STORAGE OF CARBON DIOXIDE IN DEPLETED NATURAL GAS RESERVOIRS AS GAS HYDRATE

by

DUO SUN

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M. A. Sc, Keio University, 2011

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Abstract

More than 120 depleted natural gas reservoirs in Alberta, Canada have been identified as potential sites for CO₂ storage at temperature and pressure conditions at which CO₂ may form gas hydrate. Reservoir simulations presented in the literature have demonstrated the feasibility of storing CO₂ in such reservoirs. In this thesis, the injection of CO₂ in a laboratory size reservoir (packed bed of silica particles) serving as a physical model for a depleted reservoir was studied. The hypothesis was that injecting CO₂ into the reservoir at gas hydrate formation conditions will be beneficial in terms of increased CO₂ storage density. It is noted that CO₂ is stored not only as hydrate but also some is dissolved in the residual pore water (not converted to hydrate) and some as a gas in the remaining pore space. The results indicate that hydrate formation enhances the CO₂ storage density. The work also demonstrated that substances like tapioca starch added to the water in small quantities (1 wt %) delayed the onset of hydrate nucleation in the earlier stage but subsequently more CO₂ was stored as hydrate compared to the tapioca starch-free systems. The delay in nucleation decreases the risk to form a hydrate plug in the injection system. The injection of the CO₂-rich mixture (90 mol % CO₂/10 mol % N₂), which is a typical composition of a flue gas after CO₂ capture process, into a reservoir with CH₄ (simulating residual natural gas) was also studied in the laboratory reservoir. It was found that the total CO₂ storage density (in hydrate, gaseous and dissolved state) decreased from 143 kg/m³ (the CO₂ injection into a CH₄ free reservoir) to 119 kg/m³. Finally, relevant phase equilibrium data were obtained in a constant volume high pressure vessel and by calorimetry. The results were found to be in good agreement with thermodynamic model calculated values within ± 40 kPa and ± 0.2 K, respectively.
Preface

Versions of Chapter 2 to 5 in this thesis have been published in peer-reviewed journals, in conference proceedings and presented in conferences listed below.

Published articles in peer-reviewed Journals1-4:


2. Sun, D., Englezos, P. CO₂ storage capacity in laboratory simulated depleted hydrocarbon reservoirs - Impact of salinity and additives. *Journal of Natural Gas Science and Engineering* 2016, [http://dx.doi.org/10.1016/j.jngse.2016.03.043](http://dx.doi.org/10.1016/j.jngse.2016.03.043)


4. Sun, D., Ripmeester, J., Englezos, P. Phase equilibria for the CO₂/CH₄/N₂/H₂O system in the hydrate region under conditions relevant to storage of CO₂ in depleted natural gas reservoirs. *Journal of Chemical and Engineering Date* 2016, [http://pubs.acs.org/doi/abs/10.1021/acs.jced.6b00547](http://pubs.acs.org/doi/abs/10.1021/acs.jced.6b00547)

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5. Sun, D., Englezos, P. Assessment of CO₂ storage capacity in a laboratory bed of silica sand particles. 8th International Conference on Gas Hydrate. Beijing, China, 28 July-1 August, 2014.

7. Sun, D., Englezos, P. Effect of gas injection methods, additives and salinity on CO2 storage capacity in Alberta reservoirs. 65th Canadian Chemical Engineering Conference. Calgary, Canada, 4-7 October, 2015.

Professor Peter Englezos is my principal research supervisor in Chemical and Biological Engineering Department at the University of British Columbia. Also, it is my pleasure to have fruitful discussions regarding this research project with Dr. John A. Ripmeester, a principal research officer from Steacie institute for Molecular Studies, National Research Council of Canada and Dr. Hassan Hassanzadeh, an associate professor from Schulich School of Engineering at the University of Calgary.

I was responsible for literature review, experimental design, performing experiments and data analysis under the supervision of Professor Peter Englezos. I conducted the preparation of the manuscript under careful supervision.
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<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{n}^{G-L}$</td>
<td>Gas-liquid surface area per unit volume in the block $n$ [m$^2$/m$^3$]</td>
</tr>
<tr>
<td>$A_{n}^{H}$</td>
<td>Hydrate surface area per unit volume in the block $n$ [m$^2$/m$^3$]</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>Activation energy [J]</td>
</tr>
<tr>
<td>$F_{n}^{CO_2}$</td>
<td>Mass flux of CO$_2$ transported through the gas-water surface in block $n$ [kg/m$^2$ s]</td>
</tr>
<tr>
<td>$F_{n}^{h}$</td>
<td>Heat flux flowed to the surrounding volume [J/m$^2$]</td>
</tr>
<tr>
<td>$F_{n}^{W}$</td>
<td>Mass flux of water transported through the gas-water surface in block $n$ [kg/m$^2$ s]</td>
</tr>
<tr>
<td>$f_{eq}$</td>
<td>Fugacity of CO$_2$ at the hydrate equilibrium pressure [kPa]</td>
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<tr>
<td>$f_{n}$</td>
<td>Fugacity of CO$_2$ at the pressure of block $n$ [kPa]</td>
</tr>
<tr>
<td>$H$</td>
<td>Heat [mJ]</td>
</tr>
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<td>$H_{CO_2}$</td>
<td>Enthalpy of CO$_2$ gas for energy balance modeling [J]</td>
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<td>$H_{H}$</td>
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<td>$k_{f}$</td>
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<tr>
<td>$K_{f}^{0}$</td>
<td>Intrinsic formation rate constant</td>
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<tr>
<td>$M_{H}$</td>
<td>Molecular weight of the hydrate [g/mol]</td>
</tr>
<tr>
<td>$M_{n}^{CO_2}$</td>
<td>Mass change of CO$_2$ per unit volume of block $n$ [kg/m$^3$]</td>
</tr>
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</table>
$M_n^H$ Mass change of hydrate per unit volume of block $n$ [kg/m$^3$]

$M_n^W$ Mass change of water per unit volume of block $n$ [kg/m$^3$]

$N$ Number of moles of hydrate per unit volume of block $n$ [mol]

$n$ A block in the reservoir assumed for the mass and energy balance modeling

$n_{CO2,H}$ Number of moles of CO$_2$ as hydrate in the crystallizer [mol]

$n_{CR-CO2,0}$ Number of moles of CO$_2$ as gaseous in the crystallizer at time 0 [mol]

$n_{CR-CO2,t}$ Number of moles of CO$_2$ as gaseous in the crystallizer at time $t$ [mol]

$n_{D,t}$ Number of moles of CO$_2$ dissolved in the crystallizer water at time $t$ [mol]

$n_{SV-CO2,0}$ Number of moles of CO$_2$ as gaseous in the supply vessel at time 0 [mol]

$n_{SV-CO2,t}$ Number of moles of CO$_2$ as gaseous in the supply vessel at time $t$ [mol]

$n_{W,CO2H}$ Number of moles of original reservoir water formed CO$_2$ hydrate [mol]

$n_{W,initial}$ Number of moles of original reservoir water [mol]

$P$ Pressure [kPa/MPa]

$\Delta P_0, \Delta P_2, \Delta P_4, \Delta P_{7.4}, \Delta P_{9.1}$ Pressure driving force of CO$_2$ hydrate forming in water, 2, 4, 7.4 and 9.1 wt % NaCl solutions

$\Delta P_P, \Delta P_q, \Delta P_r, \Delta P_s$ Pressure driving force at the hydrate nucleation point in experiment (p1) to (s1)

$P_{CR}$ Crystallizer pressure [kPa]

$P_{SV}$ Supply vessel pressure [kPa]

$Q_n^H$ Enthalpy of hydrate per unit volume of block $n$ [J/m$^3$]

