of 95.69 mol %, while methane corresponds to only 3.3 mol % of the mixture. Indeed, the gas sample was taken after the headspace had been evacuated and the temperature had been raised from experiment temperature to room temperature. If carbon dioxide hydrates were formed due solely to the exchange, you would expect methane to be the main component of the mixture. It appears carbon dioxide formed pure CO$_2$ hydrates in addition to being involved in the exchange. Indeed, carbon dioxide is more stable in the hydrate form than methane for temperatures
below 283.15 K (at T=245 K, the CO\textsubscript{2} hydrate equilibrium pressure is 57 psia while the CH\textsubscript{4} hydrate equilibrium pressure is 155 psia [72]).

Overall, these results imply that the carbon dioxide introduced inside the sample cell 75 hours after the beginning of the experiment mainly formed pure carbon dioxide hydrate with the remaining water. Some exchange may have taken place, but it seems that the effect of the exchange was very small compared to the formation of pure CH\textsubscript{4} hydrate followed by the formation of pure CO\textsubscript{2} hydrate. The influence of the presence of free water in the system on the performance of the replacement technique is in agreement with observations made in the literature ([43] and [44]).

5.3.3.2.2. Test 2 of the CO\textsubscript{2}-CH\textsubscript{4} exchange within hydrates

Test 2 was similar to test 1 in terms of procedure, however a lower injection pressure (P=200 psig) was used for carbon dioxide in an attempt to assess the effect of the CO\textsubscript{2} injection pressure on the exchange. The evolution of pressure with temperature obtained during test 2 of the CO\textsubscript{2}-CH\textsubscript{4} exchange within hydrates is presented in figure 5-18.
Figure 5-18: Pressure inside the reaction cell during test 2 of the CO$_2$-CH$_4$ exchange in hydrates

Once again, we can observe three different segments on the plot corresponding to: (1) the injection of CH$_4$ and formation of pure CH$_4$ hydrate, (2) the injection of CO$_2$ and exchange within hydrates and (3) the dissociation of mixed CO$_2$-CH$_4$ hydrates. The pressure inside the sample cell is decreasing with time over the 61 hours of exposure of the ice seeds to methane. This could be related to the combined effect of gas cooling from room temperature (293.15 K) to experiment temperature (245.15 K) and formation of pure CH$_4$ hydrate. Indeed, the methane hydrate formation pressure at 245.15 K is 156.06 psia (143.36 psig) [72]. Thus, the selected experimental conditions (P=330 psig; T=245.15 K) are well within the stability region of pure CH$_4$ hydrate. The interpretation of the decrease in the sample cell pressure with time also takes into account the fact that we have a constant volume system and we are minimizing the effects of leaks within the experimental set-up. The sample cell pressure reaches a value of 232 psig after 61 hours. Then, the sample cell headspace is evacuated, which is displayed by the sudden decrease
in pressure. Next, carbon dioxide is introduced into the reaction vessel and the pressure rises to reach 200 psig. The pressure stays fairly constant around 200 psig for 47 hours. This could be related to the occurrence of the exchange between carbon dioxide and methane within the hydrates. Indeed, if a CH$_4$ molecule gets released, as soon as a CO$_2$ molecule is consumed, the number of moles of gas in the free gas space as well as the pressure should remain constant, as the temperature is kept constant.

The final segment of the plot displays the evolution of pressure with temperature during the dissociation of the potentially formed hydrates through isochoric heating. It can be seen in figure 5-19.

![Pressure in the sample cell during the dissociation of mixed CO$_2$-CH$_4$ hydrates (test 2)](chart.png)

**Figure 5-19: Pressure inside the reaction cell during the dissociation cycle of test 2**

It can be observed from the plot that pressure is rising as temperature increases. Overall, the P-T curve obtained during the dissociation experiment has an S-shape which is consistent with typical gas hydrates dissociation curves seen in the literature [80]. This curve is an indication of the presence of hydrates in
the sample cell during test 2. The P-T conditions recorded throughout the dissociation experiment were plotted against pure methane and pure carbon dioxide hydrate phase diagrams in order to further ascertain the presence of hydrates and better explain the phenomena at stakes during the dissociation test. The results can be seen in figure 5-20.

Contrary to the results of the previous test, the P-T conditions recorded during the dissociation portion of test 2 remain outside the carbon dioxide hydrate and methane hydrate stability region, for the entire duration of the dissociation run. This could be related to the anomalous hydrate preservation phenomenon, which can enable some gas hydrates such as methane and carbon dioxide to exist outside of their stability regions, for temperatures below 273.15 K and pressures around 0.1 MPa [81]. This behavior has been linked to the presence of a film of ice covering the hydrates and dissociation rates.
have been shown to decrease for the aforementioned pressure and temperature conditions, due to the anomalous hydrate preservation [81]. Pressure displays an abrupt increase around 273.15 K, suggesting a fast release of the remaining gas.

Gas samples were also taken before and after dissociation in order to verify the presence of gas hydrates and determine the compositions of such hydrates. The results of the gas sample analysis performed during test 2 are presented in figures 5-21 and 5-22.

**Figure 5-21: Chromatogram obtained before dissociation during test 2 of the CO₂-CH₄ exchange in hydrates**

The gas chromatography analysis performed before dissociation for test 2 reveals the gas mixture mostly contains carbon dioxide (98.5 mol %), with methane, oxygen and nitrogen as trace components. Similarly to the results of the gas chromatography carried out during test 1, we notice the presence of oxygen and nitrogen. However, they appear in much smaller amounts. Their presence could be due to some air that was introduced either inside the experimental set-up during test 2 or inside the sample bag.
and syringe utilized for the gas sample extraction. The amount of methane present in the mixture is surprisingly low in this case (0.13 mol %) compared to the result obtained during the first trial test, which could indicate that the chemical substitution between carbon dioxide and methane within hydrates was not successful in this trial.

![Chromatogram obtained after dissociation during test 2 of the CO2-CH4 exchange in hydrates](image)

**Figure 5-22: Chromatogram obtained after dissociation during test 2 of the CO2-CH4 exchange in hydrates**

The gas chromatography analysis of the mixture obtained after the dissociation portion of test 2 shows the presence of methane and carbon dioxide, as well as oxygen and nitrogen, whose contents are higher than in the case before dissociation. This could be explained by the introduction of some air inside the sample bag or inside the syringe prior to the analysis due to human error. However, the methane and carbon dioxide contents are still quite significant. The presence of methane and carbon dioxide in the mixture at the end of the dissociation experiment confirms that gas hydrates were formed during test 2. Once again, carbon dioxide is the main component of the mixture with a concentration of 77.35 mol % while methane has a concentration of 8.59 mol %. This suggests that methane hydrate was formed...
during the first 61 hours of the experiment. In this case, carbon dioxide mostly formed pure carbon dioxide hydrate with the excess water instead of substituting the methane already trapped inside the hydrates. In addition, the CO$_2$ injection pressure used for test 2 (P=200 psig) was inferior to the one used for test 1 (P=300 psig). This may have influenced the outcome of the experiment as it was noticed in chapter 4 that the exchange method could yield low recovery ratios for deposits with low reservoir pressures. The exposure time of ice seeds to methane and carbon dioxide was also reduced, which may have influenced the success of the exchange. The impacts of the presence of free water in the system and of the initial reservoir pressure that have been noticed during test 2, are in accordance with observations reported in the literature ([43] and [44]).

5.3.3.2.3. Test 3 of the CO$_2$-CH$_4$ exchange within hydrates

Test 3 was similar to test 1 in terms of procedure. In this case, a higher experiment temperature (T=253.15 K) was applied to evaluate the effect of temperature on the exchange. The evolution of pressure with temperature recorded during test 3 of the CO$_2$-CH$_4$ exchange within hydrates is presented in figure 5-23.
Figure 5-23: Pressure inside the sample cell during test 3 of the CO\textsubscript{2}-CH\textsubscript{4} exchange in hydrates

Similarly to the previous tests, pressure is steadily decreasing after methane has been introduced inside the sample cell. This could be related to gas cooling from room temperature (293.15 K) to experiment temperature (253.15 K), as we have a constant volume system and we are assuming that any leaks within the system can be minimized. The conversion of methane gas to methane hydrate should also cause a decrease in pressure. Indeed, experimental conditions of 340 psig and 253.15 K are well within the methane hydrate stability region since the methane hydrate equilibrium pressure is 204.24 psia (189.54 psig) [72] at 253.15 K. Ice seeds remain exposed to methane for approximately 73 hours and the pressure reaches a value of 246 psig. The sample cell headspace is then evacuated, which leads to the sudden decrease in pressure at t=73 h and carbon dioxide is injected inside the sample cell, causing the pressure to increase back to 330 psig. During the carbon dioxide injection cycle, the pressure in the sample evolves differently from the previous cycle. The pressure displays an initial decrease from 330
psig to 300 psig during the three first hours of the cycle. Then, the pressure stabilizes around 300 psig. This could be explained by gas cooling from room temperature to the experiment temperature, followed by the exchange between carbon dioxide hydrate and methane hydrate. Indeed, the experimental conditions (P=330 psig, T=253.15 K) are well within the stability region of both carbon dioxide hydrate and methane hydrate. The chemical substitution between carbon dioxide and methane in the hydrates is feasible. The fact that the pressure stabilizes around 300 psig could be related to the occurrence of the exchange. Indeed, any amount of methane released should equate the amount of carbon dioxide being consumed thus resulting in the pressure in the cell being maintained for a constant volume system.

In order to confirm the occurrence of the exchange, the product from these two injection cycles was decomposed by isochoric heating from experiment temperature to room temperature. The results can be seen in figure 5-24.
Figure 5-24: Pressure inside the reaction cell during the dissociation cycle of test 3

The decomposition curve obtained from the data recorded during the dissociation cycle of test 3 has an S-shape typical for gas hydrate dissociation curves. The dissociation seems to be complete at 277 K and 90 psig. The pressure increases linearly between 280 K and 293 K, and it is in accordance with the pressure behavior observed during isochoric heating of a system containing a constant amount of gas, without any change in the gas content. The curve is similar to the decomposition curve obtained for test 2. The final decomposition pressure is higher than the one obtained during test 2, but still low compared to the decomposition pressure value obtained during test 1 (P=320 psig, T=282 K).

The decomposition curve was also plotted against the methane and carbon dioxide hydrate phase diagrams. The results can be seen in figure 5-25.
Similarly to the results of test 2, the P-T conditions recorded during the dissociation cycle of test 3 remain outside the carbon dioxide hydrate and methane hydrate stability region, for the entire duration of the experiment. This could be explained by the anomalous preservation behavior displayed by carbon dioxide and methane hydrates, for temperatures below 273.15 K and pressures around 0.1MPa. At such conditions, the dissociation rates become slower than usual and the hydrates can remain stable outside their stability regions [81]. Once 273.15 K is reached, there is an abrupt change in pressure suggesting the completion of the hydrate dissociation experiment.

Gas samples were also taken before and after dissociation in order to verify the presence of gas hydrates and determine the compositions of such hydrates. The results of the gas sample analysis performed during test 3 are presented in figure 5-26.
As mentioned in section 5.3.2, a 200 µL sample of the reaction cell headspace’s gas was analyzed via gas chromatography. The results indicate that carbon dioxide is the main component of the mixture with oxygen, nitrogen and methane as trace components. This is similar to what was obtained during test 2. It seems to show that no exchange took place during the carbon dioxide injection cycle.
Figure 5-27: Chromatogram obtained after dissociation during test 3 the CO$_2$-CH$_4$ exchange in hydrates

The gas chromatography analysis performed using a gas sample taken at the end of the decomposition experiment reveal the presence of methane and carbon dioxide in fairly significant quantities. Their concentrations are 8.45 mol % and 88.27 mol % respectively. Once again, carbon dioxide is the main component of the mixture, which may imply that the exchange was less successful during this trial. The low methane content in the mixture compared to the carbon dioxide content is an indication that a small amount of methane hydrate was formed. In addition, it seems carbon dioxide reacted with the excess water to form carbon dioxide hydrate instead of participating in the exchange with methane hydrate. Indeed, carbon dioxide stability conditions are lower than methane hydrate stability conditions for temperature below 283.15 K, making it easier for carbon dioxide hydrate to form. The presence of oxygen and nitrogen in the mixture could be related to the introduction of air into the gas sample during the extraction process or during the experiment. Test 3 was similar to test 1 in terms of the injection pressures of methane and carbon dioxide. However, a higher experiment temperature was used for test 3
(253.15 K) compared to tests 1 (245.15 K). In addition, the CO$_2$ injection cycle was shortened for test 3 (38.5 hours instead of 59.6 hours for test 1). These changes may have affected the outcome of the exchange experiment. The influence of the initial reservoir temperature as a promoter of the exchange [43] could not be noticed during this trial.

### 5.3.3.3. Simulation results for the trial tests of the exchange

The MATLAB numerical model presented in chapter 4 was modified in order to incorporate the laboratory conditions. The pressures and temperatures used during tests 1, 2 and 3 of the CO$_2$-CH$_4$ exchange within hydrates were applied to the model. As, we are creating pure hydrate samples in the laboratory, the porosity and saturation values required in the model were set to 1. The bottom of the stainless steel reaction cell was assimilated to the base rock included in the reservoir description (see figure 4-9). Additional input data describing the experimental set-up is summarized in table 5-4.

**Table 5-4: Input data for the MATLAB model of the CO$_2$-CH$_4$ exchange within hydrates applied to laboratory conditions**

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample height (hydrate zone thickness, inches)</td>
<td>1</td>
</tr>
<tr>
<td>Sample diameter (inches)</td>
<td>2.3125</td>
</tr>
<tr>
<td>Reaction cell headspace height (gas layer thickness, inches)</td>
<td>2.5</td>
</tr>
<tr>
<td>Density of base rock (kg/m$^3$)</td>
<td>8000</td>
</tr>
<tr>
<td>Thermal conductivity of base rock (W/m.K)</td>
<td>16.2</td>
</tr>
<tr>
<td>Heat capacity of base rock (J/kg.K)</td>
<td>500</td>
</tr>
<tr>
<td>Thickness of base rock (inches)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The outcomes of the model for the conditions used in tests 1, 2 and 3 of the exchange are presented in figures 5-28 through 5-30.
Figure 5-28: Results of the gas hydrate exchange model for the conditions applied for test 1

Figure 5-28 presents from left to right: (1) the calculated ratios of methane and carbon dioxide in the hydrates during the exchange, (2) the methane hydrate formation and carbon dioxide hydrate dissociation rates, (3) the evolution of the temperature of the hydrate zone and (4) the percentage of methane recovered during the exchange. It can be noticed that the model developed in chapter 4 predicts a successful exchange for the conditions used in test 1 (P_{CO2}=300 psig; T=245.15K). The model results in 22.73% of the initial methane content being recovered after about 143 hours (515000 seconds),
corresponding to the following hydrate composition: 77.27 mol% CH₄ and 22.73 mol% CO₂. The following compositions were obtained for the gas phase after the exchange: 49.25 mol% CH₄ and 50.75 mol% CO₂. The model also predicts that the methane hydrate dissociation rate stays low throughout the exchange compared to the carbon dioxide hydrate formation rate. When compared to the experimental results described in section 5.3.3.2.1, both the experiment and the model outcomes, although different, enable to conclude that some amount of methane may have been recovered through the exchange technique for the conditions of test 1. Indeed, the model predictions are based on the assumption that the exchange occurs with a hydrate block containing no free water and that all cages within the hydrates are affected by the exchange, which was not the case during test 1, as we could observe that not enough methane hydrates was formed and there was still some remaining free water when carbon dioxide was introduced into the reaction cell. In addition, the model, which only takes into account the CO₂ injection cycle of test 1, predicts an experimental duration of 143 hours in order to reach a methane recovery of 22.73%, while methane hydrate remained exposed to carbon dioxide for only 59.6 hours during test 1.

Thus, the model results for test 1 confirm that the exchange is feasible at the conditions selected for the first preliminary test. However, in order to increase the methane recovery, it seems necessary to expand the duration of the exchange to about 143 hours and to increase the amount of methane hydrate formed during the first cycle of the exchange experiment.
Figure 5-29: Results of the gas hydrate exchange model for the conditions applied for test 2

Similarly to figure 5-28, figure 5-29 displays from left to right: (1) the calculated ratios of methane and carbon dioxide in the hydrates during the exchange, (2) the methane hydrate formation and carbon dioxide hydrate dissociation rates, (3) the evolution of the temperature of the hydrate zone and (4) the percentage of methane recovered during the exchange. It can be observed that the model developed in chapter 4 predicts a successful exchange for the conditions used in test 2 ($P_{CO2}=200$ psig; $T=245.15K$). However, the model results in a lower methane recovery ratio of 20.26%, in comparison to the results of
test 1. The following compositions were obtained after the exchange: 72.29 mol% CH$_4$ and 27.71 mol% CO$_2$ in the fluid phase and 79.74 mol% CH$_4$ and 20.26 mol% CO$_2$ in the hydrate phase. The recovery ratio is reached after 143 hours (515000 seconds). The model also predicts lower methane hydrate dissociation and carbon dioxide formation rates compared to test 1. When associated with the experimental results described in section 5.3.3.2.2, both the experiment and the model outcomes, agree in showing that less methane may have been recovered during test 2 than the amount recovered in test 1. Yet, the model results in optimistic predictions as it is based on the assumption that the exchange occurs with a perfect hydrate-filled block containing no remaining water and that all cages within the hydrates are affected by the exchange. On the other hand, the experimental results of test 2 enabled to notice that carbon dioxide mostly formed pure carbon dioxide hydrate with the remaining free water and may have not been much involved in a molecular guest exchange with methane in the hydrates. Besides, the model predicts an experimental duration of 143 hours in order to reach a methane recovery of 20.26%, while methane hydrate remained exposed to carbon dioxide for 47 hours during test 2.

Thus, in the case of test 2, the model confirms the feasibility of the exchange and agrees with the experiment in showing that the conditions selected for the second preliminary test might not lead to optimum methane hydrate recovery. The simulation results show a lower methane recovery ratio for a lower carbon dioxide injection pressure, as reported in the literature ([43] and [44]). We can also conclude from the analysis of the results that the exchange section of the experiment should be extended to reach a better recovery ratio.
Figure 5-30: Results of the gas hydrate exchange model for the conditions applied for test 3

Figure 5-30 displays from left to right: (1) the calculated ratios of methane and carbon dioxide in the hydrates during the exchange, (2) the methane hydrate formation and carbon dioxide hydrate dissociation rates, (3) the evolution of the temperature of the hydrate zone and (4) the percentage of methane recovered during the exchange. It can also be seen in this case that the model predicts a successful exchange for the following conditions: $P_{CO2}=330$ psig; $T=253.15$ K. The model results in a methane recovery ratio of 27.6% which is higher than the results obtained for both tests 1 and 2. The
compositions obtained after the exchange are as follows: 56.74 mol% CH₄ and 43.26 mol% CO₂ in the fluid phase and 72.4 mol% CH₄ and 27.6 mol% CO₂ in the hydrate phase. However, the duration of the exchange is shorter in this case (about 106 hours or 380400 seconds). When associated with the experimental results described in section 5.3.3.2.3, the model leads to optimistic predictions as it is based on the assumption that the exchange occurs with a perfect hydrate-filled block containing no remaining water and that all cages within the hydrates are affected by the exchange. On the other hand, the experimental results of test 3 seem to imply that no exchange took place during the carbon dioxide injection cycle. Carbon dioxide mostly formed pure carbon dioxide hydrate with the remaining free water. It should be recalled that although the experiment temperature was raised, the carbon dioxide injection cycle only lasted 38.5 hours, while the maximum recovery ratio was reached after 106 hours through modeling.

Therefore, in the case of test 3, the model and experiment resulted in opposite results. Still, the model confirmed the feasibility of the exchange given that the procedure is started with a good quality hydrate sample. The model also confirmed the effects of the initial reservoir pressure and temperature on methane recovery as reported in the literature ([43] and [44]). Once again, it seems necessary to improve the procedure for the formation of methane hydrate and extend the exchange section of the experiment. A higher experiment temperature may also lead to an increase of the recovery ratio.

5.3.4. Summary

A series of preliminary tests have been performed in an attempt to (1) assess the effectiveness of the experimental set-up in creating synthetic hydrates and achieving the CO₂-CH₄ exchange within hydrates and (2) finding optimum conditions for the exchange. The experimental set-up was utilized to test the formation of propane-methane mixed hydrate and pure methane hydrate, as well as to evaluate the exchange within hydrate for different conditions.
Overall, these tests resulted in promising results when it comes to the formation and dissociation of hydrates. We were able to reach a conversion percent of 16.3% for the formation of propane-methane mixed hydrates. Hydrate formation was also observed during the pure methane hydrate formation test and the CO₂-CH₄ exchange tests. The dissociation curves had an S-shape typical of gas hydrate dissociation experiments and the presence of gas trapped in hydrate form was confirmed through gas chromatography analyses which were performed at the end of the tests. However, it was difficult to validate the results with mass balance calculations due most likely to the presence of leaks within the experimental system and some inconsistence between the amounts of gas measured before and after the tests. The set-up should be further improved in an effort to estimate more accurately the mass balance for the system.