$q_{n,CO2,con}^c$ Consumption rate of CO$_2$ per unit volume of block $n$ [kg/m$^3$ s]
<table>
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<th>Symbol</th>
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<tr>
<td>$q_n^{CO_2,\text{inj}}$</td>
<td>Injection rate of CO$_2$ per unit volume of block $n$ [kg/m$^3$ s]</td>
</tr>
<tr>
<td>$q_n^{H,\text{for}}$</td>
<td>Formation rate of hydrate per unit volume of block $n$ [kg/m$^3$ s]</td>
</tr>
<tr>
<td>$q_n^{W,\text{con}}$</td>
<td>Injection rate of water per unit volume of block $n$ [kg/m$^3$ s]</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant [8.314 J/K mol]</td>
</tr>
<tr>
<td>$R_{CO_2,W}$</td>
<td>Percentage of initial reservoir water formed CO$_2$ hydrate</td>
</tr>
<tr>
<td>$S_{CO_2}$</td>
<td>Saturation of CO$_2$ gas for energy balance modeling</td>
</tr>
<tr>
<td>$S_{CO_2,H}$</td>
<td>CO$_2$ hydrate saturation in the reservoir free space</td>
</tr>
<tr>
<td>$S_H$</td>
<td>Saturation of hydrate for energy balance modeling</td>
</tr>
<tr>
<td>$S_W$</td>
<td>Saturation of water for energy balance modeling</td>
</tr>
<tr>
<td>$S_{W,\text{initial}}$</td>
<td>Initial reservoir water saturation in the reservoir free space</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature [K/$^\circ$C]</td>
</tr>
<tr>
<td>$U_n$</td>
<td>Total internal energy per unit volume of block $n$ [J/m$^3$]</td>
</tr>
<tr>
<td>$V_{CR}$</td>
<td>Crystallizer volume [cm$^3$]</td>
</tr>
<tr>
<td>$V_p$</td>
<td>Porous volume in the reservoir [m$^3$]</td>
</tr>
<tr>
<td>$V_{SV}$</td>
<td>Supply vessel volume [cm$^3$]</td>
</tr>
<tr>
<td>$W_{CO_2,G}$</td>
<td>Mass of CO$_2$ stored in reservoir as gaseous form [kg]</td>
</tr>
<tr>
<td>$W_{CO_2,H}$</td>
<td>Mass of CO$_2$ stored in reservoir as hydrate form [kg]</td>
</tr>
<tr>
<td>$W_{CO_2,W}$</td>
<td>Mass of CO$_2$ stored in reservoir as dissolving in the water [kg]</td>
</tr>
<tr>
<td>$y_{CO_2,0}$</td>
<td>Mole fraction of CO$_2$ at time 0</td>
</tr>
<tr>
<td>$y_{CO_2,t}$</td>
<td>Mole fraction of CO$_2$ at time $t$</td>
</tr>
</tbody>
</table>
$z$  Compressibility factor

$\phi$  Porosity of the reservoir

$\rho_{CO_2}$  Density of CO$_2$ gas for energy balance modeling [kg/m$^3$]

$\rho_{CR}^{CO_2,H}$  Total CO$_2$ storage density (in hydrate, gaseous and dissolved state) in the reservoir [kg/m$^3$]

$\rho_{CR}^{CO_2,G}$  CO$_2$ storage density in the reservoir as gaseous form [kg/m$^3$]

$\rho_{CR}^{CO_2,H}$  The CO$_2$ storage density in the reservoir as hydrate form [kg/m$^3$]

$\rho_{CR}^{CO_2,W}$  The CO$_2$ storage density in the reservoir as dissolving in the water [kg/m$^3$]

$\rho_H$  Density of hydrate for energy balance modeling [kg/m$^3$]

$\rho_S$  Density of silica sand for energy balance modeling [kg/m$^3$]

$\rho_W$  Density of water for energy balance modeling [kg/m$^3$]
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEUB</td>
<td>Alberta Energy and Utilities Board</td>
</tr>
<tr>
<td>CO$_2$-ECBM</td>
<td>Enhanced coal-bed methane recovery using CO$_2$ injection</td>
</tr>
<tr>
<td>CO$_2$-EGR</td>
<td>Enhanced gas recovery using CO$_2$ injection</td>
</tr>
<tr>
<td>CO$_2$-EOR</td>
<td>Enhanced oil recovery using CO$_2$ injection</td>
</tr>
<tr>
<td>CR</td>
<td>Crystallizer</td>
</tr>
<tr>
<td>DAQ system</td>
<td>Data acquisition system</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>-eq</td>
<td>Equivalent</td>
</tr>
<tr>
<td>ER</td>
<td>External refrigerator</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>HP-μDSC</td>
<td>High pressure micro differential scanning calorimetry</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>KHIs</td>
<td>Kinetic hydrate inhibitors</td>
</tr>
<tr>
<td>PC</td>
<td>Personal computer</td>
</tr>
<tr>
<td>PID controller</td>
<td>Proportional integral derivative controller</td>
</tr>
<tr>
<td>PT</td>
<td>Pressure transmitter</td>
</tr>
<tr>
<td>PVCap</td>
<td>Polyvinylcaprolactam</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
</tbody>
</table>
SDS  Sodium dodecyl sulfate
SES  Sodium ethyl sulfate
SV   Supply vessel
sI, sII and sH    Structure I, II and H for hydrate
sm³   Standard cubic meter
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To my parents; Ying & Yao-Cheng
& my love; Olivia
1 Introduction and Literature Review

1.1 Emission and storage of CO$_2$

CO$_2$, one of the most prevalent greenhouse gases (GHG), took the center place of the stage where the climate change concerns have been frequently discussed in recent decades. The increased concentration of greenhouse gases in the atmosphere, as a result of human activities, has caused serious concern about global warming. Also, a consequence of rising atmospheric CO$_2$ is that more CO$_2$ dissolves in the oceans to form carbonic acid and reduces the pH of the ocean water$^6$.

It is estimated that the emission of 1,000 Gt of CO$_2$-eq leads to about 1.75 °C increase in global average temperature and the Intergovernmental Panel on Climate Change (IPCC) reported that the global average temperature has increased 0.76 °C between 1850 to 1899 and 2001 to 2005$^7$. From 2000 to 2010, the GHG emissions increased at a 2.2 % annual rate and reached 49 Gt CO$_2$-eq at 2010. Fossil fuel energy combustion is considered the major source of anthropogenic CO$_2$ emitted to the atmosphere$^8$. It is estimated that 65 % of the emissions, which is about 32 Gt originates from the fossil fuel combustion sources and industrial processes$^9$.

In Canada, as shown in Figure 1.1, it is estimated that 700 to 760 Mt of CO$_2$-eq was annually emitted in 2005 to 2013$^{10}$. Canada signed the Copenhagen Accord in 2009 and agreed to reduce its GHG emissions to 17 % below 2005 levels (749 Mt CO$_2$-eq) by 2020. Figure 1.2 and 1.3 shows the Canadian emission breakdown by components and sources in 2013$^{10}$. About 80 % of the GHG emitted is CO$_2$ and 45 % of the GHG emission were from stationary combustion sources. It is noted that it is considered easier to be collect CO$_2$ from stationary sources
compared to the GHG emitted from other sources. Capture and storage of CO$_2$ is a possible strategy that deals with the CO$_2$ emitted from the fossil fuel combustion sources in order to reduce the GHG emission and achieve the Copenhagen Accord goal.

Figure 1.1 Canadian national GHG emission, 1990 to 2013. (Adapted from Environment Canada, 2015)
Figure 1.2 Canadian emission breakdown by components. (Adapted from Environment Canada, 2015)

Figure 1.3 Canadian emission breakdown by sources. (Adapted from Environment Canada, 2015)
Table 1.1 CO₂ emission mitigation technologies

<table>
<thead>
<tr>
<th>Geological media for CO₂ storage</th>
<th>Storage capacity</th>
<th>Cost</th>
<th>Feasibility</th>
<th>Leak risk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmineable coal bed</td>
<td>Large</td>
<td>High</td>
<td>Easy</td>
<td>High</td>
</tr>
<tr>
<td>Deep saline formation</td>
<td>Very large</td>
<td>Very high</td>
<td>Hard</td>
<td>High</td>
</tr>
<tr>
<td>Depleted oil and gas reservoir</td>
<td>Large</td>
<td>Low</td>
<td>Easy</td>
<td>Very low</td>
</tr>
</tbody>
</table>

Geological storage of captured CO₂ is considered to be one of the most promising methods which can contribute towards significant reduction in CO₂ emission and permanent storage stability. Geological storage may be defined as the placement of CO₂ into a subsurface formation. CO₂ can be stored in unmineable coal beds, deep saline formations and in depleted oil and gas reservoirs. Table 1.1 shows the potential of geological storage of CO₂ in these three media. The in situ carbon mineralization is considered another form of geological CO₂ storage. Although the CO₂ storage capacity through carbon mineralization is large as 1 Gt per year, the high injection cost and slow reaction rate created a barrier for the carbon mineralization to be widely applied to reduce CO₂ emission. In addition, the CO₂ storage potential in selected coal beds for enhanced coal-bed methane recovery using CO₂ injection (CO₂-ECBM) has also been discussed and 300 to 1000 Gt of CO₂ was suggested to be stored in this manner. Saline formations/aquifers are attractive candidates for CO₂ disposal and it is important to understand the behavior of CO₂ when it is injected. Particularly CO₂ hydrate will form when injection is applied at a sufficiently high pressure. However, CO₂ hydrate formation is not always a negative occurrence on CO₂ storage. Koide et al. suggested that the storage of CO₂ emitted from...
fossil fuel power plants in depleted gas and oil reservoirs can be aided by a forming CO\textsubscript{2} hydrate gas cap to prevent leakage of stored CO\textsubscript{2}\textsuperscript{18}. The concept of the gas hydrate to seal a natural gas storage reservoir was also suggested earlier by Evrenos et al. in 1971\textsuperscript{19} and Hatzikiriakos and Englezos in 1994\textsuperscript{20}. The deep saline formations could store 2700 Gt CO\textsubscript{2}, however it requires energy to inject the CO\textsubscript{2} and store it at supercritical conditions. There is also the leakage concern\textsuperscript{21}.

CO\textsubscript{2} storage in depleted oil and gas reservoirs is indeed another option to reduce CO\textsubscript{2} and can produce oil or natural gas in the meantime\textsuperscript{18}. The reservoirs are known to have held liquids and gases for millions of years. Their geology is known and there is substantial available capacity estimated globally at 400 to 900 Gt\textsuperscript{22}. It is noted that enhanced oil recovery using CO\textsubscript{2} injection (CO\textsubscript{2}-EOR) into depleted oil field is relatively mature technology and has been applied in the petroleum industry during the past four decades\textsuperscript{15}. On the other hand, enhanced gas recovery using CO\textsubscript{2} injection (CO\textsubscript{2}-EGR) into depleted natural gas reservoirs is also a commercially viable method to store CO\textsubscript{2} and simultaneously produce natural gas\textsuperscript{15,23-26}. Depleted gas reservoirs are considered the most suitable sites to store CO\textsubscript{2} since they have already proven gas capacity and storage safety over geological time scales\textsuperscript{22}. The first industrial scale CO\textsubscript{2} storage project was the depleted Krechba gas field in the central region of Algeria, which was started in 2004\textsuperscript{27}. Another example of underground storage of CO\textsubscript{2} in porous and permeable reservoir rocks is the Sleipner West gas field in the North Sea\textsuperscript{28}. More recently, the Otway project in Australia and similar projects in Europe (Pathfinding project in the Netherlands and Germany, CO\textsubscript{2}SINK Integrated project in Germany and Lacq CO\textsubscript{2} pilot project in France) demonstrated the long term storage of CO\textsubscript{2} in a gas field\textsuperscript{26,29,30}. 
The geological storage of captured CO₂ represents an attractive method to deal with climate change concerns arising from the continued use of fossil fuels and the resulting emission of CO₂. In this work, we focus on depleted gas reservoirs because such formations have been effective in storing natural gas prior to its extraction. More specifically, we will be focusing on shallow reservoirs where the temperature conditions may favour CO₂ gas hydrate formation.

1.2 Why gas hydrate and depleted natural gas reservoirs?

A new thinking about CO₂ storage in the form of solid hydrate into depleted natural gas reservoirs was first provided in 2004. The concept of CO₂ storage into gas reservoirs is shown in Figure 1.4. Due to CO₂ injection the pressure in those gas reservoirs will increase and enter the region of thermodynamic stability of CO₂ hydrate. Preliminary research indicated that 61 gas reservoirs in Alberta (Cold Lake and Fort McMurray area) have CO₂ storage potential in hydrate form in 2010. Three years later the number of reservoirs with such CO₂ storage potential increased to 121 and the amount of CO₂ that could be stored in these gas reservoirs was estimated to be 61 Gt. The depleted gas reservoirs located at a 200 to 1400 m depth region (108 of the gas reservoirs are located 200 to 500 m underground) and consist of a porous medium containing water and residual natural gas at 2 to 5 MPa and 1 to 10 °C.

As shown in Figure 1.5 it was reported that Alberta emitted 267 Mt CO₂ in 2013 and approximately 187 Mt (70 %) of the CO₂ came from large stationary sources (e.g. power plants, refineries, oil sands operations, and petrochemical and cement plants). The injection of CO₂ into the depleted gas reservoirs in Alberta and the storage of CO₂ as gas hydrate would be able to store the CO₂ emitted from Alberta sources for 326 years.
Figure 1.4 Concept of CO₂ storage into depleted gas reservoirs. (Adapted from Zatsepina and Pooladi-Darvish, 2011)

Figure 1.5 Canadian emission breakdown by provinces. (Adapted from Environment Canada, 2015)
Gas hydrates, also called clathrate hydrates are non-stoichiometric crystalline compounds consisting of hydrogen-bonded water molecules. The water molecules, generally called “host molecules”, build a network with hydrogen bonds to stabilize molecules other than water, generally called “guest molecules”. Gas hydrates were first found by Sir Humphrey Davy in 1810, who observed that a solution of chlorine gas in water freezes faster than pure water. After that research on hydrates attracted the strong attention of scientists. In 1934, Hammerschmidt reported that formation of gas hydrates in oil or gas transportation pipelines may cause blockage\(^3\) and such hydrates were concerned as a hindrance of the natural gas industry. The idea of storing natural gas as hydrate has been presented as early as in 1945 and related applications were proposed\(^{19,36}\). It was also reported in the mid-1960s that gas hydrates occur naturally in the earth. Several applications of hydrate for the development of technologies for gas separation, gas transportation and storage, heat storage, sea water desalination, and others have been widely discussed\(^{37-44}\).

Three crystallographic structures of hydrates have been known to exist—structure I (sI), structure II (sII), and structure H (sH)—which have different lattice dimensions to accommodate the respective guest molecules\(^{45-49}\). Three structures of hydrates are shown in Figure 1.6 and also described below.

• sI:

Consist of small cavities labeled 5\(^{12}\) as it has twelve pentagonal faces and large cavities labeled 5\(^{12}6^2\) as it has twelve pentagonal and two hexagonal faces.