Concerning the CO₂-CH₄ exchange, only test 1 may have been successful. The subsequent tests seem to have resulted mainly in the formation of two separate methane and carbon dioxide hydrates. Not enough methane hydrate was formed and carbon dioxide reacted with the excess water present, instead of getting involved in the exchange with CH₄ within hydrates. This may have been related to the change in pressure and temperature or to the duration of the test. In the preliminary pure methane hydrate test, equilibrium was reached after 144 hours. The model described in chapter 4 was also used to assess the feasibility of the exchange for the conditions applied in tests 1, 2 and 3. Although the model over-predicted the methane recovery ratios, it showed that the exchange was feasible in the three cases. The obtained ratios were between 20% and 28%, the lowest corresponding to test 2 and the highest corresponding to test 3. However, these ratios could be reached after 143 hours for tests 1 and 2, and 106 hours for test 3.

These observations allow us to conclude that it may be necessary to extend the duration of the CH₄ hydrate formation cycle and CO₂ injection cycle in an attempt to reach better results during the exchange. It may also be useful to increase the experiment temperature and use CO₂ injection pressures
above the one used in test 2. Some final additional tests have been performed based on the preliminary results obtained in paragraph 5.3 and they are discussed in the following section.

5.4. Experiments performed with the modified experimental set-up

5.4.1. Description of the modified experimental set-up

The observations and results obtained in section 5.3 allowed us to make additional adjustments to the experimental set-up and to the experimental procedures used to investigate the feasibility of the chemical exchange between carbon dioxide and methane within hydrates. The modified set-up can be seen in figure 5-31.
Figure 5-31: Modified experimental apparatus

The gas supply section, the gas hydrate formation, dissociation and production section, the data acquisition section and the gas recovery section are presented in figure 5-31, from left to right. The main components of the apparatus have been kept. As aforementioned, the sample cylinder serving as gas reservoir was removed from the gas hydrate production section and the reaction cell is now directly connected to the pressurized cylinders. Concerning the gas recovery section, a choke valve was added which separates the production section from the vacuum line and the recovery section. A second choke valve enables to isolate the vacuum line from the recovery section and the gas production section. The presence of these two valves helps in releasing gas from both the recovery section and the production section without the other one being affected. The gas sample cylinder described in paragraph 5.2 was
added to the recovery section in an attempt to better estimate the amount of gas present in the system at the end of dissociation. A pressure gauge is attached to the gas sample cylinder in order to monitor the pressure during gas recovery. A schematic representation of the modified experimental apparatus is displayed in figure 5-32.

![Diagram](image)

**Figure 5-32: Schematic diagram of the modified experimental apparatus**

### 5.4.2. Formation and dissociation of pure CH₄ hydrate with the modified apparatus

#### 5.4.2.1. Experimental procedure

21.75 g of ice seeds were created as stated in paragraph 5.3.1. The seeds were incorporated into the reaction cell which had been pre-cooled at T=253.15 K. After properly sealing the reaction cell, it was pressurized with methane at P=340 psig. The ice seeds remained exposed to gas for 129.20 hours (5.38 days). Pressure and temperature changes were monitored and recorded with the PDAQView data acquisition system. A final pressure of 270 psig was reached at the end of the formation experiment.
Following this, the freezer was stopped, the reaction cell headspace was evacuated and the temperature increased from 253.3 K to 292.34 K in about 23.6 hours, thus a temperature increase rate of 1.65 K/hour. The pressure in the sample cell reached a final value of 34.75 psig.

5.4.2.2. Results and discussion

The evolution of pressure in the sample cell during the formation of pure CH₄ hydrate at P=340 psig and T=253.15 K can be seen in figure 5-33

Figure 5-33: Pressure during pure CH₄ hydrate formation with the modified apparatus

The pressure inside the sample cell is decreasing over time, which could be related to: (1) gas cooling from room temperature to experimental temperature and (2) the formation of pure methane hydrates inside the reaction vessel. The CSMHYD software [72] was used to estimate the methane hydrate equilibrium pressure at T=253.15 K and we found a pressure value of 204.24 psia (189.54 psig). Thus,
the selected initial conditions are favorable for methane hydrate formation. A blank test was run at the same experimental conditions by pressurizing an empty reaction vessel (containing no ice seeds) with methane at T=253.15 K. The pressure and temperature data recorded during the blank test was plotted against the data obtained during the formation experiment for comparison purposes. The results can be seen in figure 5-34.

![Comparison between pressure in the sample cell during the formation experiment of pure CH₄ hydrate and pressure in the sample cell during the blank test (P=340 psig; T=253.15 K)](image)

**Figure 5-34:** Comparison between the evolution of pressure during CH₄ hydrate formation and the evolution of pressure during the blank test with CH₄

The pressure values recorded during the blank test are slightly higher than the pressure values obtained during the formation experiment, which could indicate that a small amount of methane hydrates was formed during the test. However, pressure seems to be steadily decreasing over time during the blank test, which may suggest the occurrence of gas leaks in the system. The results from the dissociation experiment are displayed in figure 5-35.
Figure 5-35: Pressure in the sample cell during the dissociation experiment of pure CH$_4$ hydrate with the modified apparatus

We can notice that the dissociation curve has an S-shape, which is typical of gas hydrate dissociation [80]. Pressure is steadily rising from 10.52 psig at 253.3 K to 26.96 psig at 273.86 K, thus an increase rate of 0.8 psi/K. Between 273.86 K and 275.94 K, there is an abrupt increase in pressure from 26.96 psig to 31.5 psig, thus a pressure increase rate of 2.18 psi/K that could be related to the final release of any gas still entrapped in the hydrate structure. Water goes from the solid state to the liquid state during the dissociation experiment. The hydrogen-bonded water cages within the hydrates should be more difficult to break when water is in the solid state, which could explain why less gas molecules are able to escape between 253.3 K and 273.86 K. Hydrogen bonds in liquid water are weaker and are constantly breaking and reforming, hence enabling most of the entrapped gas to be released. Pressure seems to stabilize between 275.94 K and 277.95 K, indicating the completion of the hydrate’s decomposition.
Thus, the final dissociation conditions of the hydrates formed during that experiment are 277.95 K and 31.76 psig. This low pressure values suggest that a small amount of hydrate conversion was achieved during the test. Above 277.95 K, pressure increases linearly with pressure as typically seen during isochoric heating experiments of systems containing a constant amount of gas (see section 5.3.2.2). The gas introduced in the vessel during the blank test was also warmed via isochoric heating for comparison purposes. The evolution of pressure during that test is displayed in figure 5-36.

![Figure 5-36: Pressure in the sample cell during isochoric heating of CH₄ from 253 K to 293 K](image)

As described in section 5.3.2.2 with the real gas law, the reaction cell pressure varies linearly with temperature during isochoric heating of a system with a constant amount of gas. There is no deviation from the straight line that could indicate a change in the amount of gas present in the reaction cell. A comparison with the pressure trend displayed in figure 5-35 suggests the amount of gas in the vessel
increased from 253.3 K to about 273.86 K due to the progressive release of gas from hydrates, thus causing the elevation in pressure. The abrupt pressure increase noticed between 273.86 K and 275.94 K is indeed an indication of the final release of gas from methane hydrates. The number of moles of gas consumed by the hydrate reaction was estimated using a method similar to the one employed in section 5.3.1.2 with a free volume of 172 cc and the P-T data recorded during the formation test. Assuming that the observed pressure decrease is entirely due to hydrate formation, we obtained that 45.44 millimoles of methane were trapped in hydrates during the experiment. This outcome was compared to the amount of gas necessary for complete hydrate conversion of the 21.75 g of water that were placed in the vessel. Methane hydrates form type I hydrates that have a hydration number of 6. Thus, we obtained that 201.3 millimoles of gas would be needed. Therefore, based on these figures, we were able to achieve 22.6% of hydrate conversion during the pure methane hydrate formation test. Considering that 213.5 millimoles of methane were introduced into the reaction cell, we could have been able to reach a conversion percent of 100% if all the gas had been consumed by the hydrate reaction. We also used the dissociation data to estimate the amount of gas released from the hydrates. We obtained that 24.01 millimoles of gas were released, which translates into an 11.9% hydrate conversion. We attempted to use the gas recovery section of the modified apparatus to evaluate the amount of gas released from the dissociation experiment. Unfortunately, the final dissociation pressure was too low for enough gas to flow into the outside gas cylinder. We can infer from our calculations that we achieved an 11.9% hydrate conversion during the pure methane hydrate formation test with the modified apparatus. We decided to use the outcome obtained with the dissociation data as it is directly linked to the amount of gas that is effectively trapped in the hydrate structure. The higher hydrate conversion percent that was obtained with the formation data may be due to the optimistic assumption of minimizing the effects of leaks within the system.
We attempted to obtain a gas sample from the reaction cell headspace for analysis via gas chromatography in order to obtain another proof of the formation of pure methane hydrates during test 1. However, the pressure that was reached at the end of the experiment did not allow us to extract a significant amount of gas for the analysis. The results can be seen in figure 5-37.

Figure 5-37: Chromatogram obtained after dissociation of methane hydrate formed with the modified apparatus

The results from the analysis suggest the presence of nitrogen, oxygen, carbon dioxide and methane in the sample. The presence in large amounts of nitrogen (27.3 mol %) and oxygen (4.82 mol %) is due to the introduction of air either inside the sample bag or inside the syringe used for the analysis. Methane is the major component of the mixture with 58.95 mol %. However, this composition is low in comparison to what was expected since methane is the only gas we introduced in the reaction cell. Carbon dioxide was also detected with a composition of 8.92 mol. % probably due to the fact that the sample bag still
contained some traces of carbon dioxide from previous experiments. As stated above, the low final
dissociation pressure achieved during the dissociation test of methane hydrates led to unsuccessful gas
sample recovery and the methane content in the gas phase was diluted.

In summary, we can infer from the data gathered during the formation and dissociation tests of pure
methane hydrates that we were successful in synthetically creating pure methane hydrates with the
apparatus. We reached 11.9 % of hydrate conversion and the presence of gas hydrates in the reaction
cell was confirmed with the dissociation data and the gas chromatography analysis. However, the
hydrate conversion percent is low in comparison to what has been achieved in the literature [80].The
experimental procedures and the apparatus may need to be further improved to obtain better quality
methane hydrate samples.

5.4.3. Formation and dissociation of pure CO\textsubscript{2} hydrates with the modified apparatus

5.4.3.1. Experimental procedure

As the preliminary tests that had been performed, seem to suggest that carbon dioxide mostly formed
pure CO\textsubscript{2} hydrates with excess water instead of replacing methane in the hydrate structure, we formed
and dissociated pure CO\textsubscript{2} hydrates in an attempt to better assess the results obtained from the exchange
experiments. We created 22.46 g of ice seeds in a manner similar to what was described in paragraph
5.3.1. Next, the seeds were placed into the reaction cell that had been pre-cooled at T=253.15 K. The
reaction cell was connected back to the apparatus, sealed and slowly pressurized with carbon dioxide
until a pressure of P=260 psig was reached. Following the conclusions that were drawn from the
preliminary experiments, the seeds were left exposed to carbon dioxide for 134.27 hours (5.6 days).
Pressure and temperature were monitored with the PDAQView data acquisition system. The pressure
reached a value of 168 psig by the end of the formation experiment. The headspace was evacuated and
the freezer was stopped in order to let the temperature increase and dissociate the hydrate sample. The
sample was warmed from 253.15 K to 292.15 K in about 19 hours, thus a temperature increase rate of 2.05 K/hour. The pressure of the sample cell reached a value of 143 psig by the end of the hydrate dissociation experiment.

5.4.3.2. Results and discussion

The evolution of pressure in the reaction cell during the formation of pure carbon dioxide hydrate at T=253.15 K and P=260 psig can be seen in figure 5-38.

Figure 5-38: Pressure during pure CO$_2$ hydrate formation with modified apparatus

When observing the results presented in figure 5-38, we can notice that pressure in the reaction cell is decreasing over time and seems to stabilize around 168 psig. This trend could be explained by gas cooling and carbon dioxide hydrate formation. CSMHYD [72] was used to evaluate the carbon dioxide hydrate equilibrium pressure at T=253.15 K. We obtained 79.4 psia ($\approx$64.7 psig). As 260 psig is well
above the CO$_2$ hydrate equilibrium pressure, the selected conditions are favorable for hydrate formation. This brings some additional confirmation of the presence of carbon dioxide hydrate in the sample cell. It also suggests that carbon dioxide hydrate formation stopped before it could reach equilibrium for the given temperature, probably because a layer of carbon dioxide hydrate kept ice seeds located deeper into the sample from being contacted by the gas and form more hydrates. A blank test was performed at the same experimental conditions. An empty reaction cell (containing no ice seeds) that had been pre-cooled to 253.15 K was pressurized with carbon dioxide at P=260 psig for about 6 days. Results from the blank test are compared against the results from the hydrate formation test in figure 5-39.

![Comparison between pressure in the sample cell during the formation experiment of pure CO$_2$ hydrate and pressure in the sample cell during the blank test (P=260 psig; T=253.15 K)](image)

**Figure 5-39: Comparison between the evolution of pressure during CO$_2$ hydrate formation and the evolution of pressure during blank test with CO$_2$**

As we can see from figure 5-39, pressure stays constant when an empty reaction cell is pressurized with carbon dioxide at T=253.15 K and P=260 psig. This confirms that the pressure decrease noticed during
the formation test of pure carbon dioxide is due to carbon dioxide being consumed by the hydrate formation process in the presence of ice. The results from the dissociation experiment can be seen in figure 5-40.

![Graph showing pressure changes during dissociation experiment](image)

Figure 5-40: Pressure in the sample cell during the dissociation experiment of pure CO₂ hydrate with the modified apparatus

The dissociation curve follows the trend of a gas hydrate dissociation curve, thus proving once again that the pure carbon dioxide hydrate formation experiment was successful. There is a slow increase of pressure from T=254 K to about T=273 K, with pressures going from 12.72 psig to 42.68 psig; thus a pressure increase rate of 1.56 psi/K. Then, we can notice a sharper pressure increase between 273 K and 277 K. The pressure increase rate during that interval has been estimated at about 30 psi/K. As temperature rises from 254 K to 273 K, carbon dioxide is slowly being released from the hydrate structure. Then, water goes from the solid state to the liquid state at 273.15 K, the hydrogen bonds in
water become weaker and gas molecules should escape more easily from the hydrate structure. Indeed, a higher amount of the entrapped gas is being released at a faster rate. The highest point on the dissociation curve could be considered as the final hydrate dissociation conditions corresponding to T=276.82 K (≈277 K) and P=136.58 psig. Any additional rise in temperature beyond that point should be attributed to the fact that we have a constant volume system. A blank test was also performed for the dissociation case. The reaction cell pressurized with 260 psig of carbon dioxide was warmed from experimental temperature to room temperature. The results can be seen in figure 5-41.

![Figure 5-41: Pressure in the sample cell during heating of CO₂ from 253 K to 293 K](image)

As explained in section 5.3.2.2 with the real gas law, the pressure varies linearly with temperature, due to the isochoric heating of a system containing a constant amount of gas. There is no deviation from the straight line that could be related to a change in the number of moles of gas present in the reaction cell.
When compared with the results presented in figure 5-40, it can be once again confirmed that carbon dioxide hydrates were formed during the experiment. The number of moles of gas trapped in the hydrates was calculated in a method similar to what was discussed in section 5.3.1.2, using a free volume of 172 cc and the P-T data recorded during the formation experiment. It was found that about 69.16 millimoles of carbon dioxide were consumed by the hydrate formation. This number was compared to the ideal number of moles necessary for complete hydrate conversion based on the 22.46 g of water placed inside the reaction cell and on the fact that carbon dioxide forms type I hydrates which have a hydrate number of 6. We found that 208 millimoles of gas would have been needed for complete hydrate conversion. Thus, we were able to achieve about 33.2% conversion during our experiment. We also have to highlight that 184.9 millimoles of carbon dioxide were introduced into the reaction cell at the beginning of the experiment. A conversion percent of 88.9% would have been achieved if all the gas introduced had been consumed by the formation reaction. For confirmation purposes, the number of moles of gas released during the dissociation experiment was also estimated. We obtained that 68.06 millimoles of gas had been released during the dissociation experiment, thus a conversion percent of 32.7%. The modified gas recovery section was used in an attempt to estimate again the amount of gas trapped during the hydrate formation by measuring the volume of gas released after dissociation. The valves between the formation section of the apparatus and the recovery section were opened. The gauge pressure attached to the reaction cell read 60 psig, while the gauge pressure attached to the gas cylinder read 45 psig. We have a free space volume of 172 cc for the reaction cell and of 500 cc for the gas cylinder. These data as well as the final temperature of 292.54 K were used to estimate the gas released from the experiment. We obtained a total of 121.04 millimoles of gas (36.42 millimoles inside the reaction cell and 84.62 millimoles inside the gas cylinder). This tends to suggest that 58.2% of hydrate conversion have been achieved during the experiment.
After analyzing the results, we can infer that a hydrate conversion percent of about 33% seems more reasonable, since this result was confirmed by the data collected at the end of the formation and dissociation experiments. The highest values that have been suggested by the third calculation method indicate that there are still some issues with the ability of the apparatus to give a good estimate of the volume of gas released after hydrate decomposition.

A sample of the released gas was taken to confirm the presence of carbon dioxide via gas chromatography analysis. A 200 µL sample volume was analyzed with the thermal conductivity detector (TCD) method of the Schimadzu GC-17 A gas chromatograph and the sample composition was estimated after comparison with standard compositions of the possible components of the gas sample. The obtained results can be seen in figure 5-42.
The gas chromatography results suggest the presence of nitrogen, oxygen, methane and carbon dioxide in the sample. As expected, carbon dioxide is the major component with a composition of 89.09 mol %, which validates the formation of carbon dioxide hydrates during the experiment. As explained in previous sections, the presence of nitrogen and oxygen could be related to air being introduced either in the sample bag during gas sample extraction or in the syringe used for the gas chromatography analysis. The presence of methane could be due to the pure methane hydrate experiment that was conducted prior to the carbon dioxide hydrate experiment. Traces of methane may have stayed in the gas recovery section of the apparatus.

Overall, the results obtained during the formation and dissociation of pure carbon dioxide hydrates at the selected conditions suggest a successful synthesis of pure carbon dioxide hydrates with a conversion
percent of about 33%. The good agreement between the conversion percentages calculated at the end of the formation and dissociation experiments, indicates that less leakage occurred during the experiment. We also obtained a better hydrate conversion percent than what was experienced in the preliminary tests. We can infer from these observations that the modification of the apparatus and the extension of the experimental durations improved the quality of the synthetic hydrate obtained. Once again, the low hydrate conversion percent in comparison with the 88.9% which should have been noticed, had all the initial gas present been consumed by the formation reaction, could be related to the fact that created hydrates formed a barrier, keeping additional ice from being converted to carbon dioxide hydrates. The utilization of a rigid container to help measure and calculate the amount of gas released after decomposition of the created hydrates did not yield successful results in this case.

5.4.4. Tests of CO$_2$-CH$_4$ exchange within hydrates with the modified apparatus

5.4.4.1. Experimental procedure

We ran two tests of the CO$_2$-CH$_4$ exchange within hydrates with the modified apparatus. We first created methane hydrates in a similar manner to what was described in paragraph 5.4.2.1. Ice seeds were prepared by introducing 50 ml of distilled water into liquid nitrogen. Next, the ice pellets were collected with a pre-cooled strain and crushed into snow using a coffee grinder. The snow was incorporated into the reaction cell pre-cooled at 253.15 K. 20.81 g of ice seeds were utilized for the first test and 21 g of ice seeds, for the second test. Then, the pressure vessel was slowly pressurized with methane at P=340 psig. Based upon the observations made from the preliminary tests presented in section 5.3.3, the ice seeds remained exposed to methane for 143.47 hours (5.98 days) during test 1 and 144.13 hours (6 days) during test 2. The pressure in the reaction cell stabilized around 250 psig for both tests. Next, the reaction cell headspace was evacuated and pressurized with carbon dioxide at P=260 psig during test 1 and P=330 psig during test 2. The sample remained exposed to carbon dioxide for 154.27 hours (6.43
days) during test 1 and for 155.87 hours during test 2 (6.49 days). The experimental conditions for both tests are summarized in table 5-5.

Table 5-5: Experimental conditions during the CO$_2$-CH$_4$ exchange in hydrate tests with the modified apparatus

<table>
<thead>
<tr>
<th></th>
<th>$P_{\text{CH}_4}$ (psig)</th>
<th>$P_{\text{CO}_2}$ (psig)</th>
<th>$T$ (K)</th>
<th>$t_{\text{injCO}_2}$ (hrs)</th>
<th>$t_{\text{finalCO}_2}$ (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>340</td>
<td>260</td>
<td>253.15</td>
<td>143.47</td>
<td>154.27</td>
</tr>
<tr>
<td>Test 2</td>
<td>340</td>
<td>330</td>
<td>253.15</td>
<td>144.13</td>
<td>155.87</td>
</tr>
</tbody>
</table>

After leaving the sample exposed to carbon dioxide, the reaction cell headspace was once again evacuated. A gas sample was taken to be analyzed via gas chromatography in an attempt to determine the gas phase composition and confirm the occurrence of the exchange during the tests. Next, the freezer was stopped and the assumed mixed hydrate thus created, was decomposed by isochoric heating from experiment temperature to room temperature. At the end of the dissociation run, the reaction cell headspace was once more evacuated and another sample was taken to be analyzed with gas chromatography. The dissociation conditions observed during both tests are presented in table 5-6.

Table 5-6: Dissociation conditions during the CO$_2$-CH$_4$ exchange in hydrate tests with the modified apparatus

<table>
<thead>
<tr>
<th></th>
<th>$T_{\text{initial}}$ (K)</th>
<th>$T_{\text{final}}$ (K)</th>
<th>$P_{\text{final}}$ (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>253.15</td>
<td>293.71</td>
<td>130</td>
</tr>
<tr>
<td>Test 2</td>
<td>253.15</td>
<td>293</td>
<td>169</td>
</tr>
</tbody>
</table>

5.4.4.2. Results and discussion

5.4.4.2.1. Test 1 of the CO$_2$-CH$_4$ exchange within hydrates with the modified apparatus

The evolution of pressure with temperature during the first exchange test performed with the modified apparatus can be seen in figure 5-43.
Figure 5-43: Pressure inside the sample cell during test 1 of the CO\textsubscript{2}–CH\textsubscript{4} exchange in hydrates with the modified apparatus

Three different segments are shown on the plot corresponding each to: (1) CH\textsubscript{4} injection and the formation of CH\textsubscript{4} hydrates, (2) CO\textsubscript{2} injection and the exchange within hydrates and (3) hydrate decomposition. It can be noticed that pressure is decreasing with time after the vessel has first been pressurized with methane. This could be attributed to gas cooling and methane hydrate formation as the selected pressure is above the methane hydrate equilibrium pressure at T=253.15 K, which has been estimated at 189 psig with CSMHYD. As stated in paragraph 5.4.4.2.1, pressure reaches a value of 250 psig after about 6 days. The reaction cell headspace is evacuated and the vessel is pressurized with carbon dioxide at 260 psig, which explains the increase in pressure that is observed around t=143.47 hours. Pressure decreases again in a similar trend than what was noticed during the first segment of the experiment. Assuming the exchange corresponds to methane molecules being replaced by carbon dioxide molecules in the hydrates, the exchange should not cause any pressure decrease as the total
number of moles of gas in the reaction cell headspace should remain constant [43]. The decrease in pressure that we are noticing could be related to carbon dioxide forming pure carbon dioxide hydrate with the excess water as it was observed during the preliminary exchange tests described in section 5.3.3. These explanations are also based upon the assumptions that we have a constant volume system and the effects of leaks within the apparatus can be minimized. During the second segment of the experiment, pressure decreased from 260 psig to about 200 psig in 6 days. The third segment of the plot corresponds to the evolution of pressure during the dissociation of the hydrates. This segment can be seen in more details in figure 5-44.

![Figure 5-44: Pressure inside the reaction cell during the dissociation segment of test 1 of the exchange with the modified apparatus](image)

The pressure versus temperature curve follows a typical trend for the dissociation of hydrates as seen in previous paragraphs. There is a slow increase in pressure from about 254 K to 273 K. The reaction cell
pressure varies between 16 psig and 56 psig, thus a pressure increase rate of 2.1 psi/K. Starting from 273 K, a sharper change in pressure can be observed. Pressure varies between 56 psig at 273 K to 122 psig at 277 K, thus a pressure increase rate of 16.5 psi/K. Dissociation seems to be complete at 277 K and 122 psig. Beyond those conditions, pressure begins to increase linearly with temperature as illustrated in figure 5-41. These observations could be explained by hydrate being slowly dissociated and a small amount of gas being released as temperature rises from 254 K to 273 K. Once 273 K has been reached, water goes from the solid state to the liquid state, the hydrogen bonds of the water cages within the hydrates become weaker, probably causing more gas to be released and the dissociation to be completed within a short period of time, which is materialized by the sharp increase in pressure. Once all gas trapped within hydrates has been released, pressure continues to increase linearly with temperature until room temperature is reached, due to the fact that we have a constant volume system containing a constant amount of gas. Unfortunately, the pressure versus temperature plot does not show with certainty if any mixed hydrates were formed or if we have pure methane hydrates and pure carbon dioxide hydrates being decomposed by isochoric heating. The dissociation curve was plotted against methane and carbon dioxide hydrates phase diagrams. The results can be seen in figure 5-45.
Figure 5-45: Comparison between the dissociation data of test 1 and the stability conditions of methane and carbon dioxide in permafrost regions

The pressure and temperature conditions encountered during the dissociation experiment are outside the stability regions of both methane and carbon dioxide hydrates, for the entire duration of the dissociation experiment. This confirms that gas is being released during the experiment. Yet, hydrate dissociation is not an instant phenomenon and gas is progressively being released from the hydrate structure, although we are outside the hydrate stability regions delimited by the phase boundaries. This can be linked to the anomalous preservation of hydrates, which has been observed for temperatures below 273.15 K and pressures around 0.1 MPa [81].

In order to further confirm the formation of synthetic methane hydrate and the eventual success of the exchange for the conditions of test 1, gas samples were taken before the beginning of the decomposition run and after its completion, to be analyzed by gas chromatography. The Schimadzu GC 17-A gas
chromatograph was used to help determine the compositions of those samples. The results are presented in figures 5-46 and 5-47

**CO₂-CH₄ EXCHANGE IN HYDRATES**
**(BEFORE DISSOCIATION)**

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>CONCENTRATION (MOL %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
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</tr>
<tr>
<td>N₂</td>
<td>1.40</td>
</tr>
<tr>
<td>CH₄</td>
<td>6.79</td>
</tr>
<tr>
<td>CO₂</td>
<td>91.62</td>
</tr>
</tbody>
</table>

![Chromatogram](image)

**Figure 5-46: Chromatogram obtained before dissociation during test 1 of CO₂-CH₄ exchange within hydrates with the modified apparatus**

The results obtained from the chromatography analysis show the presence of oxygen, nitrogen, methane and carbon dioxide in the gas sample. The presence of oxygen and nitrogen could be due to the introduction of a small amount of air in the sample during gas recovery or during sampling with the syringe. Carbon dioxide is the main component of the mixture with a composition of 91.62 mol%. This is in agreement with the fact that the reaction cell headspace was filled with carbon dioxide prior to the exchange. Methane is also present in the mixture with a composition of 6.79 mol%. The presence of methane in the mixture is an indication of the occurrence of the exchange. The amount of methane present is an improvement in comparison to the methane compositions achieved during the preliminary
tests of section 5.3.3. Indeed, concerning those tests, the presence of methane in significant quantities was only noticed for test 1 with a composition of 2.32 mol%. The two subsequent tests resulted in methane content before the exchange below 0.15 mol%. We can infer from these results that the modification of the apparatus, the extension of the experimental time and the increase of the initial experimental temperature, seem to have been beneficial to the reproduction of the exchange in the laboratory.

**CO$_2$-CH$_4$ EXCHANGE IN HYDRATES**  
(AFTER DISSOCATION)

![Chromatogram](image)

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>CONCENTRATION (MOL %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>3.26</td>
</tr>
<tr>
<td>N2</td>
<td>18.41</td>
</tr>
<tr>
<td>CH4</td>
<td>16.14</td>
</tr>
<tr>
<td>CO2</td>
<td>62.19</td>
</tr>
</tbody>
</table>

Figure 5-47: Chromatogram obtained after dissociation during test 1 of the CO$_2$-CH$_4$ exchange within hydrates with the modified apparatus

The results obtained from the chromatography analysis of the sample taken after dissociation can be seen in figure 5-47. We can notice the presence of oxygen, nitrogen, methane and carbon dioxide in the gas mixture. Oxygen and Nitrogen are present in higher quantities (3.26 mol% and 18.41 mol% respectively) in this case due to the fact that the sampling bag seemed to have been perforated, allowing a larger amount of air to be introduced into the bag, than during previous analyses. As a result, the
methane and carbon dioxide contents in the mixture were diluted. We have a methane composition of 16.14 mol% and a carbon dioxide composition of 62.19 mol%. However, if we disregard the presence of nitrogen and oxygen and recalculate the compositions of methane and carbon dioxide based on the numbers of figure 5-47, we obtain a methane composition of 20.6 mol% and a carbon dioxide composition of 79.4 mol%. Considering that the sample was taken from the gas released after dissociation, these results confirm that both methane hydrates and carbon dioxide hydrates were formed during test 1. The methane composition is higher than the results acquired by chromatography analysis after dissociation, for the three preliminary tests described in section 5.3.3. This suggests that we were able to synthesize methane hydrate samples of better quality with the modified apparatus and the new experimental conditions. Besides, we can notice that carbon dioxide is present in the recovered gas in larger amounts than methane. This confirms the fact that carbon dioxide formed pure carbon dioxide hydrates with the excess water in addition to replacing methane trapped in the hydrate structure, as observed in the preliminary tests and reported in the literature ([43] and [44]).

5.4.4.2.2. Test 2 of the CO₂-CH₄ exchange within hydrates with the modified apparatus

Test 2 was comparable to test 1 in terms of procedure. However, a higher injection pressure (P=330 psig) was utilized for carbon dioxide in an attempt to evaluate the effect of pressure on the exchange and to compare it to the test conducted in section 5.3.3.2.3. The evolution of pressure with temperature observed during test 2 is represented in figure 5-48.
We can notice three segments on the plot portraying: (1) \( \text{CH}_4 \) injection and the formation of \( \text{CH}_4 \) hydrates, (2) \( \text{CO}_2 \) injection and the exchange within hydrates and (3) hydrate decomposition. After being pressurized with methane during the first segment of the test, we can notice a decrease in pressure, which could be attributed to methane hydrate formation as the injection pressure is higher than the hydrate equilibrium pressure at 253.15 K. The pressure in the reaction cell reaches a value of 250 psig after about 6 days. Then, we can notice a sudden decrease in pressure corresponding to the reaction cell headspace being evacuated. Next, the vessel is pressurized with carbon dioxide at \( P=330 \) psig. We can see an initial decrease in pressure from 330 psig to about 300 psig, probably due to cooling from room temperature to experiment temperature. Then, pressure stabilizes around 300 psig for the remainder of the experiment. This pressure trend is similar to what was observed during the preliminary tests presented in paragraph 5.3.3, but different from what we observed during test 1. It could be explained by
the fact that the effect of the exchange between carbon dioxide and methane was more significant in this case in comparison to the formation of pure carbon dioxide hydrates with excess water. It could also be a sign of a faster exchange reaction taking place due to a higher driving force and the newly formed hydrates forming a barrier keeping additional carbon dioxide from replacing methane in the hydrates located deeper inside the reaction cell. It is necessary to take a look at the dissociation curve and at the chromatography analysis results to better understand the pressure response recorded during test 2. The dissociation curve is presented in figure 5-49.

![Figure 5-49: Pressure inside the reaction cell during the dissociation segment of test 2 of the exchange with the modified apparatus](image)

The dissociation curve follows a typical trend for a gas hydrate dissociation curve as seen in previous sections. Pressure rises slowly from 254 K to about 273 K with an increase rate of 2.78 psi/K. Then, we have a sharper increase in pressure once a temperature of 273 K has been reached, with a rate of 18.08
psi/K. This is due to the fact that more gas can be released at a faster rate, as water goes from the solid state to the liquid state and the hydrogen bonds of the water cages within the hydrates become weaker. Pressure stabilizes around 156 psig between 277.25 K and 278.68 K. Beyond that temperature, pressure starts rising linearly with temperature until we reach the final temperature of 292.46 K. This could be explained by the fact that all gas is being released at P=156 psig and T=278.68 K. Thus, any further pressure increase for temperatures above 278.68 K is due to the isochoric heating process. The dissociation data allows us to confirm the presence of hydrates in the reaction cell during test 2. The data points were plotted against the methane and carbon dioxide hydrates phase diagrams. The results are displayed in figure 5-50.

Figure 5-50: Comparison between the dissociation data of test 2 and the stability conditions of methane and carbon dioxide in permafrost regions
Similarly to test 1, the pressure and temperature conditions recorded during the dissociation cycle of test 2 are outside the hydrates stability regions. This could be linked to the anomalous hydrate preservation behavior discussed in the literature [81]. We also have higher dissociation pressures in comparison to test 1 and it could suggest that more gas was trapped in the hydrate structure during the experiment. Once the dissociation experiment was completed, gas samples were taken to be analyzed by gas chromatography. The results can be seen in figure 5-51 and 5-52.

Figure 5-51: Chromatogram obtained before dissociation during test 2 of CO$_2$-CH$_4$ exchange within hydrates with the modified apparatus

The results from the chromatography analysis displayed in figure 5-51 show the presence of methane and carbon dioxide in the sample with traces of nitrogen. Once again, the presence of nitrogen can be explained by the introduction of a small amount of air in the sample during gas recovery from the apparatus or gas extraction with the gas tight syringe. Carbon dioxide is the main component of the
mixture with a composition of 97.33 mol%. Methane has a composition of 1.92 mol%. The fact that both methane and carbon dioxide are present in the mixture indicates that carbon dioxide molecules were able to replace some of the methane molecules within the hydrates. Carbon dioxide is the more abundant component due to the fact that the reaction cell headspace was completely filled with carbon dioxide after methane hydrate formation. However, the methane composition is a bit low compared to what was obtained after test 1. This comes in contradiction with the fact that a higher initial reservoir pressure should increase the recovery of methane from hydrates with the replacement technique. As previously stated, the pressure in the sample cell stabilized quickly during the second segment of test 2, implying that a barrier of hydrates may have kept more exchange from occurring. Previous experiments have also shown that carbon dioxide hydrate formation could compete with the exchange reaction in the presence of excess water. Thus, in this case, it seems that the higher carbon dioxide pressure led to a higher driving force for both the exchange and pure carbon dioxide hydrate formation with excess water and the latter may have undermined the ability of carbon dioxide to replace more methane molecules in the hydrates. When compared with the results of the third preliminary test of the exchange presented in section 5.3.3.2.3, we can see that we were able to recover a higher amount of methane. Thus, the modification of the apparatus and of the duration of the exchange experiment appears to have been beneficial, although the performance of the exchange seems to have been limited by the presence of excess water in the reaction cell.
Figure 5-52: Chromatogram obtained after dissociation during test 2 of CO$_2$-CH$_4$ exchange within hydrates with the modified apparatus

The results obtained from the gas chromatography analysis at the end of the dissociation cycle of test 2 display the presence of methane, carbon dioxide and nitrogen. Methane has a composition of 13.01 mol% and carbon dioxide, a composition of 82.12 mol%. Once more, carbon dioxide instead of methane is the main component of the gas mixture recovered from the reaction vessel at the end of the experiment. This confirms that carbon dioxide molecules formed pure carbon dioxide hydrates besides replacing methane molecules in the hydrate structure. The presence of nitrogen in the mixture can be explained by the introduction of air in the gas sample due to experimental error.

Test 1 and 2 were similar in terms of the procedure used with the main difference being the injection of carbon dioxide at a higher pressure (330 psig) during test 2 in comparison to the pressure used in test 1 (260 psig). The pressure trends observed during the test suggest the successful formation of hydrates as a decrease in pressure was observed over time due to the exposure of the hydrate formers (methane and
carbon dioxide) to water (ice). This trend was not observed during the blank tests that were described in previous sections, where the hydrate formers had been introduced in the sample cell in the absence of ice. The presence of hydrates in the reaction cell was further confirmed by the dissociation curves obtained which had a typical shape for gas hydrate dissociation. Higher pressures were achieved during the dissociation cycle of test 2, suggesting that more gas had been entrapped in the hydrate structure. Gas chromatography analyses revealed the presence of methane in the gas samples taken before dissociation for both tests, signifying that the exchange took place. Carbon dioxide was present in larger quantities as expected. Methane and carbon dioxide were also present in the gas samples obtained after dissociation of the hydrates with carbon dioxide, still as major component, indicating that pure carbon dioxide hydrates were formed during the tests. The MATLAB exchange model was used at laboratory conditions and led to methane recoveries of 25.64 % for test 1 and 27.6 % for test 2, thus showing the feasibility of the exchange.

Overall, the modification of the apparatus and of the experimental procedures allowed us to reach better results in terms of feasibility of the exchange in comparison to the preliminary tests. We could see the influence of initial pressure and initial temperature on the performance of the exchange as both tests yielded better methane contents in the gas phase after the exchange than what was achieved in the preliminary tests. However, it appears the presence of excess water still undermined the performance of the exchange and the methane recovery efficiency, such that the effect of the higher initial pressure on the recovery could not be observed during test 2.

5.5. Discussion of results

In this chapter, we attempted to experimentally examine the feasibility of the CO_2-CH_4 molecular guest exchange within hydrates, as a natural gas production method for gas hydrate reservoirs. We designed and built an experimental apparatus able to synthetically create pure hydrates and mimic the exchange at
certain conditions. We performed a series of preliminary tests, showing successful hydrate formation for methane mixed with propane and pure methane. Although, the exchange was less successful during the preliminary tests (in the exception of preliminary test 1 of the exchange), we could notice the influence of the presence of excess water in the system as mentioned in recent publications ([43] and [44]). We could also notice the effects of anomalous gas hydrate preservation described by Stern et al. (2003) [81].

The numerical model developed in chapter 4 was used at laboratory conditions to evaluate the feasibility of the exchange and the results confirmed that 20-28 % of methane recovery could be achieved at the selected experimental conditions. The model also suggested an experimental duration of 143 hours.

The apparatus and the experimental procedures were modified based on the recommendations from the preliminary tests. Pure methane and carbon dioxide hydrate formation and dissociation tests were performed with a 6 day-duration and at a higher temperature of 253.15 K. The results were compared against outcomes from blank tests at similar conditions and confirmed hydrate conversion of 33% for carbon dioxide and of 11.9% for methane. The carbon dioxide hydrate conversion ratio is an improvement in comparison to the preliminary tests. The conversion percent achieved with methane on the other hand is still low, probably due to the low magnitude of the driving force. New CO\textsubscript{2}-CH\textsubscript{4} exchange tests were also executed and generally led to higher methane contents in the gas phase after the exchange than what was observed in the preliminary tests. Although the achieved methane contents are low in comparison with the simulation results, they suggest that the modification of the apparatus, of the experimental duration and of the experimental temperature, was beneficial to the performance of the replacement technique. Anomalous hydrate preservation outside the stability region was also observed. Unfortunately, the presence of excess free water limited the efficiency of the exchange.

Overall, these experiments have enabled us not only to mimic hydrate formation, dissociation and exchange conditions, but also to assess conditions that could optimize methane recovery with the replacement technique. It seems a high initial pressure and a high initial temperature should improve
methane recovery with the exchange technique as seen in chapter 4. This is in good agreement with the observations that have been made in the literature ([43] and [44]). However, the amount of free water present in the system should be as low as possible.
Chapter 6. Life cycle assessment of the CO₂-CH₄ exchange within hydrates

Chapter 4 and 5 respectively focused on numerically and experimentally investigating the feasibility of the exchange and assessing its conditions of success when applied to class 1 hydrate deposits. In those chapters, we were mainly concerned with the possibility of reaching new sources of energy via the extraction of methane from naturally occurring gas hydrates. However, the exchange between CO₂ and CH₄ within hydrates offers the additional advantage of helping to curb emissions of anthropogenic CO₂ in the atmosphere, as CO₂ can be stored in the hydrate form while simultaneously assisting with methane extraction. In this chapter, we will apply a life cycle assessment approach to a hydrate deposit assumed to be under production via the exchange technique. We will assess the impacts on the environments of natural gas production from hydrates using CO₂ clathrate sequestration in terms of CO₂ emissions released in the atmosphere.

6.1. Methodology

Life cycle assessment or analysis (LCA) is a technique that can be used to assess the environmental burden of a process, product or activity during its lifetime ([58] and [92]). It helps identifying and quantifying energy, material usage and environmental releases by evaluating the impacts on the environment, as well as recognizing and implementing opportunities for improvements. LCA usually follows a process or activity from “cradle to grave” and captures energy and material usage, as well as releases to air, water or land during the process lifetime. In order to reach these objectives, the process is split into unit functions or smaller elements with each element having identifiable inputs and outputs ([58],[82] and [92]). A complete life cycle assessment usually incorporates the following four steps: (1) goal and scope definition, (2) inventory, (3) impact assessment and (4) improvement analysis.