• sII:
Consist of small cavities labeled $5^{12}$ as it has twelve pentagonal faces and large cavities labeled $5^{12}6^4$ as it has twelve pentagonal and two hexagonal faces.

- sH:

Consist of small cavities labeled $5^{12}$ as it has twelve pentagonal faces, large cavities labeled $5^{12}6^8$ as it has twelve pentagonal and two hexagonal faces and irregular cavities labeled $4^{3}5^{6}6^{3}$ as it has three square, six pentagonal and three hexagonal faces.

<table>
<thead>
<tr>
<th>Hydrate crystal structure</th>
<th>I</th>
<th>II</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cavity</td>
<td>Small</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>Description</td>
<td>$5^{12}$</td>
<td>$5^{12}6^2$</td>
<td>$5^{12}$</td>
</tr>
<tr>
<td>Number of cavities per unit cell</td>
<td>2</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>Average cavity radius (Å)</td>
<td>3.95</td>
<td>4.33</td>
<td>3.91</td>
</tr>
<tr>
<td>Coordination number</td>
<td>20</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>Number of waters per unit cell</td>
<td>46</td>
<td>136</td>
<td>34</td>
</tr>
</tbody>
</table>

Figure 1.6 Three common hydrate unit crystal structures. (Adapted from Sloan, 2003)
Figure 1.7 Schematic image of CO$_2$ hydrate.

Figure 1.7 shows four CO$_2$ molecules trapped in cages of CO$_2$ hydrate. Cages are formed by hydrogen bonded water molecules. Gas hydrates may contain a significant quantity of gas. For example, the volume of CO$_2$ gas stored in 1 m$^3$ of CO$_2$ hydrate is approximately 160 m$^3$ at standard temperature and pressure$^{49}$. Using the large gas storage capability of gas hydrates, novel applications, such as the storage and transportation of CO$_2$, natural gas and H$_2$, have been studied$^{38,50,51}$. Considering the large gas capacity of hydrates, trapping CO$_2$ in hydrate form to store carbon is an attractive option to significantly reduce CO$_2$ emissions to the atmosphere.

Numerical studies of geological storage CO$_2$ as gas hydrate in natural gas hydrate reservoirs have been reported recently. CO$_2$ hydrate formation due to injection and coincident CO$_2$ storage/CH$_4$ production from natural gas were demonstrated. The temperature rises indicate hydrate formation because it is an exothermic reaction. However, the continuation of gas injection could lead to near-well blockage by forming hydrate$^{52,53}$. Zatsepina and Pooladi-Darvish examined hydrate formation during a period of 270 days by employing a reservoir simulator. CO$_2$ injection was simulated into a 5 m thickness depleted natural gas reservoir. The rate of CO$_2$ injection was constant at 0.1 $\times$ 10$^6$ sm$^3$/day. Results indicated that more hydrate forms at the bottom and top
position where heat of hydrate formation diffuses to the base and cap shale. The effect of initial conditions has been discussed. The higher the initial reservoir temperature is, the later the process of hydrate formation will be. For a higher initial pressure, hydrate formation occurs earlier because larger pressure driving force was provided. The amount of hydrate decreases with increasing initial pressure. Moreover, the higher the injection temperature, the further away from the wellbore hydrate forms\textsuperscript{54-56}.

To prevent the formation of hydrate near the injection well, the effect of kinetic hydrate inhibitors (KHIs) on hydrate formation has been studied\textsuperscript{57-60}. Polyvinylpyrrolidone (PVP) and tapioca starch are known to prolong the hydrate formation induction time and reduce the hydrate crystalline growth rate\textsuperscript{61-63}. A delay in hydrate nucleation may reduce the possibility of undesirable hydrate formation in the injection system but over long periods of time may interestingly lead to improved hydrate conversion\textsuperscript{64}. PVP is a soluble polymeric compound with pendant rings structures which is suggested to be critical structures related to the mode the KHIs interact with the hydrate structures\textsuperscript{65}. Tapioca starch is a natural polymer which is usually cationized to use in industrial applications according the non-toxic and biodegradable property\textsuperscript{61}. Therefore, the assessment of the effect of the addition of KHIs on CO\textsubscript{2} hydrate formation and CO\textsubscript{2} storage capacity is of interest because it may increase the amount of CO\textsubscript{2} stored.

It is well known that natural gas and oil reservoirs may contain electrolytes and thus the salinity of the reservoir may be a consideration since it will affect the hydrate phase equilibrium conditions. Dissolved electrolytes were also reported to slightly reduce the water conversion to hydrate in the porous media\textsuperscript{66}. Canadian Geological Survey reported that up to 4 wt % salinity exists in some of the Alberta reservoirs which have CO\textsubscript{2} storage potential in the gas hydrate
form. Thus the assessment of the effect of reservoir salinity on hydrate formation and CO₂ storage capacity is required.

It is noted that although our study is motivated by our focus on hydrocarbon reservoirs in Alberta, Canada, the conclusions can be generalized to reservoirs elsewhere in the world.

According to this concept of CO₂ storage, CO₂ will be injected into a natural gas (CH₄) reservoir. The thermodynamic (P-T) conditions are such that the hydrate forming molecules in the reservoir will form hydrate with two guests (CH₄ and CO₂). The equilibrium conditions for CH₄/CO₂ hydrate are different from the hydrate formed by either CH₄ or CO₂. CH₄ hydrate requires higher pressure or lower temperature to be stabilized compared to CO₂ hydrate. Moreover, it has been suggested that at the range from 0 °C to 10 °C, CH₄ hydrate needs approximately 2 MPa more kinetics driving force to form hydrate compared to CO₂ hydrate at the same temperature. Considering that 0.5 MPa CH₄ gas originally exists in the gas reservoirs located in Alberta, 2 MPa to 3.5 MPa of CO₂ can be injected to form mixed hydrate without liquefaction of CO₂.

In order to advance further our understanding of the parameters affecting CO₂ storage we need to take into account the fact that CO₂ gas captured from large stationary sources is mixed with impurities like N₂ and O₂. In order to render the CO₂ capture (separation) process economically viable the CO₂ concentration in the treated flue gas is about 90 mol % . Comparing to CO₂, it requires much higher pressure for N₂ to form hydrate according to the hydrate equilibria calculation using CSMGem software. Thus the effect of presence of CH₄ and N₂ in the reservoir on hydrate formation need to be studied.
Recently, the studies of hydrate formation and dissociation behaviors in the presence of KHIs and gas mixture have been conducted with the techniques using high pressure reactor and differential scanning calorimetry (DSC) in terms of achieving efficient experimental test. These apparatuses were also applied in this experimental study.

1.3 Research objectives and thesis organization

As seen in the previous sections, numerical simulation of CO₂ injection into depleted natural gas reservoirs accompanied by gas hydrate formation has given merit to the idea of storing CO₂ into such reservoirs. Our first objective in the present thesis was to demonstrate this CO₂ storage concept in a laboratory reservoir at temperature and pressure conditions found in Alberta. In addition, our objective was to assess the effects of additives in the reservoir to enhance the conversion of CO₂ into hydrate and thus store more CO₂. Finally, our objective was also to determine the effects of N₂ in the injection gas, the residual CH₄ in place in the reservoir, and the presence of salinity in the reservoir on hydrate formation and CO₂ storage density. The hypothesis was that the injection of CO₂ into the reservoir at gas hydrate formation conditions will improve CO₂ storage capacity and the addition of additives will benefit in terms of increasing hydrate formation and thus storage capacity.