The goal and scope definition step of an LCA enables to properly define its objectives, the boundaries that will be accounted for while assessing the use of resources and their impacts on the environment, and
the functional units that will be employed to describe the process. The inventory serves in quantifying raw material usage and emissions occurring during the process lifetime. The impact assessment characterizes the potential environmental problems resulting from the reported emissions, releases and usage such as climate change, stratospheric ozone depletion, tropospheric ozone creation, eutrophication, acidification, toxicological stress on human health and ecosystems, depletion of resources, water use, land use, noise and others [83]. Finally, the improvement analysis evaluates improvements to the product, process or activity that could significantly reduce its environmental load. A diagram summarizing the life cycle assessment framework is presented in figure 6-1.

Figure 6-1: Summary of the life cycle assessment framework ([82] and [84])

For the sake of this research, the four steps of the life cycle assessment technique were utilized; however we focused on evaluating the CO$_2$ emissions associated to the exchange process and on ways to reduce the calculated emission amounts as regards the impact assessment and improvement analysis steps of the LCA methodology.
6.2. Base case scenario: CO\textsubscript{2} captured from a coal-fired power plant

6.2.1. General description

Since the production of natural gas from hydrate deposits has not yet been proven commercially viable, we designed an in-house case study encompassing methane extraction from a class 1 permafrost hydrate reservoir via CO\textsubscript{2} injection. We assumed the existence of one injection well and one production well at the location, with a well spacing of 400 m. The reservoir conditions are P=78.95 atm (1160 psia) and T=280.15 K. We considered the gas layer to be filled with methane before the beginning of production.

The parameters used to describe the reservoir are tabulated in table 6-1

Table 6-1: Reservoir parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir Area (m\textsuperscript{2})</td>
<td>502655</td>
</tr>
<tr>
<td>Hydrate zone (m)</td>
<td>50</td>
</tr>
<tr>
<td>Gas zone (m)</td>
<td>50</td>
</tr>
<tr>
<td>Cap rock thickness (m)</td>
<td>50</td>
</tr>
<tr>
<td>Hydrate saturation (Hydrate zone)</td>
<td>0.8</td>
</tr>
<tr>
<td>Gas saturation (Gas zone)</td>
<td>1</td>
</tr>
<tr>
<td>Porosity (Hydrate zone)</td>
<td>0.3</td>
</tr>
<tr>
<td>Porosity (Gas zone)</td>
<td>0.9</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>280.15</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>78.95</td>
</tr>
<tr>
<td>Initial free gas in place (SCM)</td>
<td>2.1922\times10\textsuperscript{9}</td>
</tr>
<tr>
<td>Initial gas trapped in hydrate (SCM)</td>
<td>9.7092\times10\textsuperscript{8}</td>
</tr>
<tr>
<td>Well depth (m)</td>
<td>750</td>
</tr>
<tr>
<td>Tubing size (I.D., m)</td>
<td>0.062</td>
</tr>
<tr>
<td>Permeability(md)</td>
<td>74.68</td>
</tr>
</tbody>
</table>

A coal-fired power plant can emit up to 6 or 8 Mt of CO\textsubscript{2} in the atmosphere annually; an oil-fired power plant emits 25 % less and a natural gas combined cycle power plant emits about half of the CO\textsubscript{2} emissions that come from coal power plants ([59] and [60]). Thus, coal-based electricity was selected as the primary source of carbon dioxide, in this case. It has been estimated that the emissions of one power plant of 1000 MW capacity need to be captured for the daily supply of CO\textsubscript{2} to the injection site. Carbon dioxide is then transported via pipeline from the capture facility to the injection site. The power plant and transportation parameters are contained in table 6-2
Table 6-2: Power plant, capture process and transportation parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant capacity (MW)</td>
<td>1000</td>
</tr>
<tr>
<td>Capacity factor (%)</td>
<td>80</td>
</tr>
<tr>
<td>Efficiency (HHV)</td>
<td>32</td>
</tr>
<tr>
<td>Capture factor (%)</td>
<td>90</td>
</tr>
<tr>
<td>Pipeline length (km)</td>
<td>641.95</td>
</tr>
<tr>
<td>Pipeline diameter (m)</td>
<td>0.305</td>
</tr>
</tbody>
</table>

6.2.2. Goal and scope definition

We included in our evaluation, the emissions associated with: (1) coal mining, processing and transportation to the power plant, (2) electricity generation, (3) carbon dioxide capture and storage, (4) carbon dioxide transportation, (4) methane extraction and (5) methane combustion. We disregarded emissions related to natural gas handling at processing plants and to the transportation of natural gas to the consumer. The boundary of the CO₂-CH₄ exchange within hydrate system is presented in figure 6-2.

Figure 6-2: LCA system boundary for the base case scenario
6.2.3. Inventory

6.2.3.1. Total amount of carbon dioxide needed

It is essential to define the injectivity of carbon dioxide into the selected hydrate deposit. Indeed parameters such as the injection pressure and the injection rate should be consistent with the reservoir properties and well design parameters.

The injection pressure needs to be selected so that the injected carbon dioxide does not induce fractures inside the reservoir. The fracture gradient of artic permafrost hydrates is taken as 0.65 psi/ft [85]. This corresponds to a pressure of about 1600 psia at 750 m. This pressure is the maximum bottom hole injection pressure for carbon dioxide. We have assumed an injection pressure of 1500 psia.

Using Darcy’s law and considering pseudo-steady state, homogeneous, isentropic and single phase flow from the injection point to the production point inside the reservoir, the following equation can be used to determine the CO$_2$ injection flow rate for a radial flow geometry:

$$q_{\text{inj}} = \frac{0.00708h(P_{\text{inj}} - P_{\text{res}})}{k} \frac{r}{(\ln(\frac{r_e}{r_w}) - \frac{3}{4})} \frac{k}{\mu}$$

(Eq 6-1)

where $q_{\text{inj}}$ is the injection rate (resbbl/D); $P_{\text{inj}}$ is the bottom hole injection pressure (psia); $P_{\text{res}}$ is the reservoir pressure (psia); $k$ is the permeability (md); $\mu$ is the average carbon dioxide viscosity (cP), estimated at reservoir temperature and an average pressure between the injection and the reservoir pressures $P_{\text{avg}} = \frac{P_{\text{inj}} + P_{\text{res}}}{2}$; $r_e$ is the drainage radius (ft) and $r_w$ is the wellbore radius(ft).

Carbon dioxide injection rate was found to be equal to 36667 resbbl/D which corresponds to 5430.76 tCO$_2$/D using CO$_2$ density at reservoir temperature and the average pressure between the injection and production point inside the reservoir: $T=280.15 \; \text{K}$ and $P=90.5 \; \text{atm}$ (1330 psia). The CO$_2$-CH$_4$ exchange
program presented in chapter 4 was used to estimate the amount of CO₂ needed to fill the gas layer at the
beginning of the exchange. It was found that 18.3 MtCO₂ would be required for that purpose. It would
take about 3378 days (9 years) to fill the reservoir with the selected injection rate.

We used the equation for the pressure drop across the well to estimate the surface injection pressure. We have:

\[ P_{surf} = P_{inj} - \Delta P_{hydrostatic} + \Delta P_{friction} \]  

(Eq 6-2)

where \( P_{surf} \) is the pressure at the wellhead (psia, atm or MPa); \( P_{inj} \) is the bottom hole injection pressure
(psia, atm or MPa); \( \Delta P_{hydrostatic} \) is the pressure drop due to the weight of the column of fluid (psia, atm or
MPa) and \( \Delta P_{friction} \) is the pressure drop due to friction (psia, atm or MPa). The pressure drop due to the
change in kinetic energy is neglected here, as we have a constant flow rate and a constant pipe diameter.

\[ \Delta P_{hydrostatic} = \rho_{avg} gh \]  

(Eq 6-3)

where \( \rho_{avg} \) is the fluid density (kg/m³), evaluated at average pressure and temperatures between the
surface and bottom hole conditions \( T_{avg} = \frac{T_{inj} + T_{surf}}{2} \) and \( P_{avg} = \frac{P_{inj} + P_{surf}}{2} \); \( g \) is the acceleration of
gravity (m.s⁻²) and \( h \) is the well depth (m). We are using the average fluid density for equation 6-3, as
CO₂ density varies between surface and reservoir conditions. The friction pressure drop can be
estimated as follows

\[ \Delta P_{friction} = \frac{32f \rho_{avg} Lq^2}{\pi^2 gD^5} \]  

(Eq 6-4)

\[ f_f = \frac{1}{\left[-4 \log\left(\frac{\varepsilon}{3.7065} \cdot \frac{5.0452}{N_{Re}} \log(\frac{1.1098}{2.8257} \cdot \left(\frac{7.149}{N_{Re}}\right)^{0.8981})\right)\right]^2} \]
where $f_f$ is the fanning friction factor (dimensionless); $D$ is the pipe diameter (m); $N_{Re}$ is the Reynolds number (dimensionless); and $\epsilon$ is the pipe roughness (dimensionless). Once again, the density ($\rho_{avg}$) and viscosity ($\mu_{avg}$) are evaluated at average pressure and temperature between surface conditions and bottom hole injection conditions, because of the changes in CO$_2$ density with pressure and temperature. Although the volumetric flow rate will be affected by such changes, the mass flow rate will remain constant. Thus, we will use the following equations instead, to estimate the pressure drop due to friction:

We have:

$$Q = \rho_{avg} q$$  \hspace{1cm} (Eq 6-5)

Thus:

$$\Delta P_{friction} = \frac{32 f_f L Q^2}{\pi^2 g D^4 \rho_{avg}}$$  \hspace{1cm} (Eq 6-6)

And

$$N_{Re} = \frac{4Q}{\pi \mu_{avg} D}$$  \hspace{1cm} (Eq 6-7)

where $Q$ is the mass flow rate in (kg.s$^{-1}$).

Since we need to know the average fluid density in order to perform the calculations, we assumed $P=148.04$ atm (2175.6 psia) for the wellhead pressure and $T=288.15$ K for the surface temperature. Thus, equation 6-3 will help us validate that assumption. The values of the parameters needed are contained in table 6-3.
Table 6-3: Parameters used for the calculation of the surface pressure

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{\text{avg}} ) (atm)</td>
<td>125.04 (12.67 MPa, 1837.6 psia)</td>
</tr>
<tr>
<td>( T_{\text{avg}} ) (K)</td>
<td>284.15</td>
</tr>
<tr>
<td>( \rho_{\text{avg}} ) (kg/m(^3)) [86]</td>
<td>934.58</td>
</tr>
<tr>
<td>( \mu_{\text{avg}} ) ((\mu)Pa.s) [86]</td>
<td>100.94</td>
</tr>
<tr>
<td>( h, L ) (m)</td>
<td>750</td>
</tr>
<tr>
<td>( Q ) (kg/s)</td>
<td>62.856 (5430.76 tCO(_2)/D)</td>
</tr>
<tr>
<td>( N_{\text{Re}} ) (dimensionless)</td>
<td>1.2788x10(^7)</td>
</tr>
<tr>
<td>( \varepsilon ) (dimensionless)</td>
<td>0.0121</td>
</tr>
<tr>
<td>( D ) (m)</td>
<td>0.062</td>
</tr>
<tr>
<td>( f_f ) (dimensionless)</td>
<td>0.01011</td>
</tr>
<tr>
<td>( g ) (m.s(^{-2}))</td>
<td>9.81</td>
</tr>
<tr>
<td>( \Delta P_{\text{hydrostatic}} ) (atm)</td>
<td>67.9 (6.88 MPa, 997.86 psia)</td>
</tr>
<tr>
<td>( \Delta P_{\text{friction}} ) (atm)</td>
<td>114.09 (11.56 MPa, 1676.6 psia)</td>
</tr>
</tbody>
</table>

After incorporating the parameters listed in table 6-3 into equation 6-2, we obtained a value of 148.24 atm (15.02 MPa) for \( P_{\text{surf}} \) that is consistent with our assumptions.

6.2.3.2. Emissions from power generation

In this section, we are going to estimate carbon dioxide emissions resulting from power generation. We are including the emissions of coal mining, processing and transportation as stated in section 6.2.2. From the calculations performed in section 6.2.3.1, we can conclude that 5430.76 tCO\(_2\) are needed daily to fill the gas layer associated with the hydrate deposit, prior to the exchange. We will be evaluating the daily carbon dioxide output from a 1000 MW coal-fired power plant with the following design parameters:

Table 6-4: Power plant design parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant capacity (MW)</td>
<td>1000</td>
</tr>
<tr>
<td>Capacity factor (%)</td>
<td>80</td>
</tr>
<tr>
<td>Efficiency (HHV)</td>
<td>32</td>
</tr>
<tr>
<td>Capture factor (%)</td>
<td>90</td>
</tr>
<tr>
<td>Type of coal</td>
<td>US bituminous coal</td>
</tr>
<tr>
<td>Heating value (MJ/kg of coal) [87]</td>
<td>27.8</td>
</tr>
</tbody>
</table>
The following equations serve in the calculation of the daily energy output and the associated CO₂ emissions:

\[
\text{Daily energy output} = CF \times \text{Capacity} \times \Delta T \\
\text{Amount of CO}_2 \text{ emitted} = EF \times \text{Energy}
\]

(Eq 6-8) \hspace{1cm} (Eq 6-9)

where CF is the plant capacity factor (fraction), Capacity is the plant capacity (MW), \( \Delta T \) corresponds to the duration of energy supply (hours), EF is the emission factor (gCO₂/MJ) and Energy is the amount of energy generated (MJ). We used an emission factor of 87.3 gCO₂/MJ for the U.S bituminous coal [87].

In an effort to estimate the emissions resulting from coal mining, processing and transportation, we needed to evaluate the amount of coal (raw material) utilized for power generation. The daily amount of coal used can be obtained with the given equation:

\[
\text{Amount of Coal} = \frac{\text{Energy}}{\text{Efficiency} \times \text{Heatingvalue}}
\]

(Eq 6-10)

where Efficiency stands for the plant efficiency (fraction) and Heatingvalue is the heating value of the raw materials used (MJ/kg of coal, in this case). An emission factor of 4.99 gCO₂/MJ [62] was utilized to determine the emissions associated with coal mining, processing and transportation. The results for the selected power plant based upon equations 6-8 through 6-10 are contained in table 6-5.

**Table 6-5: Emission results for the coal-fired power plant**

<table>
<thead>
<tr>
<th></th>
<th>Coal-fired power plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily energy output (MJ/D)</td>
<td>6.912 \times 10^7</td>
</tr>
<tr>
<td>Daily amount of Coal used (t/D)</td>
<td>7769.8</td>
</tr>
<tr>
<td>Total emissions from power generation (tCO₂/D)</td>
<td>6034.18</td>
</tr>
<tr>
<td>Total emissions from coal mining, processing and transportation (tCO₂/D)</td>
<td>1077.8</td>
</tr>
</tbody>
</table>
6.2.3.3. Emissions from carbon dioxide capture and storage

We assumed that the flue gases from the power plant would be gathered at a separated capture and storage facility. We also assumed that 90% of carbon dioxide could be captured from the flue gases via chemical absorption ([59], [60] and [62]) which is a post-combustion carbon dioxide capture process. The remaining 10% would be released into the atmosphere. Carbon dioxide capture by chemical absorption involves a reaction between carbon dioxide and a chemical solvent to form a compound that is later on broken down by the application of heat. The chemical solvent is then regenerated. Energy is needed for the process to be performed. We assumed that 3.41 GJ would be necessary per ton of CO$_2$ (947.22 kWh/tCO$_2$) [87]. An emission factor of 712 kgCO$_2$/MWh [62] was employed to determine the emissions related to the energy used in the capture process. That energy was considered to be taken from the electricity grid and is separate from the energy supplied by the power plant. The amount of carbon dioxide captured for transportation, the amount released into the atmosphere after capture and the amount emitted due to the energy used in the absorption process are tabulated in table 6-6.

Table 6-6: Emission results for the CO$_2$ capture process

<table>
<thead>
<tr>
<th>CO$_2$ capture facility</th>
<th>Amount of CO$_2$ captured for transportation (tCO$_2$/D)</th>
<th>Amount of CO$_2$ released into the atmosphere after capture (tCO$_2$/D)</th>
<th>Emissions from the use of CO$_2$ capture technology (tCO$_2$/D)</th>
<th>Total emissions from CO$_2$ capture and storage (tCO$_2$/D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5430.76</td>
<td>603.42</td>
<td>3662.6</td>
<td>4266</td>
</tr>
</tbody>
</table>

Looking at the results presented in table 6-6, we can notice that the entire amount of carbon dioxide captured from the 1000 MW coal-fired power plant can be stored daily at the injection site. We are also considering that the captured carbon dioxide can be brought to a suitable pressure for transportation, here 148.04 atm (15 MPa, 2175.6 psia). Carbon dioxide is transported through a 12 inch diameter pipeline that is 641.95 km long. The pipe roughness is 0.0457 ([88] and [89]). The outlet pressure is 9
MPa. The equation describing the pressure drop across a horizontal pipe can be used to verify that the selected pipeline can carry the daily supply of carbon dioxide. We have in this case:

\[
P_{\text{inlet}} - P_{\text{outlet}} = \Delta P_{\text{friction}} = \frac{32 f_f L Q^2}{\pi^2 g D^5 \rho_{avg}}
\]  
(Eq 6-11)

We assume no change in elevation and no change in kinetic energy (constant flow-rate, constant pipe diameter). The Reynolds number and Fanning friction factor are estimated with the same method as in section 6.2.3.1. The parameters used in the calculation are contained in table 6-7.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_{avg}) (atm)</td>
<td>118.43 (12 MPa, 1740.5 psia)</td>
</tr>
<tr>
<td>(T_{avg}) (K)</td>
<td>288.15</td>
</tr>
<tr>
<td>(\rho_{avg}) (kg/m³)</td>
<td>907.8</td>
</tr>
<tr>
<td>(\mu_{avg}) (μPa.s)</td>
<td>93.544</td>
</tr>
<tr>
<td>h, L (m)</td>
<td>6.4195x10⁵</td>
</tr>
<tr>
<td>Q (kg/s)</td>
<td>62.856 (5430.76 tCO₂/D)</td>
</tr>
<tr>
<td>(N_{Re}) (dimensionless)</td>
<td>1.684x10⁶</td>
</tr>
<tr>
<td>(\varepsilon) (dimensionless)</td>
<td>0.0457</td>
</tr>
<tr>
<td>D (m)</td>
<td>0.305</td>
</tr>
<tr>
<td>(f_f) (dimensionless)</td>
<td>0.01715</td>
</tr>
<tr>
<td>g (m.s⁻²)</td>
<td>9.81</td>
</tr>
<tr>
<td>(\Delta P_{friction}) (atm)</td>
<td>59.21 (6 MPa, 870.23 psia)</td>
</tr>
</tbody>
</table>

The results obtained confirm our assumptions for pipeline transportation. No compression is needed during transportation. Therefore, there are no emissions related to carbon dioxide transportation from the capture facility to the injection site.

### 6.2.3.4. Emissions at the injection site

The carbon dioxide captured from the power plant is transported to the injection site by pipeline. It is recompressed at the site from 9 MPa to 15 MPa. We assumed that the gas layer associated with the hydrate deposit was initially filled with methane. CO₂ injection could help extract gas contained in the hydrate free layer similarly to carbon sequestration enhanced gas recovery. Indeed, simultaneous CO₂
injection deep in the reservoir coupled with CH\textsubscript{4} production should cause the reservoir re-pressurization and CH\textsubscript{4} displacement toward the production well ([90] and [91]). Gas trapped in hydrates could then be accessed via CO\textsubscript{2}-CH\textsubscript{4} exchange within hydrates without causing the dissociation of the hydrate deposit. Depressurization could reach the same goal; however, it would cause hydrate dissociation, which might lead to structure stability issues and uncontrolled methane release into the atmosphere.

6.2.3.4.1. CH\textsubscript{4} production before the exchange

First, we estimated the volume of methane contained in the hydrate free layer using the following equation, based on the real gas law:

\[ V_{\text{CH}_4,sc} = \frac{P V_{\text{CH}_4,\text{res}} M_{\text{CH}_4}}{Z R T P_{\text{CH}_4,sc} \times 1000} \]  
(Eq 6-12)

where \( V_{\text{CH}_4,sc} \) is the volume of methane in the gas layer at standard conditions (scm), \( V_{\text{CH}_4,\text{res}} \) is the volume of methane in the gas layer at reservoir conditions (m\textsuperscript{3}), \( P \) is the reservoir pressure (Pa), \( T \) is the reservoir temperature (K), \( Z \) is the compressibility factor (dimensionless), \( R \) is the real gas constant (Pa.m\textsuperscript{3}.mol\textsuperscript{-1}.K\textsuperscript{-1}) and \( M_{\text{CH}_4} \) is the molar mass of methane (g/mol). The Z-factor was determined with the Soave Redlich and Kwong equation of state at \( P=78.95 \) atm and \( T=280.15 \) K.

As mentioned in section 6.2.3.1, the MATLAB exchange model served to determine the amount of carbon dioxide needed to completely fill the hydrate-free layer. We obtained that 18.3 MtCO\textsubscript{2} would be needed. Equation 6-12 resulted in 2.1922x10\textsuperscript{9} scm which correspond to 1.47 MtCH\textsubscript{4}. The ratio of the volume of CH\textsubscript{4} produced per volume of CO\textsubscript{2} injected can be evaluated as follows:

\[ \text{CO}_2 \text{ effectiveness ratio} = \frac{V_{\text{CH}_4,sc}}{V_{\text{CO}_2,sc}} = \frac{m_{\text{CH}_4}}{\rho_{\text{CH}_4,sc}} \times \frac{\rho_{\text{CO}_2,sc}}{m_{\text{CO}_2}} \]  
(Eq 6-13)
where \( V_{\text{CO}_2,sc} \) is the volume of CO\(_2\) needed to fill the gas layer at standard conditions (scm); \( \rho_{\text{CO}_2,sc} \) is the CO\(_2\) density at standard conditions (kg/m\(^3\)); \( m_{\text{CO}_2} \) is the mass of CO\(_2\) needed to fill the gas layer (Mt); \( \rho_{\text{CH}_4,sc} \) is the CH\(_4\) density at standard conditions (kg/m\(^3\)) and \( m_{\text{CH}_4} \) is the mass of CH\(_4\) contained in the gas layer (Mt). We obtained that about 9 scm of CO\(_2\) need to be injected to produce 2 scm of CH\(_4\), which corresponds to 1000 kg of CO\(_2\) injected for every 80.17 kg of CH\(_4\) produced. As seen in section 6.2.3.1, we will be injecting 5430.76 t of CO\(_2\) per day. This should lead to a methane production rate before exchange of 435.38 t/D (648920 scm/D), using the CO\(_2\) effectiveness ratio estimated above. The design parameters utilized in the calculation of the methane production rate are summarized in table 6-8.

Table 6-8: Parameters used for the calculation of methane production rate prior to the exchange

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P ) (atm)</td>
<td>78.95 (8 MPa, 1160 psia)</td>
</tr>
<tr>
<td>( T ) (K)</td>
<td>280.15</td>
</tr>
<tr>
<td>( \rho_{\text{CH}_4,sc} ) (kg/m(^3)) [86]</td>
<td>0.67093</td>
</tr>
<tr>
<td>( \rho_{\text{CO}_2,sc} ) (kg/m(^3)) [86]</td>
<td>1.8472</td>
</tr>
<tr>
<td>( V_{\text{CH}_4,\text{res}} ) (m(^3))</td>
<td>2.2619 \times 10(^7)</td>
</tr>
<tr>
<td>( V_{\text{CH}_4,sc} ) (scm)</td>
<td>2.1922 \times 10(^9)</td>
</tr>
<tr>
<td>( V_{\text{CO}_2,sc} ) (scm)</td>
<td>9.9323 \times 10(^9)</td>
</tr>
<tr>
<td>( M_{\text{CH}_4} ) (g/mol)</td>
<td>16.043</td>
</tr>
<tr>
<td>( m_{\text{CH}_4} ) (Mt)</td>
<td>1.4708</td>
</tr>
<tr>
<td>( m_{\text{CO}_2} ) (Mt)</td>
<td>18.347</td>
</tr>
<tr>
<td>( R ) (J.mol(^{-1}).K(^{-1}))</td>
<td>8.314</td>
</tr>
</tbody>
</table>

We assumed that 40 kWh/ton of natural gas are required for methane extraction ([59] and [60]). An additional 148 kWh/ton of natural gas serves for gas handling, processing and compression for sales pipelines [89]. Thus, using equation 6-9 and an emission factor for electricity use of 712 kgCO\(_2\)/MWh, we obtain that 58.277 tCO\(_2\) will be emitted daily, due to methane production prior to the exchange. We considered the compression of CO\(_2\) at the injection site from 9 MPa to 15 MPa will require 5 kWh/ton of CO\(_2\) ([59] and [60]). This results in a power requirement of 27.154 MWh for the daily CO\(_2\) injection,
thus emissions of 19.334 tCO₂. These results and the total emissions resulting from methane extraction prior to the exchange are contained in table 6-9.

<table>
<thead>
<tr>
<th></th>
<th>Injection site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of CO₂ injected (tCO₂/D)</td>
<td>5430.76</td>
</tr>
<tr>
<td>Amount of CH₄ produced prior to exchange (tCO₂/D)</td>
<td>435.38</td>
</tr>
<tr>
<td>Emissions from CO₂ compression and injection (tCO₂/D)</td>
<td>19.334</td>
</tr>
<tr>
<td>Emissions from CH₄ production prior to the exchange (tCO₂/D)</td>
<td>58.277</td>
</tr>
<tr>
<td>Total emissions at the injection site prior to the exchange (tCO₂/D)</td>
<td>77.611</td>
</tr>
</tbody>
</table>

6.2.3.4.2. CH₄ production after the exchange

The CO₂-CH₄ exchange model served to estimate the amount of CH₄ that could potentially be extracted from the deposit, after the exchange. The reservoir properties described in table 6-1 were taken as input parameters and the model was run at P=78.95 atm and T=280.15 K. The results can be seen in figure 6-3.
Figure 6-3: Results of the CO$_2$–CH$_4$ exchange model at $P=78.95$ atm and $T=280.15$ K

As displayed in figure 6-3, the CO$_2$–CH$_4$ exchange model predicts that 99.28% of the methane initially trapped in the hydrate can be released by the end of the exchange. Prior to the exchange, the gas layer had been filled with 18.3 Mt of CO$_2$ corresponding to $4.1688 \times 10^{11}$ moles. At the end of the exchange, the hydrate-free layer contains 10.97 mol% of CH$_4$ and 89.03 mol% of CO$_2$ which correspond to 0.73 Mt of CH$_4$ and 16.3 Mt of CO$_2$ respectively. The released gas can now be recovered through conventional production methods; however, the reservoir pressure should not get below the equilibrium pressure of
the mixed CO₂-CH₄ hydrate that resulted from the exchange at reservoir pressure, as this would lead to hydrate decomposition.

As stated in chapter 4, the exchange should result in an increase of the reservoir temperature. We can infer from the model results that the final temperature after the exchange is 282.1 K. The final composition of the hydrate structure (0.72 mol% of CH₄ and 99.28 mol% of CO₂) was incorporated as an input to determine the equilibrium pressure at 282.1 K. The CSMHYD software [72] was used to estimate the equilibrium pressure at such conditions and we found P=36.41 atm (535.14 psia). We estimated the moles of fluid that would be present in the hydrate layer at T=282.1 K and P=36.41 atm, via equation 4-9. The Z-factor of the fluid mixture was calculated with the help of the Soave, Redlich and Kwong equation of state using 10.97 mol% of CH₄ and 89.03 mol% of CO₂ as the composition. We obtained that the hydrate-free layer would contain 4.6806x10¹⁰ moles of fluid at such conditions.

These results allowed us to determine the amounts of carbon dioxide and methane that are recoverable after the exchange in order to avoid dissociation of the mixed hydrate resulting from the exchange. The following equations served in the calculation:

\[
\text{m}_{\text{CO}_2,\text{recoverable}} = \text{m}_{\text{CO}_2,\text{after exchange}} - \text{m}_{\text{CO}_2,\text{after production}} = \frac{y_{\text{CO}_2} (\text{molefreesgas}_{\text{after exchange}} - \text{molefreesgas}_{\text{after production}}) \text{M}_{\text{CO}_2}}{10^6} \quad (\text{Eq 6-14})
\]

\[
\text{m}_{\text{CH}_4,\text{recoverable}} = \text{m}_{\text{CH}_4,\text{after exchange}} - \text{m}_{\text{CH}_4,\text{after production}} = \frac{y_{\text{CH}_4} (\text{molefreesgas}_{\text{after exchange}} - \text{molefreesgas}_{\text{after production}}) \text{M}_{\text{CH}_4}}{10^6} \quad (\text{Eq 6-15})
\]

where \(\text{m}_{\text{CO}_2,\text{recoverable}}\) is the mass of carbon dioxide and \(\text{m}_{\text{CH}_4,\text{recoverable}}\) is the mass of methane that can be recovered without dissociating the hydrate structure (Mt), \(\text{m}_{\text{CO}_2,\text{after exchange}}\) is the mass of carbon dioxide and \(\text{m}_{\text{CH}_4,\text{after exchange}}\) is the mass of methane in the hydrate-free layer at the end of the exchange (Mt), \(\text{m}_{\text{CO}_2,\text{after production}}\) is the mass of carbon dioxide and \(\text{m}_{\text{CH}_4,\text{after production}}\) is the mass of methane in the hydrate-
free layer at the end of recovery (Mt), \( y_{CO_2} \) is the carbon dioxide molar fraction and \( y_{CH_4} \) the methane molar fraction in the hydrate-free layer (dimensionless), \( M_{CO_2} \) is the molar mass of carbon dioxide and \( M_{CH_4} \) is the molar mass of methane (g/mol), \( molefreegas_{after\ exchange} \) is the amount of fluid in the hydrate-free layer after the exchange (mol) and \( molefreegas_{after\ production} \) is the amount of fluid in the hydrate-free layer after production. The calculated amounts and the parameters used in the calculation are contained in table 6-10.

Table 6-10: Amounts of carbon dioxide and methane recoverable after the exchange

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( y_{CO_2} ) (dimensionless)</td>
<td>0.8903</td>
</tr>
<tr>
<td>( y_{CH_4} ) (dimensionless)</td>
<td>0.1097</td>
</tr>
<tr>
<td>( M_{CO_2} ) (g/mol)</td>
<td>44.01</td>
</tr>
<tr>
<td>( M_{CH_4} ) (g/mol)</td>
<td>16.043</td>
</tr>
<tr>
<td>( molefreegas_{after\ exchange} ) (mol)</td>
<td>4.1688x10^{11}</td>
</tr>
<tr>
<td>( molefreegas_{after\ production} ) (mol)</td>
<td>4.6806x10^{10}</td>
</tr>
<tr>
<td>( m_{CO_2,after\ exchange} ) (Mt)</td>
<td>16.334</td>
</tr>
<tr>
<td>( m_{CO_2,after\ production} ) (Mt)</td>
<td>1.8339</td>
</tr>
<tr>
<td>( m_{CH_4,after\ exchange} ) (Mt)</td>
<td>0.73381</td>
</tr>
<tr>
<td>( m_{CH_4,after\ production} ) (Mt)</td>
<td>0.08237</td>
</tr>
<tr>
<td>( m_{CO_2,recoverable} ) (Mt)</td>
<td>14.5</td>
</tr>
<tr>
<td>( m_{CH_4,recoverable} ) (Mt)</td>
<td>0.6514</td>
</tr>
</tbody>
</table>

We can infer from the calculations that 15.1 Mt of fluid should be recoverable after the exchange, without dissociating the new hydrate structure. Assuming that the production well design parameters can be adapted to sustain a constant production rate for 7 years, 5674.8 tons of fluid will be produced on a daily basis, corresponding to 5430.76 t/D of CO\(_2\) and 244.04 t/D of CH\(_4\). We will also assume that carbon dioxide produced alongside methane can be recycled and re-injected into the hydrate-free layer. We will use 4.71 kWh/ton of CO\(_2\) for CO\(_2\) recycling and reinjection [89]; 40 kWh/ton of fluid for fluid recovery ([59] and [60]) and 148 kWh/ton of natural gas for gas handling, processing and compression to sales pipeline requirements [89]. The emissions related to fluid recovery at the injection site post-
exchange can be estimated based on the assumptions mentioned above. The computed results are contained in table 6-11.

Table 6-11: Emission results for the injection site post-exchange

<table>
<thead>
<tr>
<th>Emission source</th>
<th>Injection site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of fluid recovered (t/D)</td>
<td>5674.8</td>
</tr>
<tr>
<td>Amount of CH₄ produced post-exchange (tCH₄/D)</td>
<td>244.04</td>
</tr>
<tr>
<td>Amount of CO₂ recycled and re-injected (tCO₂/D)</td>
<td>5430.76</td>
</tr>
<tr>
<td>Emissions from fluid production post-exchange (tCO₂/D)</td>
<td>161.62</td>
</tr>
<tr>
<td>Emissions from gas handling and processing (tCO₂/D)</td>
<td>25.716</td>
</tr>
<tr>
<td>Emissions from CO₂ recycling and re-injection (tCO₂/D)</td>
<td>18.212</td>
</tr>
<tr>
<td>Total emissions at injection site post-exchange (tCO₂/D)</td>
<td>205.55</td>
</tr>
</tbody>
</table>

6.2.3.5. Total emissions of the process

The total daily emission amounts that have been evaluated from section 6.2.3.1 through section 6.2.3.4 are multiplied by the total production time before and after the exchange (3378 days and 2670 days respectively) in an attempt to obtain the total emissions from the use of the CO₂-CH₄ exchange process as a production technique for the selected hydrate deposit. The emissions from natural gas combustion after extraction from the reservoir have also been taken into account. We used a heat content of 37.3 kJ/m³ and an emission factor of 50 gCO₂/MJ [87]. The results are presented in table 6-12.

Table 6-12: Total emissions of the system for the base case scenario

<table>
<thead>
<tr>
<th>Emissions (tCO₂)</th>
<th>Pre-exchange</th>
<th>Post-exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal mining, processing and transportation</td>
<td>3.64x10⁶</td>
<td>0</td>
</tr>
<tr>
<td>Power generation (net emissions after capture)</td>
<td>2.04x10⁶</td>
<td>0</td>
</tr>
<tr>
<td>Carbon dioxide capture process</td>
<td>12.4x10⁶</td>
<td>0</td>
</tr>
<tr>
<td>Operations at injection site</td>
<td>2.62x10⁷</td>
<td>5.49x10⁷</td>
</tr>
<tr>
<td>Methane combustion</td>
<td>4088.4</td>
<td>1810.7</td>
</tr>
<tr>
<td>Total emissions</td>
<td>18.3x10⁷</td>
<td>5.51x10⁷</td>
</tr>
</tbody>
</table>
We can infer from the values contained in table 6-12 that 18.8 MtCO$_2$ will be emitted in the atmosphere during the entire process lifetime ($\approx$ 16 years). A schematic diagram of the production process and the allocated emissions can be seen in figure 6-4.

Figure 6-4: Total emissions related to the production of CH$_4$ from hydrate deposits with CO$_2$ sequestration: base case scenario

6.3. Alternative case scenario: CO$_2$ captured from a natural gas-fired power plant

6.3.1. General description and system boundary

Since natural gas (assimilated here to methane) is the main commodity that can be recovered from the use of the replacement technique with class 1 hydrate deposits and is a cleaner fuel than coal, an alternative case scenario was designed based on the utilization of carbon dioxide emitted from a natural gas–fired power plant for the recovery of methane from gas hydrate reservoirs. We kept the same reservoir parameters as the ones presented in table 6-1. We also kept the same pipeline transportation parameters. However, a 500 MW Natural Gas Combined Cycle (NGCC) power plant with a capacity factor of 80% and an efficiency of 50.2 % was selected for this case.
The system boundary includes emissions associated with: (1) natural gas extraction, processing and transportation for power plant supply, (2) electricity generation, (3) carbon dioxide capture and storage, (4) carbon dioxide transportation, (4) methane extraction and (5) methane combustion. Similarly to the case presented in section 6.2, we did not incorporate emissions related to natural gas handling at processing plants or to the transportation of natural gas to the consumer into our analysis. A diagram portraying the system boundary can be seen in figure 6-5.

![Diagram of LCA system boundary for the alternative case scenario](image)

Figure 6-5: LCA system boundary for the alternative case scenario

6.3.2. Inventory

6.3.2.1. Total amount of carbon dioxide needed

As seen in section 6.2.3.1, we determined the carbon dioxide injection rate, assuming an injection pressure of 1256 psia which is lower than the fracture pressure of about 1600 psia that was obtained in section 6.2.3.1. Using equation 6-1, the carbon dioxide injection rate was found to be 10578 resbbl/D which corresponds to about 1555.2 tCO₂/D for a CO₂ density calculated at reservoir temperature and the average pressure between the injection point and the production point inside the reservoir: T=280.15 K and P=82.2 atm (1208 psia). Considering that this injection rate can be maintained constant throughout
the project lifetime and 18.3 MtCO\textsubscript{2} are needed to fill the hydrate free layer of the reservoir, it should take 11797 days (32 years) to completely saturate the gas layer with carbon dioxide.

Equations 6-2 through 6-10 served to determine the surface injection pressure in a method similar to what has been described in section 6.2.3.1. The parameters needed to evaluate the surface pressure are contained in table 6-13.

Table 6-13: Parameters used for the calculation of the surface pressure

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{avg}}$ (atm)</td>
<td>116.75 (8.33 MPa, 1716 psia)</td>
</tr>
<tr>
<td>$T_{\text{avg}}$ (K)</td>
<td>284.15</td>
</tr>
<tr>
<td>$\rho_{\text{avg}}$ (kg/m\textsuperscript{3})</td>
<td>928.70</td>
</tr>
<tr>
<td>$\mu_{\text{avg}}$ (μPa.s)</td>
<td>99.271</td>
</tr>
<tr>
<td>$h$, L (m)</td>
<td>750</td>
</tr>
<tr>
<td>Q (kg/s)</td>
<td>18 (1555.2 tCO\textsubscript{2}/D)</td>
</tr>
<tr>
<td>$N_{\text{Re}}$ (dimensionless)</td>
<td>3.7236x10\textsuperscript{6}</td>
</tr>
<tr>
<td>$\varepsilon$ (dimensionless)</td>
<td>0.795</td>
</tr>
<tr>
<td>D (m)</td>
<td>0.062</td>
</tr>
<tr>
<td>$f_f$ (dimensionless)</td>
<td>0.13981</td>
</tr>
<tr>
<td>g (m.s\textsuperscript{2})</td>
<td>9.81</td>
</tr>
<tr>
<td>$\Delta P_{\text{hydrostatic}}$ (atm)</td>
<td>67.4 (6.83 MPa, 990.51 psia)</td>
</tr>
<tr>
<td>$\Delta P_{\text{friction}}$ (atm)</td>
<td>130.27 (13.2 MPa, 1914.4 psia)</td>
</tr>
</tbody>
</table>

After incorporating the results in equation 6-2, we obtained a value of 148.33 atm for $P_{\text{surf}}$ that is consistent with the assumptions used in the calculation process.

6.3.2.2. Emissions from power generation

In this section, we will be estimating the carbon dioxide emissions stemming from power generation. We are including the emissions from natural gas extraction, processing and transportation for power supply into the study system’s boundary, as stated in section 6.3.1. Carbon dioxide will be captured from a 500 MW NGCC power plant with the following design parameters summarized in table 6-14:
Table 6-14: Power plant design parameters

<table>
<thead>
<tr>
<th></th>
<th>Natural Gas-fired power plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant capacity (MW)</td>
<td>500</td>
</tr>
<tr>
<td>Capacity factor (%)</td>
<td>80</td>
</tr>
<tr>
<td>Efficiency (HHV)</td>
<td>50.2</td>
</tr>
<tr>
<td>Capture factor (%)</td>
<td>90</td>
</tr>
<tr>
<td>Type of fuel</td>
<td>Natural gas</td>
</tr>
<tr>
<td>Heating value (kJ/m³)</td>
<td>37.3</td>
</tr>
</tbody>
</table>

Equations 6-8 through 6-10 have been used to determine the emissions related to power generation from the selected power plant. An emission factor of 89.5 gCO₂/kg of natural gas ([59] and [60]) served for the calculation of the emissions associated with natural gas supply to the power plant. The estimated emission values are tabulated in table 6-15:

Table 6-15: Emission results for the natural gas-fired power plant

<table>
<thead>
<tr>
<th></th>
<th>Natural Gas-fired power plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily energy output (MJ/D)</td>
<td>3.456x10⁷</td>
</tr>
<tr>
<td>Daily amount of natural gas</td>
<td>1845.7</td>
</tr>
<tr>
<td>used (t/D)</td>
<td></td>
</tr>
<tr>
<td>Total emissions from power</td>
<td>1728</td>
</tr>
<tr>
<td>generation (tCO₂/D)</td>
<td></td>
</tr>
<tr>
<td>Total emissions from natural</td>
<td>165.19</td>
</tr>
<tr>
<td>gas extraction, processing and</td>
<td></td>
</tr>
<tr>
<td>transportation (tCO₂/D)</td>
<td></td>
</tr>
</tbody>
</table>

6.3.2.3. Emissions from carbon dioxide capture and storage

As stated in section 6.2.3.3, we assumed that the flue gases from the power plant would be gathered at a carbon dioxide capture facility. We also assumed that 90% of the carbon dioxide content could be captured through chemical absorption ([59], [60] and [62]) similarly to what was described in section 6.2.3.3. The remaining 10% would eventually be released into the atmosphere. 3.41 GJ (947.22 kWh) [87] need to be supplied per ton of carbon dioxide captured for the process to be performed. An emission factor of 712 kgCO₂/MWh [62] was used to evaluate the emissions related to the capture process. The results can be seen in table 6-16.
Table 6-16: Emission results for the carbon dioxide capture facility

<table>
<thead>
<tr>
<th>CO₂ capture facility</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of CO₂ captured for transportation (tCO₂/D)</td>
<td>1555.2</td>
</tr>
<tr>
<td>Amount of CO₂ released into the atmosphere after capture (tCO₂/D)</td>
<td>172.8</td>
</tr>
<tr>
<td>Emissions from the use of CO₂ capture technology (tCO₂/D)</td>
<td>1048.8</td>
</tr>
<tr>
<td>Total emissions from CO₂ capture and storage (tCO₂/D)</td>
<td>1221.6</td>
</tr>
</tbody>
</table>

Similarly to what was obtained for the base case scenario, it can be noticed that the total amount of carbon dioxide captured daily can be injected into the reservoir for the selected reservoir parameters, as well as the surface and bottom-hole injection pressures. We are also considering that the daily amount of carbon dioxide captured can be transported daily to the injection site through a 12 inch diameter pipeline which is 641.95 km long. We assumed the inlet and outlet pressures would respectively be 15 MPa and 9 MPa. These assumptions were verified using equation 6-11 in the same way described in section 6.2.3.3. The parameters required in this case are summarized in table 6-17.