In this work, the demonstration of CO₂ hydrate formation under physical CO₂ injection into laboratory scaled reservoir and the comparison of the amount of CO₂ stored as hydrate under various gas injection methods were shown in Chapter 2. The effects of PVP, tapioca starch and saline solution on hydrate formation were discussed in Chapter 3. The effects of N₂ in the injection gas and CH₄ in the reservoir on hydrate formation were assessed in Chapter 4. The dissociation temperature and pressure of the hydrate formed in typical depleted natural gas
reservoir conditions were measured in a stirred high pressure crystallizer and by a high pressure micro differential scanning calorimetry and their consistency with the calculation data was described in Chapter 5. The discussion of CO₂ storage density with and without hydrate technology, the economic evaluation and a mass and energy balance model were shown in Chapter 6. Finally, the conclusions of this experimental work and recommendations for the future work were presented in Chapter 7.
2 Injection of CO₂ into a Partially Water Saturated Reservoir

2.1 Materials

Silica sand obtained from Sigma-Aldrich with particle diameter ranging from 150 to 630 μm, average size of 329 μm and deionized water were employed to form a sand bed to simulate the Alberta depleted natural gas reservoirs. CO₂ obtained from Praxair has a purity of 99.5 %.

2.2 Injection of CO₂ in a gas cap under batch, series-batch and constant pressure mode

2.2.1 Experimental setup and methods

Figure 2.1 shows the schematic of the apparatus. The crystallizer (CR) has an inner diameter of 10.16 cm and inner height of 15.24 cm. The inside volume of crystallizer is calculated as 1236 cm³. The crystallizer was immersed in a water bath the temperature of which was adjusted by an external chiller (VWR Scientific, model 1187). A pressure transmitter obtained from Rosemount Inc. was employed to measure pressure in crystallizer with a maximum uncertainty of 0.075 % of the span 0 to 15000 kPa. Four thermocouples obtained from Omega Engineering Inc. were used to measure the crystallizer inner temperature in different positions inside the crystallizer. The uncertainty of thermocouples is 0.1 K. The crystallizer pressure was regulated by a PID controller and a control valve obtained from Fisher Bauman. A DAQ (data acquisition system) and the LabView 8.0 software obtained from National Instrument Inc. were used to send order to the control valve and collect the pressure and temperature data.
The injection of CO$_2$ from the top of the silica sand bed will be called *gas cap CO$_2$ injection*. This configuration may not necessarily correspond to an actual reservoir injection and it is used for convenience in this work. Nevertheless, the configuration allows observation of essential
features of the process of hydrate formation at the lab scale\textsuperscript{87}. Figure 2.2 shows the schematic of injection of CO\textsubscript{2} in a gas cap. Before starting a gas injection experiment, the sand bed was prepared. The amount of silica sand was placed in the crystallizer is 1650 g. The volume of water required to fill the void space of sand to make water saturation of 0.25 is found to be 90 mL. Silica sand and water were alternately and equably placed into crystallizer. In this case, silica sand and water consisted a sand bed to fill the inside volume of the crystallizer but left a 81 cm\textsuperscript{3} gas phase area (gas cap) above sand bed and a 270 cm\textsuperscript{3} gas phase area among the sand bed due to 0.75 gas saturation. The aspects ratio of the sand bed is 1.00 (W/H). The total volume of gas phase is 351 cm\textsuperscript{3}. A thermocouple was set to measure the temperature of gas cap and another three were placed into the sand bed to measure the temperatures of top, middle and bottom position of the sand bed.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{schematic.png}
\caption{Figure 2.2 Schematic of injection of CO$_2$ into a gas cap.}
\end{figure}

After setting up the sand bed and placing the thermocouples, the crystallizer was closed and placed into a temperature controlled water bath at 274.15 K. When the crystallizer temperatures
indicated a temperature of 274.15 K the crystallizer was pressurized with CO\textsubscript{2} to 1500 kPa and depressurized to atmospheric pressure for three times to eliminate the presence of air in the crystallizer. Then the CO\textsubscript{2} gas was injected into the crystallizer from the CO\textsubscript{2} cylinder or a supply vessel (SV) which was immersed in the same water bath as the CR. The amount of CO\textsubscript{2} in the hydrate phase, percent of initial water converted to hydrate, hydrate saturation and CO\textsubscript{2} storage density were calculated to evaluate the CO\textsubscript{2} storage capacity as hydrate formed in the sand bed. The CO\textsubscript{2} injections were conducted and the metrics were calculated as the following three modes of operation:

(a) \textit{Batch gas injection:} The crystallizer was pressurized with CO\textsubscript{2} to 3200 kPa and without any further injection of gas. The pressure dropped due to hydrate formation and the experiment was stopped after 24 h.

The total number of moles of CO\textsubscript{2} consumed to form hydrate in the process at any given time is the change in the number of moles of CO\textsubscript{2} in gas phase in the crystallizer \((n_{CR-CO2,0} - n_{CR-CO2,t})\) and the number of moles of CO\textsubscript{2} \((n_{D,t})\) dissolved in the water phase.

\[
n_{CO2,H} = (n_{CR-CO2,0} - n_{CR-CO2,t}) - n_{D,t} \tag{2.1}
\]

where \(n_{CO2,H}\) is the number of moles of CO\textsubscript{2} in the hydrate form. The number of moles in the hydrate phase at the start of experiments is 0. Hence, the number of moles of CO\textsubscript{2} stored in the hydrate at a given time \(t\) is

\[
n_{CO2,H} = n_{CR,0} - n_{CR,t} - n_{D,t} = \left(\frac{P_{CR}V_{CR}}{zRT}\right)_{CR,0} - \left(\frac{P_{CR}V_{CR}}{zRT}\right)_{CR,t} - n_{D,t} \tag{2.2}
\]
where $P_{CR}$ and $T$ are the pressure and temperature in the crystallizer, $V_{CR}$ is the volume of gas in the crystallizer, $z$ is the compressibility factor calculated by Pitzer’s correlation\textsuperscript{88} and $R$ is the gas constant. The mole fraction of CO$_2$ dissolved in the water phase is 0.016 at 274.15 K, 1850 kPa based on an interpolation from experimental data\textsuperscript{89}.

The percentage of initial water converted to hydrate was calculated below

$$R_{CO_2W} = \frac{n_{W,CO_2H}}{n_{W,initial}} = \frac{n_{CO_2H} \times 6.17}{n_{W,initial}} \times 100\% \quad (2.3)$$

where $n_{W,CO_2H}$ indicates the number of moles of water consumed to form hydrate, $n_{W,initial}$ indicates the number of moles of initial water. The mole ratio of CO$_2$ and water is called hydration number. It has been shown that the CO$_2$ occupied 95 to 100% of the large cages and 60 to 80% of the small cages\textsuperscript{90-94}. In this work the hydration numbers were calculated using the CSMGem software\textsuperscript{49}. The value for the hydration number of CO$_2$ hydrate was used is 6.17.

The CO$_2$ hydrate saturation indicates the concentration of CO$_2$ hydrate in Hydrate-Water-Gas system, which can be calculated as follows

$$S_{CO_2H} = R_{CO_2W} \times S_{w,initial} \times 1.1 \quad (2.4)$$

where $S_{W,initial}$ indicates the original water saturation in the sand bed. When water converts to hydrate the volume expands and it can be considered as 1.1 times larger than original water\textsuperscript{49}.