Table 6-17: Parameters required for the calculation of the pressure drop across the CO₂ transportation pipeline

<table>
<thead>
<tr>
<th>Parameter (dimensionless)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>P̄ (atm)</td>
<td>118.43 (12 MPa, 1740.5 psia)</td>
</tr>
<tr>
<td>T̄ (K)</td>
<td>288.15</td>
</tr>
<tr>
<td>ρ̄ (kg/m³) [86]</td>
<td>907.8</td>
</tr>
<tr>
<td>μ̄ (μPa.s) [86]</td>
<td>93.544</td>
</tr>
<tr>
<td>h, L (m)</td>
<td>6.4195x10⁵</td>
</tr>
<tr>
<td>Q (kg/s)</td>
<td>18 (1555.2 tCO₂/D)</td>
</tr>
<tr>
<td>N_Re (dimensionless)</td>
<td>8.0328x10⁵</td>
</tr>
<tr>
<td>ε̄ (dimensionless)</td>
<td>1.05</td>
</tr>
<tr>
<td>D (m)</td>
<td>0.305</td>
</tr>
<tr>
<td>f̄ (dimensionless)</td>
<td>0.2083</td>
</tr>
<tr>
<td>g (m.s⁻²)</td>
<td>9.81</td>
</tr>
<tr>
<td>ΔP_fricción (atm)</td>
<td>59.21 (≈6 MPa, 870.23 psia)</td>
</tr>
</tbody>
</table>

We assume that no compression would be necessary during transportation of carbon dioxide to the injection site. Therefore, we do not account for any emissions due to CO₂ transportation.
6.3.2.4. Emissions at the injection site

After being transported to the injection site, carbon dioxide is compressed from 9 MPa to 15 MPa and then injected into the reservoir. As stated in section 6.2.3.4, the hydrate free layer is initially filled with methane. Thus, CO₂ injection could help recover that gas prior to the exchange.

6.3.2.4.1. CH₄ production before the exchange

The amount of CH₄ initially contained in the hydrate free layer was estimated to be 1.47 MtCH₄. The total amount of CO₂ required to fully saturate the hydrate free layer was evaluated to be 18.3 MtCO₂. Thus, using the same CO₂ effectiveness ratio as in section 6.2.3.4.1, the daily injection of 1555.2 tons of CO₂ should enable the daily production of 124.68 tons of CH₄. In the same manner portrayed in section 6.2.3.4.1, we assumed that 40 kWh/ton of natural gas would be required for methane extraction ([59] and [60]). An additional 148 kWh/ton of natural gas [89] would serve for the handling, processing and compression to sale pipeline requirements of the produced gas. We also considered that 5 kWh/ton of CO₂ ([59] and [60]) would be used for compression and injection at the site. The calculated emissions are contained in table 6-18.

Table 6-18: Emission results for the injection site prior to the exchange

<table>
<thead>
<tr>
<th></th>
<th>Injection site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of CO₂ injected (tCO₂/D)</td>
<td>1555.2</td>
</tr>
<tr>
<td>Amount of CH₄ produced prior to exchange (tCO₂/D)</td>
<td>124.68</td>
</tr>
<tr>
<td>Emissions from CO₂ compression and injection (tCO₂/D)</td>
<td>5.5365</td>
</tr>
<tr>
<td>Emissions from CH₄ production prior to the exchange (tCO₂/D)</td>
<td>16.689</td>
</tr>
<tr>
<td>Total emissions at the injection site prior to the exchange (tCO₂/D)</td>
<td>22.226</td>
</tr>
</tbody>
</table>
6.3.2.4.2. CH₄ production after the exchange

The total amount of fluid recoverable after the exchange has been estimated in section 6.2.3.4.2 and we obtained 15.1 Mt. Considering that the production well design parameters could be adjusted to sustain a constant daily production for about 25 years (9323 days), 1625.1 tons of fluid should be produced daily. This will correspond to 1555.2 tCO₂/D and 69.9 tCH₄/D. Carbon dioxide produced alongside methane will be recycled and re-injected into the reservoir. As stated in section 6.2.3.4.2, a value of 4.71 kWh/ton of CO₂ [89] was used for the power requirement related to CO₂ recycling and re-injection. We considered that 40 kWh/ton of fluid ([59] and [60]) are required for fluid recovery and 148 kWh/ton of natural gas [89] serve for gas handling, processing and compression to sale pipeline requirements. The final results are summarized in table 6-19.

<table>
<thead>
<tr>
<th>Injection site</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of fluid recovered (t/D)</td>
<td>1625.1</td>
</tr>
<tr>
<td>Amount of CH₄ produced post-exchange (tCH₄/D)</td>
<td>69.9</td>
</tr>
<tr>
<td>Amount of CO₂ recycled and re-injected (tCO₂/D)</td>
<td>1555.2</td>
</tr>
<tr>
<td>Emissions from fluid production post-exchange (tCO₂/D)</td>
<td>46.283</td>
</tr>
<tr>
<td>Emissions from gas handling and processing (tCO₂/D)</td>
<td>7.3656</td>
</tr>
<tr>
<td>Emissions from CO₂ recycling and re-injection (tCO₂/D)</td>
<td>5.2154</td>
</tr>
<tr>
<td>Total emissions at injection site post-exchange (tCO₂/D)</td>
<td>58.864</td>
</tr>
</tbody>
</table>

6.3.2.5. Total emissions of the process

The total daily emission amounts that have been evaluated from section 6.3.2.1 through section 6.3.2.4 have been multiplied by the total production time before and after the exchange for the alternative case scenario (11797 days and 9323 days) in order to obtain the total emissions resulting from the use of the CO₂-CH₄ replacement process as a production technique for the selected hydrate deposit with the
utilization of carbon dioxide captured from a NGCC power plant. The emissions related to natural gas combustion after extraction from the reservoir are also included. We considered a heat content of 37.3 kJ/m$^3$ and an emission factor of 50 gCO$_2$/MJ for natural gas [87]. The produced natural gas could be reused as fuel for the NGCC power plant, thus leading to cost reduction. However, the daily natural gas production rates pre- and post-exchange in this case, were lower than the daily amount of natural gas required by the NGCC plant. Therefore, this option was not accounted for in the calculations. The final results are tabulated in table 6-20.

**Table 6-20: Total emissions of the system for the alternative case scenario**

<table>
<thead>
<tr>
<th>Emissions (tCO$_2$)</th>
<th>Pre-exchange</th>
<th>Post-exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas extraction, processing and transportation</td>
<td>1.95x10$^6$</td>
<td>0</td>
</tr>
<tr>
<td>Power generation (net emissions after capture)</td>
<td>2.04x10$^6$</td>
<td>0</td>
</tr>
<tr>
<td>Carbon dioxide capture process</td>
<td>12.4x10$^6$</td>
<td>0</td>
</tr>
<tr>
<td>Operations at injection site</td>
<td>2.62x10$^5$</td>
<td>5.49x10$^3$</td>
</tr>
<tr>
<td>Methane combustion</td>
<td>4088.4</td>
<td>1810.7</td>
</tr>
<tr>
<td>Total emissions</td>
<td>16.6x10$^6$</td>
<td>5.51x10$^3$</td>
</tr>
</tbody>
</table>

We can infer from the values contained in table 6-20 that 17.2 MtCO$_2$ will be emitted in the atmosphere during the entire process lifetime ($\approx$ 57 years). A schematic diagram of the production process with the allocated emissions can be seen in figure 6-6.
6.4. Summary and analysis

The life cycle assessment approach was applied to two case scenarios in this chapter: a base case scenario involving carbon dioxide capture from a coal power plant and an alternative case scenario involving carbon dioxide capture from a natural gas combined cycle power plant.

This allowed us to establish that the application of the exchange technique to the selected hypothetical hydrate deposit with capture of carbon dioxide from a 1000 MW coal-fired power plant, results in the total emissions of 18.8 MtCO₂ in the atmosphere. It should also be possible to store 18.3 MtCO₂ in the reservoir with 2 MtCO₂ trapped in hydrate form and 16.3 MtCO₂ in the hydrate-free layer. Thus, the process should cause a net release of 0.5 MtCO₂ in the atmosphere. A total of 2.12 MtCH₄ can be extracted through the use of the replacement technique coupled with CO₂ injection, therefore the process results in 0.24 tons of CO₂ emitted per ton of CH₄ produced.
For the case involving a 500 MW natural gas combined cycle power plant, we were able to see that the entire production process results in the total emissions of 17.2 MtCO2 in the atmosphere. 18.3 MtCO2 are also stored in the hydrate reservoir similarly to the base case scenario. Thus, in this case, there are no net emissions related to methane extraction from the hydrate reservoir. The use of carbon dioxide captured from a NGCC power plant leads to an emission-neutral gas extraction process. When comparing the final emission outcomes from both scenarios summarized in tables 6-12 and 6-20, it can be observed that the main difference between both cases is linked to the emissions related to raw material supply to the power plant. Indeed, based on selected emission factors for both units, coal mining, processing and transportation seem to generate higher carbon dioxide emissions than natural gas extraction, processing and transportation to the power plant. An additional observation that can be made about both cases is that the process lifetime is shorter in the case of the coal power plant (16 years) than in the case of the NGCC power plant (57 years) due to the fact that natural gas is cleaner than coal and gas power plants emit less carbon dioxide than coal power plants. It should be interesting to see how this aspect and the possibility of using produced methane as supply for the gas power plant, could affect the economics of the project.

We also calculated emissions resulting from the hypothetical production of the same amount of methane over the same duration without carbon dioxide injection. This should cause the emissions of $2.9 \times 10^5$ tCO2 into the atmosphere (gas extraction, gas handling and gas combustion), thus a ratio of 0.14 tons of CO2 emitted per ton of CH4 produced. When compared with the base case and alternative case scenarios, we can see once again that for the selected hydrate deposit, the use of carbon dioxide from a NGCC power plant for the exchange technique is more beneficial and leads to a decrease in the process emissions. For the case of the coal power plant, the higher net emission value of 0.24 tons of CO2 per ton of CH4 produced can be explained not only by the emissions resulting from coal mining, processing and transportation, but also by the fact that the carbon dioxide capture process requires the use of a great
amount of energy (947.22 kWh/ton of CO\textsubscript{2} captured) \cite{87}, which causes a large amount of emissions to be released into the atmosphere. If we assume that the energy requirement of the carbon capture process is instead 330 kWh/ton of CO\textsubscript{2} captured \cite{59}, we obtain 4.31 MtCO\textsubscript{2} for the emissions resulting from the carbon dioxide capture process. Thus, the total emissions related to methane production with CO\textsubscript{2} clathrate sequestration are estimated to be 10.8 MtCO\textsubscript{2}, which is less than the amount being stored (18.3 MtCO\textsubscript{2}). Therefore, in that case, the use of the exchange technique with carbon dioxide captured from a coal power plant results in a 100% emission reduction when compared to methane production without CO\textsubscript{2} injection. The alternative case scenario still leads to emission-neutral methane production with total emissions of 9.12 MtCO\textsubscript{2} in the atmosphere. Lowering the energy requirement of the capture process should also lead to lower gas production costs as similar studies (\cite{87} and \cite{89}) have demonstrated that oil and or gas production with CO\textsubscript{2} capture from power plants could be uneconomical due to the high cost of the carbon dioxide capture process.

Through this analysis, we were able to assess the potential of the exchange technique in terms of CO\textsubscript{2} emission reduction. We could see that carbon dioxide clathrate sequestration associated with natural gas extraction from hydrate deposits can lead to emission-neutral gas production when carbon dioxide is captured from a NGCC power plant. However, the process lifetime may be longer in that case and this could influence the economics of the project. A shorter process lifetime can be achieved if carbon dioxide is captured from a coal power plant. Yet, the process will result in larger emission amounts than in the case of gas production without CO\textsubscript{2} injection. This issue can be solved by lowering the energy requirement of the carbon dioxide capture process. We could see that the cost and energy requirement of the CO\textsubscript{2} capture process have a significant impact on the efficiency of the technique.
Chapter 7. Conclusions and Final recommendations

The overall objective of this study was to examine the potential of the chemical substitution of methane by carbon dioxide within hydrates as a gas hydrate production technique by the application of numerical, experimental and life cycle assessment methods. We had the following measurable goals:

(1) Numerical modeling of the CO$_2$-CH$_4$ molecular guest exchange for a gas hydrate formation with estimation of CO$_2$ consumption rates, CH$_4$ yield rates and CH$_4$ recovery efficiencies with time

(2) Laboratory synthesis of pure hydrates and reproduction of the CO$_2$-CH$_4$ exchange

(3) Experimental and numerical investigation of selected factors which could influence the performance of the exchange

(4) Life-cycle assessment of the exchange process applied to a hypothetical hydrate reservoir

The conclusions and recommendations from our investigation are presented in the next sections.

7.1. Conclusions

First, we succeeded in developing a MATLAB numerical model capable of simulating the CO$_2$-CH$_4$ molecular guest exchange within hydrates. We estimated the consumption rates of carbon dioxide and yield rates of methane throughout the exchange for different cases. We evaluated the changes in temperature and methane recovery percentages. We also compared the performance of the model to a depressurization model by Gerami and Pooladi-Darvish (2007) [55]. With the results from our simulation scenarios, we were able to establish the following:

(1) Initial reservoir pressure and temperature have an impact on the performance of the exchange and their increase should yield higher methane recovery ratios

(2) Higher recoveries and faster reaction rates are obtained with the use of liquid CO$_2$
(3) Class 1 hydrate reservoirs with a large hydrate zone thickness and porosity that are associated to a thin gas layer may lead to low recovery ratios for the CO$_2$-CH$_4$ molecular guest exchange within hydrates.

(4) The cap rock thermal conductivity does not affect recovery which is instead more affected by the enthalpy of the exchange reaction. Higher enthalpy values lead to higher recovery ratios and higher hydrate block temperatures at the end of the exchange.

(5) Depressurization could yield lower recovery ratios than the CO$_2$-CH$_4$ molecular guest exchange within hydrates if the selected operating pressures are not low enough relative to the initial reservoir pressure.

We obtained different methane recovery ratios depending on the initial reservoir conditions as noticed in the literature. The effect of the initial reservoir pressure and temperature, as well as the effect of the use of liquid CO$_2$ on methane recovery from the exchange, were demonstrated through the simulations presented in chapter 4. These results are in accordance with the recent observations that have been made in the literature ([43] and [44]). Yet, it is essential to recall that these results fall under the assumptions of deep decomposition within the hydrates, perfect hydrate stoichiometry and exchange within all hydrate cages, thus making them optimistic. Besides, the conclusions that we reached concerning the influence of thickness on exchange recovery might be erroneous, since we did not account for changes in parameters such as the heat capacity and the thermal conductivity with temperature, as well as temperature changes with the thickness of the layers. It is also important to emphasize that the comparison we performed between our exchange model and the depressurization model by Gerami and Pooladi-Darvish [55] focused mainly on estimating the amount of methane released from the hydrates via the use of those techniques, which could be different from the amount of methane produced at the wellhead from fluid flow. Although, the results from this comparison allowed us to further demonstrate the potential of the hydrates’ replacement technique as a legitimate gas hydrate production method, they
do not imply that the use of the exchange technique would yield better results than depressurization, in terms of methane recovery, under all circumstances.

Secondly, we successfully built and designed an experimental apparatus able to synthetically create pure hydrates and mimic the exchange at certain conditions. We performed a series of preliminary tests allowing us to validate the ability of the apparatus to generate pure hydrates and reproduce the exchange. Results from these tests enabled us to modify the apparatus in an attempt to obtain better quality hydrate samples and methane recovery efficiencies for the exchange. We performed new pure methane and carbon dioxide hydrates formation and dissociation tests with a 6-day duration and an experimental temperature of 253.15 K. We reached hydrate conversion percentages of 33% for CO$_2$ hydrates and 11.9% for CH$_4$ hydrates. We also obtained higher methane contents in the gas phase after the exchange, in comparison to the preliminary tests. Thus, the modification of the apparatus, of the experimental time and of the experimental temperature appeared to be beneficial to the performance of the exchange. The MATLAB exchange model was also used to simulate the exchange at laboratory conditions and the model’s outcomes validated the feasibility of the exchange with recovery ratios varying from 20% to 28% of the initial methane content within hydrates.

The experiments allowed us to assess conditions which could optimize methane recovery from the use of the replacement technique. We could see improvements related to the increase of initial reservoir pressure and temperature as stated in chapter 4 and in recent publications ([43] and [44]). We noticed the anomalous hydrate preservation behavior during dissociation runs as described by Stern et al. (2003) [81]. We also noticed that the presence of excess free water in the reaction cell could minimize methane recovery from the exchange since carbon dioxide molecules formed pure CO$_2$ hydrates besides displacing methane molecules from the hydrate structure.
Finally, we applied the life-cycle assessment approach to methane extraction from a hypothetical hydrate deposit with CO\textsubscript{2} clathrate sequestration. We considered a base case scenario where CO\textsubscript{2} was captured from a coal power plant and an alternative case scenario where CO\textsubscript{2} was captured from a natural gas combined cycle power plant. We could see that carbon dioxide clathrate sequestration associated with natural gas extraction from hydrate deposits can lead to emission-neutral gas production when carbon dioxide is captured from a NGCC power plant. However, the process lifetime may be longer in that case and this could influence the economics of the project. A shorter process lifetime can be achieved if carbon dioxide is captured from a coal power plant. Yet, the process will result in larger emission amounts than in the case of gas production without CO\textsubscript{2} injection. This issue can be solved by lowering the energy requirement of the carbon dioxide capture process. We could see that the cost and energy requirement of the CO\textsubscript{2} capture process have a significant impact on the efficiency of the technique.

7.2. Recommendations

Although this research project allowed us to gain additional understanding of the exchange within hydrates as a production technique through the application of numerical, experimental and life cycle assessment methods, it should be interesting to undertake future studies on the following aspects:

(1) The exchange model developed in this project should be extended to account for exchange at the interface between the hydrate phase and the fluid phase, non-stoichiometric hydrates formed with natural gas instead of pure methane and exchange only within the large cages of the hydrates. Changes of properties such as thermal conductivity and heat capacity with temperature should also be incorporated, as well as the evolution of temperature with the thickness of the different layers and any potential volume changes due to the exchange. The effect of the surface area on recovery from the exchange should be more closely analyzed.
(2) The proposed experimental apparatus should be modified to accommodate higher pressures and to mimic conditions that are closer to naturally occurring gas hydrate reservoir pressures and temperatures. Exchange experiments should be performed using liquid CO$_2$, CO$_2$ emulsions and hot supercritical CO$_2$ for bulk hydrates and hydrates within porous media. The effect of water saturation on the performance of the exchange should be more precisely evaluated. Flow-through experiments and the addition of a gas chromatograph directly connected to the current apparatus should be evaluated to enable the performance of compositional analysis throughout the exchange for the visualization of the evolution of methane and carbon dioxide contents over time. An increase of the surface area during experiments could lead to a better performance of the exchange and the use of fracturing and proppants simultaneous to the exchange could be studied with more advanced experiments. The use of magneto-acoustic stimulation could also be investigated.

(3) An economic analysis should be tied to the life cycle assessment to evaluate the commercial viability of natural gas extraction from hydrate deposits while sequestrating carbon dioxide captured from power plants.
References


Appendices

Appendix A: MATLAB CO\textsubscript{2}-CH\textsubscript{4} exchange model

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%  
%% CH\textsubscript{4}-CO\textsubscript{2} REPLACEMENT IN GAS HYDRATES: BASE CASE SCENARIO  
%% ANNICK NAGO  
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%  
disp('new run:');  
%% Reservoir properties  
Ares=40468.56; % reservoir area in m\textsuperscript{2}  
Ares=pi*400^2;  
Porh=0.3; % porosity of the hydrate layer  
Sh=0.8; % hydrate saturation  
h=10; % hydrate zone thickness in m  
hg=10; % gas zone thickness in m  
Sg=1; % gas saturation in the gas zone  
Porg=0.9;  
hrock=10; % cap rock thickness in m  
Tres=268.15; % reservoir temperature in K  
Tfreegas=Tres;  
Thyd=Tres;  
Trock=Tres;  
Pres=28; % reservoir pressure in atm  
Pf reveredgas=Pres*14.696; % pressure of free gas injected in reservoir for production, in psia  
disp('Pfreegas:'); disp(Pfreegas);  
Pc_CO2=1070; % CO\textsubscript{2} critical pressure in psia  
Tc_CO2=87.76; % CO\textsubscript{2} critical temperature in fahrenheit  
w_CO2=0.2239; % CO\textsubscript{2} accentric factor  
%% CO\textsubscript{2} hydrate equilibrium pressure  
if (0<Thyd) && (Thyd<=283.17)  
    Peq_CO2=exp(44.580-10246.28/Thyd)*1000*145.04*10^-6; % CO\textsubscript{2} hydrate equilibrium pressure in psia  
elseif 283.17<Thyd  
    Peq_CO2=3.34*10^-4*(Thyd/273.15)^264.4*145.04; % CO\textsubscript{2} hydrate equilibrium pressure in psia  
end  
disp('P_{eq,CO2}:'); disp(Peq_CO2);  
Pc_CH4=667; %CH\textsubscript{4} critical pressure in psia  
Tc_CH4=-116.66; % CH\textsubscript{4} critical temperature in fahrenheit  
w_CH4=0.0115; % accentric factor for methane  
%% CH\textsubscript{4} hydrate equilibrium pressure calculation  
if (0<Thyd) && (Thyd<=273.15)  
    %P_{eq,CH4}=exp(38.980-8533.80/Thyd)*1000*145.04*10^-6; % CH\textsubscript{4} hydrate equilibrium pressure at Tres in Psia; % CO\textsubscript{2} hydrate equilibrium pressure in psia  
    Peq_CH4=exp(14.717-1886.79/Thyd)*1000*145.04*10^-6;  
elseif 273.15<Thyd  
    Peq_CH4=exp(38.980-8533.80/Thyd)*1000*145.04*10^-6;  
end  
Omegaa=0.4274802;  
Omegab=0.08664035;  
Rsi=8.314; % gas constant in m\textsuperscript{3}.Pa.mol^-1.K^-1  
Tsc=288.7; % standard temperature (60 degree fahrenheit) in K  
Psc=101325; % standard pressure in Pa  
Bch4=181; % hydrate gas formation factor in SCM/m\textsuperscript{3}  
Bco2=168; % co2 hydrate gas formation factor in SCM/m\textsuperscript{3}
Kd_0=3.6*10^4;
Kd_ch4=Kd_0*exp(-9400/Thyd);  % dissociation rate constant in kmol.m^-2.kPa^-1.s^-1
Kf_co2=0.35*10^-10;  % formation rate constant in kmol.m^-2.kPa^-1.s^-1
Delta_h_ch4hyd=477*10^3;  % enthalpy of dissociation of methane hydrate in J/kg
Delta_h_co2hyd=-500*10^3;  % enthalpy of formation of co2 hydrate in J/kg
Delta_h_reaction=Delta_h_co2hyd+Delta_h_ch4hyd;
heatcaphyd=1600;  % heat capacity of methane hydrate in J.kg^-1.K^-1
molech4released_old=0;
molec2hyd_old=0;
rhoc4hyd=913;  % density of methane hydrate in kg/m^3
Mch4hyd=17.7;  % molecular weight of methane hydrate in kg/kmol
Mch4g=16;  % molecular weight of methane gas in kmol/kg
Mco2hyd=21.6;  % molecular weight of carbon dioxide hydrate in kg/kmol
Mco2g=44;  % molecular weight of co2(g) in kmol/kg
molefrach4inhyd=0.1481;  % mole fraction of hydrate former (8 molecules of ch4 for 54 total molecules per unit cell of hyd)
molehydinitial=Ares*Porh*Sh*h*rhoc4hyd*1000/Mch4hyd;  % initial moles of hydrate
molec4initial=molefrach4inhyd*molehydinitial;
Vfree=Ares*Porg*Sg*hg;
Ahs=3*10^5;  % specific surface area of hydrate particles in m^-1
Adec=Porh*Sh*Ahs;  % area of decomposition per unit volume in m^-1
rhocaprock=2650;  % density of the cap rock in kg/m^3
Kcr=1.5;  % Thermal conductivity of the rock in W/m.K
heatcapcr=800;  % heat capacity of the rock
alphacr=Kcr/(rhocaprock*heatcapcr);  % rock thermal diffusivity in m^2/s
rhowater=1000;
heatcapwater=4180;
rhowhyd=(1-Porh)*rhocaprock+Porh*Sh*rhoc4hyd+Porh*(1-Sh)*rhowater;
heathyd=(1-Porh)*heatcapcr+Porh*Sh*heatcaphyd+Porh*(1-Sh)*heatcapwater;
sumratech4hyd=0;
sumrateco2hyd=0;
deltat=60;  % time step in seconds
ntime=860;  % number of time steps
time=linspace(0,ntime,ntime+1);  
1st time step:
% 1st time step
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
[2rootco2g,fugco2g]=fugacitypurecompsubroutine(Pfreegas,Tfreegas,Pc_CO2,Tc_CO2,Omegaa,Omegab,w_CO2);
disp('2rootco2g:'); disp(2rootco2g);
disp('fugco2g:'); disp(fugco2g);
molec2initial=Pres*101325*Vfree/(2rootco2g*Rsi*Tres);  % initial number of moles of CO2
fugco2g0=fugco2g;  
fugco2g=fugco2g*6.895;  % fugacity of CO2 in gas phase at Pfreegas in kPa
fugco2h0=0;  % no carbon dioxide in the hydrate phase initially
fugco2h=fugco2h0;
deltafugco2=fugco2g-fugco2h;
fugch4g=0;  % no methane initially in the gas phase
fugch4g0=fugch4g;
[2rootch4h,fugch4h]=fugacitypurecompsubroutine(Peq_CH4,Thyd,Pc_CH4,Tc_CH4,Omegaa,Omegab,w_CH4);
fugch4h0=fugch4h;
fugch4h=fugch4h*6.895;  % fugacity of methane gas in equilibrium with methane hydrate at Tres and Peq(Tres) in kPa
\[
\begin{align*}
\delta f_{\text{CH}_4} &= f_{\text{CH}_4\text{h}} - f_{\text{CH}_4\text{g}}; \\
\text{rate}_{\text{CH}_4\text{hyd}} &= K_{\text{d CH}_4} M_{\text{CH}_4\text{hyd}} A_{\text{dec}} A_{\text{res}} h \delta f_{\text{CH}_4}; \\
\text{rate}_{\text{CH}_4\text{hyd}} &= -\frac{dm_{\text{CH}_4\text{hyd}}}{dt}; \\
\text{rate}_{\text{CH}_4\text{hyd}} &= \text{rate}_{\text{CH}_4\text{hyd}0} + \text{sumrate}_{\text{CH}_4\text{hyd}} + \text{rate}_{\text{CH}_4\text{hyd}}; \\
\text{mole}_{\text{CH}_4\text{released} \text{new}} &= \text{mole}_{\text{CH}_4\text{released} \text{old}} + 0.1481 \text{rate}_{\text{CH}_4\text{hyd}} \delta t / M_{\text{CH}_4\text{hyd}}; \\
\text{mole}_{\text{CH}_4\text{released} \text{new}0} &= \text{mole}_{\text{CH}_4\text{released} \text{new}}; \\
% Mass of CO2 Trapped in Hydrate (in kmol) %%%%%%%%%%%%%%%%%%%%%%%%%% \\
\text{rate}_{\text{CO}_2\text{hyd}} &= K_f \text{CO}_2 M_{\text{CO}_2\text{hyd}} A_{\text{dec}} A_{\text{res}} h \delta f_{\text{CO}_2}; \\
\text{rate}_{\text{CO}_2\text{hyd}} &= +\frac{dm_{\text{CO}_2\text{hyd}}}{dt}; \\
\text{rate}_{\text{CO}_2\text{hyd}} &= \text{rate}_{\text{CO}_2\text{hyd}0} + \text{sumrate}_{\text{CO}_2\text{hyd}} + \text{rate}_{\text{CO}_2\text{hyd}}; \\
\text{mole}_{\text{CO}_2\text{hyd} \text{new}} &= \text{mole}_{\text{CO}_2\text{hyd} \text{old}} + \text{rate}_{\text{CO}_2\text{hyd}} \delta t / M_{\text{CO}_2\text{hyd}}; \\
\text{mole}_{\text{CO}_2\text{hyd} \text{new}0} &= \text{mole}_{\text{CO}_2\text{hyd} \text{new}}; \\
\text{Cor} &= M_{\text{CH}_4\text{hyd}} \text{sumrate}_{\text{CO}_2\text{hyd}} / (M_{\text{CO}_2\text{hyd}} \text{sumrate}_{\text{CH}_4\text{hyd}}); \\
\text{co2trappedcumul0} &= 0.1481 \text{mole}_{\text{CO}_2\text{hyd} \text{new}0} / \text{Cor}; \\
% New temperatures (Hydrate block, Gas phase, Cap rock) after exchange %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\text{Kprime1} &= (\rho_{\text{hyd layer}} h * \text{heat hyd layer} / K_{\text{cr}}) * (\alpha_{\text{cr}} \pi / \delta t)^{0.5}; \\
\text{Kprime2} &= (\delta t_{\text{reaction}} / (K_{\text{cr}} A_{\text{res}})) * (\alpha_{\text{cr}} \pi / \delta t)^{0.5}; \\
\text{Thyd}_{\text{new}} &= \text{Kprime1} / (1 + \text{Kprime1}) \times \text{Thyd}_{\text{new}} - \text{Kprime2} / (1 + \text{Kprime1}) \times \text{rate}_{\text{CH}_4\text{hyd}} + 1 / (1 + \text{Kprime1}) \times \text{T}_{\text{res}}; \\
\text{Thydgradient0} &= (\text{Thyd}_{\text{new}} - \text{Thyd}) / \delta t; \\
\text{Trockbottom} &= \text{Thyd}_{\text{new}} \times \text{erfc}((h_{\text{rock}}) / (2 * (\alpha_{\text{cr}} * \delta t)^{0.5})) + \text{T}_{\text{res}} * (1 - \text{erfc}((h_{\text{rock}}) / (2 * (\alpha_{\text{cr}} * \delta t)^{0.5})); \\
\text{Trockavg} &= \text{Thyd}_{\text{new}} - \text{T}_{\text{res}} * (2 * (\alpha_{\text{cr}} * \delta t)^{0.5}) / h_{\text{rock}} * (h_{\text{rock}} / (2 * (\alpha_{\text{cr}} * \delta t)^{0.5}) * \text{erfc}(h_{\text{rock}} / (2 * (\alpha_{\text{cr}} * \delta t)^{0.5})) - \exp(-h_{\text{rock}}^2 / (4 * \alpha_{\text{cr}} \delta t)) / \pi^{0.5} + 1 / \pi^{0.5}) + \text{T}_{\text{res}}; \\
\text{Thyd}_{\text{new0}} &= \text{Thyd}_{\text{new}}; \\
\text{Tfreegas}_{\text{new0}} &= \text{Tfreegas}_{\text{new}}; \\
\text{Trockbottom0} &= \text{Trockbottom}; \\
\text{Trockavg0} &= \text{Trockavg}; \\
\text{Trockbottom0} &= \text{Trockbottom}; \\
\text{Trockavg0} &= \text{Trockavg}; \\
% New gas pressure after exchange %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Material balance %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\text{molegascurrent} &= \text{mole}_{\text{gas initial}} * 10^{-3} - \text{co2trappedcumul0} + \text{mole}_{\text{CH}_4\text{released new}}; \\
\text{molegascurrent0} &= \text{molegascurrent}; \\
\text{ych}_4 &= \text{mole}_{\text{CH}_4\text{released new}} / \text{molegascurrent}; \\
\text{ych}_40 &= \text{ych}_4; \\
\text{yco2} &= (\text{mole}_{\text{CO}_2\text{initial}} * 10^{-3} - \text{co2trappedcumul0}) / \text{molegascurrent}; \\
\text{yco20} &= \text{yco2}; \\
\text{molefractionch4inhyd} &= (\text{mole}_{\text{CH}_4\text{initial}} * 10^{-3} - \text{mole}_{\text{CH}_4\text{released new}}) / (\text{mole}_{\text{CH}_4\text{initial}} * 10^{-3}); \\
\text{molefractionch4inhyd0} &= \text{molefractionch4inhyd}; \\
\text{molefractionco2inhyd} &= \text{co2trappedcumul0} / (\text{mole}_{\text{CH}_4\text{initial}} * 10^{-3}); \\
\text{molefractionco2inhyd0} &= \text{molefractionco2inhyd}; \\
% Calculation of Zfactor for the mixture with cubic EOS %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\text{numcomp} &= 2; \% number of components of the gas mixture \\
\text{compos} &= \{\text{ych}_4, \text{yco2}\}; \% vector composition of gas mixture \\
\text{Pcritical} &= \{P_{\text{C CH}_4}, P_{\text{C CO}_2}\}; \% vector of critical pressures in psia \\
\text{Tcritical} &= \{T_{\text{C CH}_4 + 460}, T_{\text{C CO}_2 + 460}\}; \% vector of critical temperatures in degree \\
\text{Rankine} &= \{w_{\text{CH}_4}, w_{\text{CO}_2}\}; \% vector ofacentric factors for the mixture
\end{align*}
\]
bininter=[0 0; 0 0]; % matrix of binary interaction coefficients for the mixture
Tfreegas_newr=Tfreegas_new*1.8; % new gas phase temperature in Rankine
Zmixinit=Zrootco2g; % initial Z at initial experimental conditions Pfreegas and Tres
Tresinit=Tres*1.8; % initial temperature in rankine
[D,E]=coefcalculation2(compos,Pcritical,Tcritical,w,Zmixinit,numcomp,Pfreegas,Tfree

gas_newr,Tresinit,moleco2initial,molegascurrent*10^3));
disp('E'); disp(E);
disp('D'); disp(D);
Zmixture=E/D;
Zmixture0=Zmixture;
disp('Zmixture:'); disp(Zmixture);
Pfreegasnew=molegascurrent*10^3*Zmixture*Rsi*Tfreegas_new/Vfree; % pressure in Pa
disp('Pfreegasnew:'); disp(Pfreegasnew);
Pfreegasnew0=Pfreegasnew; % storing free gas pressure in Pa
disp('Tfreegas_new:'); disp(Tfreegas_new);
disp('Thyd_new:'); disp(Thyd_new);
disp('Trockbottom:'); disp(Trockbottom);
disp('Trockavg:'); disp(Trockavg);
disp('molegascurrent:'); disp(molegascurrent);
disp('Thydgradient0:');disp(Thydgradient0);

2nd time step:

% 2nd time step
% CO2 hydrate equilibrium pressure
if (0<Thyd_new)&&(Thyd_new<=283.17)
    Peq_CO2=exp(44.580-10246.28/Thyd_new)*1000*145.04*10^-6; % CO2 hydrate
end
% CH4 hydrate equilibrium pressure calculation
if (0<Thyd_new)&&(Thyd_new<=273.15)
    Peq_CH4=exp(14.717-1886.79/Thyd_new)*1000*145.04*10^-6; % CH4 hydrate
end

fug=fugacitymixsubroutin1(compos,Pcritical,Tcritical,w,bнтер,Pfreegasnew*145.04
*10^-6,numcomp,Tfreegas_newr,Zmixture);
fugco2g1=fug(2);
fugch4g1=fug(1);
fugco2g=fug(2)*6.895; % fugacity of CO2 in gas phase at PRes in kPa
[Zrootco2h,fugco2h]=fugacitypurecompsubroutine(Peq_CO2,Thyd_new,Pc_CO2,Tc_CO2,Omega
a,Omegab,w_CO2);
fugco2h1=fugco2h;
fugco2h=fugco2h*6.895; % fugacity of CO2 at hydrate equilibrium pressure in kPa
deltafugco2=fugco2g-fugco2h;
fugch4g=fug(1)*6.895; % fugacity of CH4 in gas phase at PC4(i-1) in kPa
[Zrootch4h,fugch4h]=fugacitypurecompsubroutine(Peq_CH4,Thyd_new,Pc_CH4,Tc_CH4,Omega
a,Omegab,w_CH4);
fugch4h1=fugch4h;
fugch4h=fugch4h*6.895;
deltafugch4=fugch4h-fugch4g;

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% Mass of CH4 released from hydrate (in kmol) %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
Kd_ch4=Kd_0*exp(-9400/Thyd_new);
ratech4hyd=Kd_ch4*Mch4hyd*Adec*Ares*h*deltafugch4;
ratech4hyd_2=ratech4hyd;
sumratech4hyd=sumratech4hyd+ratech4hyd;
molech4released_new=molech4released_new+0.1481*ratech4hyd*deltat/Mch4hyd;
molech4released_new1=molech4released_new;

% Mass of CO2 Trapped in hydrate (in kmol) %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
rateco2hyd=Kf_co2*Mco2hyd*Adec*Ares*h*deltafugco2;
rateco2hyd_2=rateco2hyd;
sumrateco2hyd=sumrateco2hyd+rateco2hyd;
moleco2hyd_new=moleco2hyd_new0+rateco2hyd*deltat/Mco2hyd;
moleco2hyd_new1=moleco2hyd_new;
Cor=Mch4hyd*sumrateco2hyd/(Mco2hyd*sumratech4hyd);
c02trappedcumul1=0.1481*moleco2hyd_new1/Cor;
disp('c02trappedcumul1'); disp(co2trappedcumul1);

%% New temperatures (Hydrate block, Gas phase, Cap rock) after exchange
%%%%%%%%%%%%%%%%%%%%%%%%%%%
Kprime1=(rhohydlayer*h*heathydlayer/Kcr)*(alphacr*pi/deltat)^0.5;
Kprime2=(deltah_reaction/(Kcr*Ares))*(alphacr*pi*deltat)^0.5;
Thyd_new=(Kprime1/(1+Kprime1))*Thyd_new0-(Kprime2/(1+Kprime1))*ratech4hyd+1/(1+Kprime1)*Trockavg0; % new temperature in K
Thygradient1=(Thyd_new-Thyd_new0)/deltat;
Tfreegas_new=Tfreegas;
Trockbottom=Thyd_new*erfc((hrock)/(2*(alphacr*deltat)^0.5))+Trockavg0*(1-erfc((hrock)/(2*(alphacr*deltat)^0.5)); % new rock temperature in K
Trockavg=(Thyd_new-Trockavg0)*((2*(alphacr*deltat)^0.5)/hrock*(hrock/(2*(alphacr*deltat)^0.5)*erfc(hrock/(2*(alphacr*deltat)^0.5))-exp(-hrock*2/(4*alphacr*deltat))/pi^0.5+1/pi^0.5)+Trockavg0;
Thyd_new=Thyd_new;
Tfreegas_new1=Tfreegas_new;
Trockbottom1=Trockbottom;
Trockavg1=Trockavg;

%% New gas pressure after exchange
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%% Material balance
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
molegascurrent=moleco2initial*10^-3-co2trappedcumul1+molech4released_new;
molegascurrent1=molegascurrent;
ych4=molech4released_new/molegascurrent;
yco2=(moleco2initial*10^-3-co2trappedcumul1)/molegascurrent;
yco21=yco2;
molefractionch4inhyd=(molech4initial*10^-3-molech4released_new)/(molech4initial*10^-3);
molefractionch4inhyd1=molefractionch4inhyd;
molefractionco2inhyd=co2trappedcumul1/(molech4initial*10^-3);
molefractionco2inhyd1=molefractionco2inhyd;