The mass of CO$_2$ (kg) stored in the reservoir within the pore volume (kg/m$^3$) is given by the following equation

$$\rho_{CR}^{CO_2} = \rho_{CR}^{CO_2,H} + \rho_{CR}^{CO_2,G} + \rho_{CR}^{CO_2,W} = \frac{W_{CO_2,H}}{V_p} + \frac{W_{CO_2,G}}{V_p} + \frac{W_{CO_2,W}}{V_p} \quad (2.5)$$
where \( W_{C02,H}, W_{C02,G} \) and \( W_{C02,W} \) indicate the mass of CO\(_2\) stored in sand bed as hydrate and gas form and dissolved in water, \( V_p \) indicates the pore volume in the sand bed. Note that 25 % of the pore volume was occupied by water and CO\(_2\) gas occupied the remaining space. On the other hand, because not all the initial water was converted to hydrate and the amount of CO\(_2\) dissolved into water was also considered. The CO\(_2\) storage density was calculated as the total of the three different forms.

(b) **Series-batch gas injection**: The crystallizer was pressurized with CO\(_2\) to 3200 kPa. After 6 and 20 h of operation the crystallizer was again pressurized with CO\(_2\) to restore the pressure to 3200 kPa. The experiment was stopped after 24 h.

*Series-batch gas injection* experiment can be considered as three *batch gas injection* experiments in series (0-6 h, 6-20 h, and 20-24 h). The total number of moles of CO\(_2\) consumed to form hydrate after 24 h experiment is the sum of CO\(_2\) uptake in these three time periods.

\[
n_{C02,H} = n_{H,0-6} + n_{H,6-20} + n_{H,20-24}
\]

(2.6)

The mole fraction of CO\(_2\) dissolved in the water phase is approximately 0.016 at 274.15 K, 3180 kPa which is the temperature and pressure condition of crystallizer after 24 h. It is noted that the solubility of CO\(_2\) in water in the presence of hydrates decreases with decreasing temperature in the hydrate formation region and is not a strong function of pressure over the hydrate formation region\(^{89}\).

The calculations of \( R_{C02,W}, S_H \) and \( \rho_{C02}^{CR} \) were the same as (a) *Batch gas injection*.

(c) **Constant pressure gas injection**: The crystallizer was pressurized with CO\(_2\) to 3200 kPa then the pressure in the crystallizer was maintained constant at 3200 kPa by continuously injecting
CO\textsubscript{2} with the help of the PID controller from the supply vessel. The experiment was stopped after 24 h.

A constant crystallizer pressure was maintained by delivering CO\textsubscript{2} from a supply vessel. The number of moles of CO\textsubscript{2} consumed to form hydrate in the crystallizer \(n_{C02,H}\) is the change in the number of moles of CO\textsubscript{2} in the supply vessel \(n_{SV-C02,0} - n_{SV-C02,t}\) which can be calculated by the supply vessel pressure change. The number of moles of CO\textsubscript{2} \(n_{D,t}\) dissolved in the water phase in the crystallizer was also be taken into account.

\[
n_{C02,H} = n_{SV-C02,0} - n_{SV-C02,t} - n_{D,t} = \left(\frac{P_{SV}V_{SV}}{zRT}\right)_{SV,0} - \left(\frac{P_{SV}V_{SV}}{zRT}\right)_{SV,t} - n_{D,t} \tag{2.7}
\]

where \(P_{SV}\) and \(T\) are the pressure and temperature in the supply vessel, \(V_{SV}\) is the volume of the supply vessel. The mole fraction of CO\textsubscript{2} in water at 274.15 K and 3200 kPa is 0.016\textsuperscript{89}.

The calculations of \(R_{CO2,W}^C\), \(S_{CO2,H}^C\) and \(\rho_{CR}^{CO2}\) were the same as (a) \textit{Batch gas injection}.

2.2.2 Results and discussion

Figure 2.3 shows the pressure profiles in the crystallizer corresponding to experiments (a1), (b1) and (c1) for the CO\textsubscript{2} injection in a gas cap for 24 h. Due to the hydrate formation and gas dissolution the pressure in the crystallizer decreased. The amount of CO\textsubscript{2} dissolved in water is small compared to that consumed to form hydrate. During the (a) \textit{Batch gas injection} experiment, the pressure dropped quickly in the first 3 h and then moderately. A rapid pressure decrease can also be observed under the (b) \textit{Series-batch gas injection} experiment during the first 3 h. After the crystallizer was pressurized again to 3200 kPa at the 6 h mark, the crystallizer pressure dropped quickly in 20 min and then exhibited a moderate decrease to about 3000 kPa. The
pressure decreased very moderately after pressurization at the 20 h mark which is likely due to the fact that there is less water available for hydrate formation. Under the case of (c) Constant pressure gas injection experiment, a constant crystallizer pressure was maintained at 3200 ± 3 kPa.

Figure 2.3 Pressure profiles in the crystallizer in gas cap mode CO$_2$ injection experiments for 24 h. (a1) Batch gas injection, (b1) Series-batch gas injection, and (c1) Constant pressure gas injection experiments.
Figure 2.4 Temperature profiles in the crystallizer in gas cap mode CO$_2$ injection experiments for 24 h. (a1) Batch gas injection, (b1) Series-batch gas injection, and (c1) Constant pressure gas injection experiments.
Figure 2.4 shows the temperature profiles in the crystallizer corresponding to experiments (a1), (b1) and (c1) for the CO₂ injection in a gas cap for 24 h and Figure 2.5 shows the temperature profiles for the first 60 min. Hydrate crystal formation is an exothermic process and a corresponding temperature rise is seen to occur at the 1 to 5 min mark in all of the three experiments. This point marks the onset of hydrate crystal formation (nucleation). After that the crystallizer temperatures were back to the initial set temperature. In (b) *Series-batch gas injection* experiment, temperature rises were observed when crystallizer was pressurized at the 6 and 20 h mark indicating the hydrate crystal formation.
Figure 2.5 Temperature profiles in the crystallizer in gas cap mode CO$_2$ injection experiments for the first 60 min. (a1) Batch gas injection, (b1) Series-batch gas injection, and (c1) Constant pressure gas injection experiments.
Figure 2.5 clearly shows the temperature changes corresponding to experiments (a1), (b1) and (c1) when hydrate started to form. In all the three experiments, the temperatures of top and middle positions of the crystallizer are higher than the temperature of bottom position during the 5 to 60 min mark. This indicates that more hydrate formed in the top and middle area of sand bed than the bottom area in the crystallizer. The crystallizer was sitting on a rubber pad in the water bath and the thermal conductivity of rubber is less than water. Thus when the heat generated from the hydrate formation in the crystallizer transferred to the water bath higher temperature changes were observed at the bottom area of the crystallizer. In (a) Batch gas injection experiment and (b) Series-batch gas injection experiment, the temperatures in all positions decreased just after the first temperature rise. However, in (c) Constant pressure gas injection experiment, the temperatures of top and middle positions kept at 281 K for 15 min and 10 min respectively. This shows that more hydrate formed.

Table 2.1 shows the number of moles of CO$_2$ in the CO$_2$ hydrate phase, percentage of water converted to hydrate, CO$_2$ hydrate saturation and CO$_2$ storage density of the three gas cap mode CO$_2$ injection experiments. Results indicate that under the (c) Constant pressure gas injection mode more CO$_2$ is stored compared to the other two injection modes. It was observed that 42 %, 44 % and 51 % of the original water converted to hydrate in (a) Batch, (b) Series-batch and (c) Constant pressure gas injection experiments, respectively. After 24 h, CO$_2$ hydrate saturation results 0.11 to 0.14. The rest in the pore space of the sand bed can be considered to be unconverted water and gaseous CO$_2$. Based on the above data the gas cap injection is able to achieve conversion of only half of the water available. The CO$_2$ storage density as hydrate form was 40 to 50 kg/m$^3$. 
Table 2.1 The number of moles of CO\textsubscript{2} stored in hydrate \((n_{C02,H})\), the percent of water formed hydrate \((R_{C02,W})\), the CO\textsubscript{2} hydrate saturation \((S_{C02,H})\), the CO\textsubscript{2} storage density as the form of hydrate \((\rho_{CR}^{CO2,H})\) and the induction time for gas cap mode CO\textsubscript{2} injection experiments.

<table>
<thead>
<tr>
<th>Injection mode</th>
<th>Exp.</th>
<th>(n_{C02,H}) (mol)</th>
<th>(R_{C02,W}) (%)</th>
<th>(S_{C02,H})</th>
<th>(\rho_{CR}^{CO2,H}) (kg/m\textsuperscript{3})</th>
<th>Induction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Batch gas injection</td>
<td>a1</td>
<td>0.342</td>
<td>42.2</td>
<td>0.12</td>
<td>41.8</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>a2</td>
<td>0.335</td>
<td>41.3</td>
<td>0.11</td>
<td>40.9</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>a3</td>
<td>0.337</td>
<td>41.6</td>
<td>0.12</td>
<td>41.2</td>
<td>2</td>
</tr>
<tr>
<td>(b) Series-batch gas injection</td>
<td>b1</td>
<td>0.355</td>
<td>43.8</td>
<td>0.12</td>
<td>43.3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>b2</td>
<td>0.360</td>
<td>44.4</td>
<td>0.13</td>
<td>44.0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>b3</td>
<td>0.368</td>
<td>45.5</td>
<td>0.13</td>
<td>45.0</td>
<td>5</td>
</tr>
<tr>
<td>(c) Constant pressure gas injection</td>
<td>c1</td>
<td>0.415</td>
<td>51.2</td>
<td>0.14</td>
<td>50.7</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>c2</td>
<td>0.414</td>
<td>51.1</td>
<td>0.14</td>
<td>50.6</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>c3</td>
<td>0.410</td>
<td>50.6</td>
<td>0.14</td>
<td>50.1</td>
<td>2</td>
</tr>
</tbody>
</table>
2.3 Injection of CO$_2$ using spiral tubing under constant pressure mode

2.3.1 Experimental setup and methods

An alternative injection mode was also followed by using a stainless steel spiral tubing. Figure 2.6 (A) shows the injection of CO$_2$ using the spiral tubing. The initial temperature was set at 277.15 K in the spiral tubing mode CO$_2$ injection experiments to reflect the fact that this is a more likely reservoir temperature. It is noted that only Constant pressure gas injection was conducted and the metrics are the same as in the gas cap mode Constant pressure gas injection experiments. The mole fraction of CO$_2$ dissolved in the water phase is 0.019 at 277.15 K, 3200 kPa according to interpolation from experimental data$^{89}$. Figure 2.6 (B) shows a picture of the spiral tubing. Each tubing has 15 holes with the diameter of 0.5 mm that opened in the same direction perpendicular to the spiral plane on the 1/8” stainless steel tubing in order to inject CO$_2$ into the crystallizer. Silica sand and water placed in the crystallizer were 1800 g and 98 ml to obtain a 0.25 initial water saturation sand bed in this mode. In this case, silica sand and water (sand bed) filled the inside volume of the crystallizer but left a 8 cm$^3$ gas phase area (gas cap) above the sand bed and a 292 cm$^3$ gas phase area in the silica sand. Thus the total volume of the gas phase is 300 cm$^3$. The aspects ratio of the sand bed is 0.74 (W/H). The CO$_2$ injection was conducted by the following three methods:

(d) Single top spiral tubing gas injection: A spiral tubing was placed above the sand bed in the crystallizer. Holes were open facing down to inject CO$_2$ gas.

(e) Single bottom spiral tubing gas injection: A spiral tubing was placed at the bottom of the sand bed in the crystallizer. Holes were open facing up to inject CO$_2$ gas.
(f) *Double spiral tubing (Top + Bottom) gas injection*: Two spiral tubing were placed at the top and bottom of the sand bed in the crystallizer. Holes were opening up and down respectively to inject CO₂ gas.

![Schematic of CO₂ injection using spiral tubing](image)

**Figure 2.6** Schematic of injection of CO₂ using spiral tubing (A) and the spiral tubing (B).

### 2.3.2 Results and discussion

The pressure was kept constant at 3200 kPa in this case so the pressure profile is similar to that of the *Constant pressure gas injection* experiment in Figure 2.3. Figure 2.7 shows the temperature profiles in the crystallizer corresponding to experiments (d1), (e1) and (f1) in spiral tubing mode CO₂ injection experiments and Figure 2.8 shows the temperature profiles during the first 120 min. 4 K temperature rises appeared at the Top, Middle and Bottom positions at the 10 to 20 min mark.
Figure 2.7 Temperature profiles in the crystallizer in spiral tubing mode CO₂ injection experiments for 24 h. (d1) Single spiral tubing gas injection (Top), (e1) Single spiral tubing gas injection (Bottom), and (f1) Double spiral tubing gas injection (Top + Bottom) experiments.
Figure 2.8 Temperature profiles in the crystallizer in spiral tubing mode CO$_2$ injection experiments for the first 60 min. (d1) Single spiral tubing gas injection (Top), (e1) Single spiral tubing gas injection (Bottom), and (f1) Double spiral tubing gas injection (Top + Bottom) experiments.
Figure 2.8 clearly shows the temperature changes when hydrate started to form. In experiment (d1), the temperature at Bottom position decreased just after the first temperature rise and temperatures of Top and Middle position kept at 280.5 K for 30 mins then started to decrease. The reason that the temperature profiles show flat top is considered the temperatures in the crystallizer reached the CO\(_2\) hydrate phase boundary (280.7 K, 3200 kPa)\(^9\). Thus no more temperature rises were observed. In experiment (e1), the temperatures kept 280 K to 280.5 K for 10 min in Middle and Bottom position and 40 min in Top position. In experiment (f1), the temperature of Bottom position decreased just after the first temperature rise and temperatures of Top and Middle position kept at 281 K for 30 and 10 min respectively then started to decrease. Temperature remained approximately 7 K higher than the initial crystallizer temperature in the Top position for a longer period than in the Middle and Bottom positions. It indicates that more hydrate formed in the top area of sand bed than in the other area. All of the temperatures of Top, Middle and Bottom positions of sand bed fell back to near 277 K at 120 min and no temperature jump was observed until the end of experiments.

Table 2.2 shows the number of moles of CO\(_2\) in the CO\(_2\) hydrate phase, percentage of water converted to hydrate, CO\(_2\) hydrate saturation and CO\(_2\) storage density of the three spiral tubing mode CO\(_2\) injection experiments. The (f) \textit{Double spiral tubing gas injection} experiment results in more CO\(_2\) consumed to form hydrate. For all three experiments the percent of water converted to hydrate exceed 50 \%. After 24 h, CO\(_2\) hydrate saturation results in 0.15 to 0.16 and hydrate form CO\(_2\) storage density was 50 to 60 kg/m\(^3\). Results indicate that more CO\(_2\) was stored in the spiral tubing mode CO\(_2\) injection as compared to the gas cap mode CO\(_2\) injection, which points to an opportunity to improve the hydrate conversion by proper design of the injection method.
Table 2.2 The number of moles of CO\(_2\) stored in hydrate (\(n_{CO2,H}\)), the percent of water formed hydrate (\(R_{CO2,W}\)), the CO\(_2\) hydrate saturation (\(S_{CO2,H}\)), the CO\(_2\) storage density as the form of hydrate (\(\rho_{CR}^{CO2,H}\)) and the induction time for spiral tubing mode CO\(_2\) injection experiments.