%% Calculation of Zfactor for the mixture with cubic EOS
numcomp=2; % number of components of the gas mixture
compos=[ych4;yco2]; % vector composition of gas mixture
Pcritical=[Pc_CH4;Pc_CO2]; % vector of critical pressures in psia
Tcritical=[Tc_CH4+460;Tc_CO2+460]; % vector of critical temperatures in degree Rankine
w=[w_CH4;w_CO2]; % vector of accentric factors for the mixture
bininter=[0 0;0 0]; % matrix of binary interaction coefficients for the mixture
Tfreegas_newr=Tfreegas_new*1.8; % new reservoir temperature in Rankine
Zmixinit=Zrootco2g; % intial Z at initial experimental conditions Pfreegas and Tres
Tresinit=Tres*1.8; % initial temperature in rankine
[D,E]=coefcalculation2(compos,Pcritical,Tcritical,w,Zmixinit,numcomp,Pfreegas,Tfreegas_newr,Tresinit,moleco2initial,molegascurrent*10^3);
Zmixture=E/D;
Zmixture1=Zmixture;
disp('Zmixture:'); disp(Zmixture);
Pfreegasnew=molegascurrent*10^3*Zmixture*Rsi*Tfreegas_new/Vfree;% pressure in Pa
Pfreegasnew1=Pfreegasnew;
disp('Pfreegasnew:'); disp(Pfreegasnew);
disp('Tfreegas_new:'); disp(Tfreegas_new);
disp('Thyd_new:'); disp(Thyd_new);
disp('Trockbottom:'); disp(Trockbottom);
disp('Trockavg:'); disp(Trockavg);
disp('molegascurrent:'); disp(molegascurrent);
disp('Thydgradient1:');disp(Thydgradient1);
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Creating the vectors
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
PFREEGAS=zeros(ntime+1,1);
PFREEGAS(1)=Pres*1.01325*10^5; % pressure in Pa
PFREEGAS(2)=Pfreegasnew0; % pressure in Pa after one time step
PFREEGAS(3)=Pfreegasnew1;
TFREEGAS=zeros(ntime+1,1);
TFREEGAS(1)=Tfreegas;
TFREEGAS(2)=Tfreegas_new0;
TFREEGAS(3)=Tfreegas_new1;
THYD=zeros(ntime+1,1);
THYD(1)=Thyd;
THYD(2)=Thyd_new0;
THYD(3)=Thyd_new1;
TROCKAVG=zeros(ntime+1,1);
TROCKAVG(1)=Tres;
TROCKAVG(2)=Trockavg0;
TROCKAVG(3)=Trockavg1;
TROCKBOTTOM=zeros(ntime+1,1);
TROCKBOTTOM(1)=Tres;
TROCKBOTTOM(2)=Trockbottom0;
TROCKBOTTOM(3)=Trockbottom1;
MOLEFREEGAS=zeros(ntime+1,1);
MOLEFREEGAS(1)=moleco2initial*10^-3;
MOLEFREEGAS(2)=molegascurrent0;
MOLEFREEGAS(3)=molegascurrent1;
MOLECH4RELEASED=zeros(ntime+1,1);
MOLECH4RELEASED(2)=molech4released_new0;
MOLECH4RELEASED(3)=molech4released_new1;
MOLECO2HYD=zeros(ntime+1,1);
MOLECO2HYD(2)=moleco2hyd_new0;
MOLECO2HYD(3)=moleco2hyd_new1;
CO2TRAPPEDCUMUL=zeros(ntime+1,1);
CO2TRAPPEDCUMUL(2)=co2trappedcumul0;
CO2TRAPPEDCUMUL(3)=co2trappedcumul1;
YCH4=zeros(ntime+1,1);
YCH4(2)=ych40;
YCH4(3)=ych41;
YCO2=zeros(ntime+1,1);
YCO2(1)=1;
YCO2(2)=yco20;
YCO2(3)=yco21;
CH4HYDFRAC=zeros(ntime+1,1);
CH4HYDFRAC(1)=1;
CH4HYDFRAC(2)=molefractionch4inhyd0;
CH4HYDFRAC(3)=molefractionch4inhyd1;
CO2HYDFRAC=zeros(ntime+1,1);
CO2HYDFRAC(1)=0;
CO2HYDFRAC(2)=molefractionco2inhyd0;
CO2HYDFRAC(3)=molefractionco2inhyd1;
RATECO2HYD=zeros(ntime+1,1);
RATECO2HYD(1)=0;
RATECO2HYD(2)=rateco2hyd0;
RATECO2HYD(3)=rateco2hyd_2;
RATECH4HYD=zeros(ntime+1,1);
RATECH4HYD(1)=0;
RATECH4HYD(2)=ratech4hyd0;
RATECH4HYD(3)=ratech4hyd_2;
FUGCO2G=zeros(ntime+1,1);
FUGCO2G(1)=fugco2g0;
FUGCO2G(2)=fugco2g0;
FUGCO2G(3)=fugco2g1;
FUGCO2H=zeros(ntime+1,1);
FUGCO2H(1)=fugco2h0;
FUGCO2H(2)=fugco2h0;
FUGCO2H(3)=fugco2h1;
FUGCH4G=zeros(ntime+1,1);
FUGCH4G(1)=fugch4g0;
FUGCH4G(2)=fugch4g0;
FUGCH4G(3)=fugch4g1;
FUGCH4H=zeros(ntime+1,1);
FUGCH4H(1)=fugch4h0;
FUGCH4H(2)=fugch4h0;
FUGCH4H(3)=fugch4h1;
THYDGRADIENT=zeros(ntime+1,1);
THYDGRADIENT(2)=Thydgradient0;
THYDGRADIENT(3)=Thydgradient1;
ZMIXTURE=zeros(ntime+1,1);
ZMIXTURE(1)=Zrootco2g;
ZMIXTURE(2)=Zmixture0;
ZMIXTURE(3)=Zmixture1;

for i=4:ntime+1
    disp('new time step:');
    if MOLECH4RELEASED(i-1)<=molech4initial*10^-3
        \% each time step
        % CO2 hydrate equilibrium pressure
        if (0<THYD(i-1)) && (THYD(i-1)<=283.17)
            Peq_CO2=exp(44.580-10246.28/THYD(i-1))*1000*145.04*10^-6; \% CO2 hydrate equilibrium pressure in psia
        elseif 283.17<THYD(i-1)
            Peq_CO2=3.34*10^-4*(THYD(i-1)/273.15)^264.4*145.04; \% CO2 hydrate equilibrium pressure in psia
        end
    end
%% CH4 hydrate equilibrium pressure calculation
if (0<THYD(i-1)) && (THYD(i-1)<=273.15)
    Peq_CH4=exp(14.717-1886.79/THYD(i-1))*1000*145.04*10^-6; % CH4 hydrate equilibrium pressure in psia
elseif 273.15<THYD(i-1)
    Peq_CH4=exp(38.980-8533.80/THYD(i-1))*1000*145.04*10^-6;
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
numcomp=2; % number of components of the gas mixture
compos={[YCH4(i-1);YCO2(i-1)]}; % vector composition of gas mixture
Pcritical={[Pc_CH4;Pc_CO2]}; % vector of critical pressures in psia
Tcritical={[Tc_CH4+460;Tc_CO2+460]}; % vector of critical temperatures in degree Rankine
w=[w_CH4;w_CO2]; % vector of accentric factors for the mixture
bininter=[0 0 0 0]; % matrix of binary interaction coefficients for the mixture

Tfreegas_newr=TFREEGAS(i-1)*1.8; % new free gas temperature in Rankine
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
fug=fugacitymixsubroutine1(compos,Pcritical,Tcritical,w,bininter,PFREEGAS(i-1)*145.04*10^-6,numcomp,Tfreegas_newr,2MIXTURE(i-1));

FUGCO2G(i)=fug(2);
FUGCH4G(i)=fug(1);

if (FUGCO2G(i)<=FUGCO2G(i))&& (FUGCH4G(i)<=FUGCH4G(i))
    fugco2g=fug(2)*6.895; % fugacity of CO2 in gas phase at Pres in kPa
    fugch4g=fug(1)*6.895; % fugacity of CH4 in gas phase at PCH4(i-1) in kPa
endif

deltafugco2=fugco2g-fugco2h;
deltafugch4=fugch4g-fugch4h;

%% Mass of CH4 released from hydrate (in moles)

Kd_ch4=Kd_0*exp(-9400/THYD(i-1));
ratech4hyd=Kd_ch4*Mch4hyd*Adec*Ares*h*deltafugch4;
sumratech4hyd=sumratech4hyd+ratech4hyd;
MOLECH4RELEASED(i)=MOLECH4RELEASED(i-1)+0.1481*ratech4hyd*deltat/Mch4hyd;

%% Moles of CO2 trapped in hydrate
rateco2hyd=Kf_co2*Mco2hyd*Adec*Ares*h*deltafugco2;
sumrateco2hyd=sumrateco2hyd+rateco2hyd;

MOLECO2HYD(i)=MOLECO2HYD(i-1)+rateco2hyd*deltat/Mco2hyd;

Cor=Mch4hyd*sumrateco2hyd/(Mco2hyd*sumratech4hyd);

CO2TRAPPEDCUMUL(i)=0.1481*MOLECO2HYD(i)/Cor;

%% New temperatures (Hydrate block, Gas phase, Cap rock) after exchange

Kprime1=(rhohydlayer*h*heathydlayer/Kcr)*(alphacr*pi/deltat)^0.5;
Kprime2=(deltah_reaction/(Kcr*Ares))*(alphacr*pi*deltat)^0.5;
\[
\text{THYD}(i) = \frac{K_{\text{prime1}}}{(1+K_{\text{prime1}})} \times \text{THYD}(i-1) - \frac{K_{\text{prime2}}}{(1+K_{\text{prime1}})} \times \text{ratech4hyd}/\text{TROCKAVG}(i-1); \quad \% \text{new temperature in K}
\]
\[
\text{THYDGRADIENT}(i) = \frac{\text{THYD}(i) - \text{THYD}(i-1)}{\text{deltat}};
\]
\[
\text{TROCKBOTTOM}(i) = \text{THYD}(i) \times \text{erfc}\left(\frac{h_{\text{rock}}}{2(\alpha_{\text{cr}} \times \text{deltat})^{0.5}}\right) + \text{TROCKAVG}(i-1) \times (1 - \text{erfc}\left(\frac{h_{\text{rock}}}{2(\alpha_{\text{cr}} \times \text{deltat})^{0.5}}\right)) - \exp(-h_{\text{rock}}^2/(4\alpha_{\text{cr}}\times \text{deltat}))/\pi^{0.5} + \frac{1}{\pi^{0.5}} + \text{TROCKAVG}(i-1);
\]

% New gas pressure after exchange

% Material balance

\[
\text{MOLEFREEGAS}(i) = \text{moleco2initial} \times 10^{-3} - \text{CO2TRAPPEDCUMUL}(i) + \text{MOLECH4RELEASED}(i); \quad \% \text{calculation of } Z \text{factor for the mixture with cubic EOS}
\]
\[
\text{numcomp} = 2; \quad \% \text{number of components of the gas mixture}
\]
\[
\text{compos} = \left[ \text{YCH4}(i); \text{YCO2}(i) \right]; \quad \% \text{vector composition of gas mixture}
\]
\[
\text{Pcritical} = \left[ \text{Pc}_{\text{CH4}}; \text{Pc}_{\text{CO2}} \right]; \quad \% \text{vector of critical pressures in psia}
\]
\[
\text{Tcritical} = \left[ \text{Tc}_{\text{CH4}}+460; \text{Tc}_{\text{CO2}}+460 \right]; \quad \% \text{vector of critical temperatures in degree Rankine}
\]
\[
\text{w} = \left[ \text{w}_{\text{CH4}}; \text{w}_{\text{CO2}} \right]; \quad \% \text{vector of accentric factors for the mixture}
\]
\[
\text{bininter} = \left[ 0 0; 0 0 \right]; \quad \% \text{matrix of binary interaction coefficients for the mixture}
\]
\[
\text{Tfreegas\_newr} = \text{TFREEGAS}(i) \times 1.8; \quad \% \text{new reservoir temperature in Rankine}
\]
\[
\text{Tresinit} = \text{Tres} \times 1.8; \quad \% \text{initial temperature in rankine}
\]
\[
\text{Zmixinit} = \text{Zrootco2g}; \quad \% \text{initial } Z \text{ at initial experimental conditions}
\]
\[
\text{Pfreesg and Tres}
\]
\[
\text{Tresinit} = \text{Tresinit} \times 1.8; \quad \% \text{initial temperature in rankine}
\]
\[
[D, E] = \text{coefcalculation2(compos, Pcritical, Tcritical, w, Zmixinit, numcomp, Pfreegas, Tfreegas\_newr, Tresinit, moleco2initial, MOLEFREEGAS(i) \times 10^{-3})};
\]
\[
\text{ZMIXTURE(i)} = \frac{E}{D}; \quad \% \text{pressure in Pa}
\]
\[
\text{PFREEGAS(i)} = \text{MOLEFREEGAS(i) \times 10^{-3} \times ZMIXTURE(i) \times Rsi \times TFREEGAS(i)/Vfree;}
\]


elseif \text{FUGCO2H}(i) > \text{FUGCO2G}(i) \break

elseif \text{FUGCH4G}(i) > \text{FUGCH4H}(i) \break
\end

else \break
\end

Appendix B: MATLAB Fugacity calculation subroutine

function [Zroot, fug] = fugacitypurecompsubroutine(P, T, Pc, Tc, Omegaa, Omegab, w)
R = 10.73; % gas constant in psia*ft^3/lbmol^-1*R^-1
Pint = P; % pressure of interest in psia
Tint = T*1.8; % temperature of interest in degree rankine
Pcrit = Pc;
Tcrit = Tc+460;

% CALCULATE a, b, m, A, B AND alpha
a = Omegaa*R^2*Tcrit^2/Pcrit;
b = Omegab*R*Tcrit/Pcrit;
m = 0.48+1.547*w-0.176*w^2;
Tr = Tint/Tcrit;
alpha = (1+m*(1-Tr^0.5))^2;

% SOLVING FOR Z
A = a*alpha*Pint/(R^2*Tint^2);
B = b*Pint/(R*Tint);
v(1) = 1;
v(2) = -1;
v(3) = A-B-B^2;
v(4) = -A*B;
Z = roots(v);
for j = 1:3
    Z(j) = isreal(Z(j))*Z(j);
end
Zroot = max(Z);

% FUGACITY CALCULATION WITH SRK EOS
Infugcoef = Zroot-1-log(Zroot-B)-(A/B)*log(1+B/Zroot);
fug = exp(Infugcoef)*Pint; % fugacity in psia
end
%% Function fugacitymixsubroutine1
function fug=fugacitymixsubroutine1(c,Pc,Tc,w,delta,P,nc,T,Zmix)
%these values are exclusively for the SRK EOS.
c = composition vector; Pc, Tc vectors of critical properties; w vector of
%acentric factors; delta matrix of interaction coefficients;
P = pressure of interest in psia;
nc = number of components; T temperature of interest in Rankine
R=10.73; % gas constant in psia.ft^3.lbmol^-1.R^-1
m1 = 0;
m2 = 1;
Omegaai = 0.4274802;
Omegabi = 0.08664035;
m = zeros(nc,1);
for i = 1:nc
    m(i) = 0.48 + 1.574*w(i) - 0.176*w(i)^2;
end
% CALCULATING Pr AND Tr
Pr = P./Pc;
Tr = T./Tc;
% FUGACITY CALCULATION FOR A MIXTURE USING SRK EOS
Av = zeros(nc,1);
Bv = zeros(nc,1);
for i = 1:nc
    Av(i) = Omegaai*(1 + m(i)*(1 - Tr(i)^0.5))^2*Pr(i)/(Tr(i)^2);
    Bv(i) = Omegabi*Pr(i)/Tr(i);
end
Am = zeros(nc,nc);
for i = 1:nc
    for j = 1:nc
        Am(i,j) = (1 - delta(i,j))*(Av(i)*Av(j))^0.5;
    end
end
A = 0;
B = 0;
for i = 1:nc
    B = B + c(i)*Bv(i);
    for j = 1:nc
        A = A + c(i)*c(j)*Am(i,j);
    end
end
Phi = zeros(nc,1);
fug = zeros(nc,1);
for i = 1:nc
    sumAC = 0;
    for j = 1:nc
        sumAC = Am(i,j)*c(j) + sumAC;
    end
    Phi(i) = exp(-log(Zmix) + (A/((m1-m2)*B))*(2*sumAC/A - Bv(i)/B)*log((Zmix+m2*B)/(Zmix+m1*B)) + Bv(i)/B*(Zmix-1));
    fug(i) = Phi(i)*c(i)*P;
end
Appendix C: MATLAB Z-factor calculation subroutine for the exchange model

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%
%% Function coefcalculationZ
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
function
[D,E]=coefcalculationZ(c,Pc,Tc,w,Zinit,nc,Pginit,T,Tresinit,mginit,mgcurrent)

%% Parameters of the function
%% c: composition vector of the gas mixture; Pc, Tc: critical properties
%% vectors of the gas mixture; w: accentric factor vector; delta: matrix of
%% interaction coefficients; Z: current Z factor in NR iteration; Zinit:
%% initial Z factor of the gas; nc: number of components of the gas; Pginit:
%% initial pressure of the gas in psia; T: current temperature of the gas in
%% Rankine;
%% Tresinit: initial temperature of the gas in Rankine; mginit: initial
%% moles of gas; mgcurrent: current moles of gas;
Omegaai = 0.4274802;
Omegabi = 0.08664035;
m=zeros(nc,1);
Acoef=zeros(nc,1);
Bcoef=zeros(nc,1);
for i = 1:nc
    m(i) = 0.48 + 1.574*w(i) - 0.176*w(i)^2;
end
% % % CALCULATING Pr AND Tr
Tr = T./Tc;
% % % SOLVING THE EOS FOR THE CALCULATION OF THE Z-FACTOR
for i = 1:nc
    Acoef(i) = Omegaai*(1 + m(i)*(1 - Tr(i)^0.5))^2*mgcurrent*Pginit*Tc(i)^2/(mginit*Zinit*Tresinit*Pc(i)*T);
    Bcoef(i)=Omegabi*mgcurrent*Tc(i)*Pginit/(mginit*Tresinit*Pc(i)*Zinit);
end
E=1-(c(1)*Acoef(1)^0.5+c(2)*Acoef(2)^0.5)^2+(c(1)*Acoef(1)^0.5+c(2)*Acoef(2)^0.5)^2*(c(1)*Bcoef(1)+c(2)*Bcoef(2))+(c(1)*Bcoef(1)+c(2)*Bcoef(2))*T;
D=1-(c(1)*Bcoef(1)+c(2)*Bcoef(2))^2;
end
Appendix D: MATLAB Z-factor calculation for the hydrate formation and dissociation experiments

```matlab
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %
%%% Z-FACTOR ESTIMATION DURING HYDRATE FORMATION AND DISSOCIATION EXPERIMENTS
%% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %

% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %

% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %
% INPUT DATA
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %
load hydratedissociationdata7.txt;
HydData=dlmread('hydratedissociationdata7.txt');
T=HydData(:,1);
P=HydData(:,3);

%% Conversion of temperature from K to Rankine and of pressure from psig to % psia
T=T*1.8;
P=P+14.7*ones(length(P),1);

M=input('input molecular weight in lbm/lbmole:');
R=10.73;
Omegaa=0.427480;
Omegab=0.086640;

Tc=input('input critical temperature in Rankine:');
Pc=input('input critical pressure in psia:');
w=input('input accentric factor:');

% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %
% CALCULATE a,b,m,A,B AND alpha
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %
a=Omegaa*R^2*Tc^2/Pc;
b=Omegab*R*Tc/Pc;
m=0.48+1.574*w-0.176*w^2;
Tr=zeros(length(P),1);
alpha=zeros(length(P),1);
A=zeros(length(P),1);
B=zeros(length(P),1);
Am=zeros(length(P),4);
Zroot=zeros(length(P),1);

% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %
% SOLVING FOR Z
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% %
for i=1:length(P)
    Tr(i)=T(i)/Tc;
    alpha(i)=(1+m*(1-Tr(i)^0.5))^2;
    A(i)=a*alpha(i)*P(i)/(R^2*T(i)^2);
    B(i)=b*P(i)/(R*T(i));
end

for i=1:length(P)
    for j=1:4
        Am(i,j)=1;
        Am(i,2)=-1;
        Am(i,3)=A(i)-B(i)-B(i)^2;
        Am(i,4)=-A(i)*B(i);
    end
end
for i=1:length(P)
    v=Am(i,:);
```
Z=roots(v);
for j=1:3
    Z(j)=isreal(Z(j))*Z(j);
end
Zroot(i)=max(Z);
end

Zfac=Zroot;
disp('end of run');
Vita

Annick Nago was born in Abidjan, Cote d’Ivoire. After completing junior high school in Abidjan at Lycee Sainte Marie of Cocody, she moved to France where she attended Lycee Prive Mongazon. She graduated from high school with the French baccalaureate in 2003 and attended the Lycee Prive Sainte Genevieve pre-engineering school with options in Advanced Mathematics and Physics. She began her engineering studies in 2005 at Ecole Centrale of Nantes. In 2007, she was selected for a double-degree program with Penn State in the United States and began her Master of Science studies in Petroleum Engineering. She graduated in 2009 with a Master of Science in Petroleum Engineering from Penn State and a Master of Engineering Science from Ecole Centrale of Nantes. In fall 2009, Annick started the doctoral program at Penn State in Energy and Mineral Engineering with option in Petroleum and Natural Gas Engineering. Annick was conferred the degree of Doctor of Philosophy in Energy and Mineral Engineering (Petroleum Engineering Option) in May 2013.