<table>
<thead>
<tr>
<th>Injection mode</th>
<th>Exp.</th>
<th>(n_{CO2,H}) (mol)</th>
<th>(R_{CO2,W}) (%)</th>
<th>(S_{CO2,H})</th>
<th>(\rho_{CR}^{CO2,H}) (kg/m(^3))</th>
<th>Induction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d) Single top spiral tubing gas</td>
<td>d1</td>
<td>0.483</td>
<td>54.7</td>
<td>0.15</td>
<td>54.2</td>
<td>9</td>
</tr>
<tr>
<td>injection</td>
<td>d2</td>
<td>0.486</td>
<td>55.1</td>
<td>0.15</td>
<td>54.6</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>d3</td>
<td>0.486</td>
<td>55.1</td>
<td>0.15</td>
<td>54.6</td>
<td>11</td>
</tr>
<tr>
<td>(e) Single bottom spiral tubing</td>
<td>e1</td>
<td>0.481</td>
<td>54.5</td>
<td>0.15</td>
<td>54.0</td>
<td>18</td>
</tr>
<tr>
<td>gas injection</td>
<td>e2</td>
<td>0.479</td>
<td>54.3</td>
<td>0.15</td>
<td>53.8</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>e3</td>
<td>0.478</td>
<td>54.2</td>
<td>0.15</td>
<td>53.7</td>
<td>10</td>
</tr>
<tr>
<td>(f) Double spiral tubing gas</td>
<td>f1</td>
<td>0.525</td>
<td>59.5</td>
<td>0.16</td>
<td>58.9</td>
<td>10</td>
</tr>
<tr>
<td>injection</td>
<td>f2</td>
<td>0.522</td>
<td>59.2</td>
<td>0.16</td>
<td>58.6</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>f3</td>
<td>0.523</td>
<td>59.3</td>
<td>0.16</td>
<td>58.7</td>
<td>12</td>
</tr>
</tbody>
</table>
2.4 Injection of CO₂ using vertical tubing under constant pressure mode and constant flow rate followed by constant pressure mode

2.4.1 Experimental setup and methods

Figure 2.9 shows the apparatus of CO₂ injection under constant pressure and constant flow rate followed by constant pressure mode. Figure 2.10 (A) shows the injection of CO₂ using vertical tubing and Figure 2.10 (B) shows a picture of the vertical tubing. The tubing has four 1.0 mm diameter holes in each one of 5 positions located at a distance of 2.5 cm from each other. The end of the vertical tubing was sealed. The sand bed was prepared by placing 10 layers of 180 g of silica sand and 40 mL of deionized water in the crystallizer and finally placing 36 g of silica sand on top. Thus, the reservoir consists of 1836 g of silica sand and 400 mL of water. In this way the silica sand was fully water saturated in the crystallizer (water saturation = 1.00). Subsequently, compressed air was injected into the crystallizer to drain the water out of the sand bed. This operation was conducted until no water came out from the crystallizer. About 60 hours were required to complete this sand bed preparation. The volume of the drained water was found to be 312 mL and thus, the water that remained in the reservoir was 88 mL. The water saturation in the reservoir was therefore found to be 0.22 and the rest of the pore space was occupied by air. The aspects ratio of the sand bed is 0.67 (W/H). The vertical tubing was located in the center of the sand bed to deliver CO₂ gas into the simulated reservoir.
Figure 2.9 CO$_2$ injection setup for the experiments under constant pressure and constant flow rate followed by constant pressure mode gas injection method.
Figure 2.10 Schematic of injection of CO₂ using vertical tubing (A) and the picture of vertical tubing (B).

CO₂ injection under (g) *Vertical tubing constant pressure gas injection* and (h) *Vertical tubing constant flow rate followed by constant pressure gas injection* into the simulated reservoir were conducted. The experiment of (g) *Vertical tubing constant pressure gas injection* was run three times for 24 h. The CO₂ injection method and the metrics calculation were the same as (c) *Constant pressure gas injection in a gas cap*. In the experiment (h) *Vertical tubing constant flow rate followed by constant pressure gas injection*, a Quizix Q5000 pump shown in Figure 2.9 was employed to provide a 5 mL/min constant flow rate gas delivery from the supply vessel to the reservoir. When the crystallizer pressure increased to 3200 kPa the gas injection was switched to the constant pressure mode until 24 h of the operation. This experiment was also run three times and an additional experiment was run for 120 h. Because a constant crystallizer pressure was
maintained through the continuous supply of CO\textsubscript{2} from the supply vessel, the number of moles of CO\textsubscript{2} uptake to form hydrate in the crystallizer \(n_{\text{C02,H}}\) is given by the following formula

\[
 n_{\text{C02,H}} = \left( n_{\text{SV-C02,0}} - n_{\text{SV-C02,t}} \right) - \left( n_{\text{CR-C02,t}} - n_{\text{CR-C02,0}} \right) - n_{D,t}
\]

\[
 = \left[ \left( \frac{P_{SV}V_{SV}}{zRT} \right)_{SV,0} - \left( \frac{P_{SV}V_{SV}}{zRT} \right)_{SV,t} \right] - \left[ \left( \frac{P_{CR}V_{CR}}{zRT} \right)_{CR,t} - \left( \frac{P_{CR}V_{CR}}{zRT} \right)_{CR,0} \right] - n_{D,t} \tag{2.8}
\]

where, the change in the number of moles of CO\textsubscript{2} in the supply vessel is \(n_{\text{SV-C02,0}} - n_{\text{SV-C02,t}}\), the change in the number of moles of CO\textsubscript{2} in the crystallizer is \(n_{\text{CR-C02,t}} - n_{\text{CR-C02,0}}\), \(P_{SV}\) and \(P_{CR}\) indicate the pressure of the supply vessel and the crystallizer, \(T\) indicates the temperature, \(V_{SV}\) and \(V_{CR}\) indicate the volume of the supply vessel and the crystallizer. The other metrics calculations were the same as (c) Constant pressure gas injection in a gas cap.

### 2.4.2 Results and discussion

Figure 2.11 shows the temperature profiles when CO\textsubscript{2} was injected into the crystallizer. These correspond to experiment (g1). The reservoir pressure was maintained at 3200 kPa by continuously supplying CO\textsubscript{2} gas delivered from the supply vessel. The temperature profiles for the other two experiments were similar with the induction times varying as seen in Table 2.3. A temperature rise of 3.5 K was seen to occur at around the 12 min at three different positions in the reservoir. This is an indication of hydrate crystal formation owing to the exothermic nature of the process. While the three temperature peaks are the same the decaying profiles are different suggested different amounts of hydrate crystals formed. More hydrate crystals formed at the top of the reservoir. As seen from the data in Table 2.3, 0.467 mol of CO\textsubscript{2} was stored in hydrate form and 58.9 % of the original water converted to hydrate after 24 h. Unconverted water and gas phase CO\textsubscript{2} were considered to fill the rest of the pore space in the sand bed.
Figure 2.11 Temperature profiles in the reservoir corresponding to experiment (g1) for injection of CO$_2$ under constant pressure (3200 kPa) into the crystallizer for 24 h and the first 120 min.
The pressure and temperature profiles in the reservoir corresponding to experiment (h4) for the injection of CO₂ under constant flow rate followed by constant pressure into pure water reservoir for 24 h, the first 360 min and 120 h are seen in Figure 2.12. The reservoir pressure increased gradually until 2500 kPa under a constant flow rate of 5 mL/min CO₂ gas injection. Rapid temperature rises and pressure drop were observed due to the hydrate formation. It is noted that the pressure drop at about 74 min was due to higher rate of CO₂ gas consumption to form hydrate as compared to the rate of CO₂ injection. The temperature rise was about 1.5 K higher than the initial point. The pressure reached the target value of 3200 kPa at about 6 h and remained constant during the 24 h and 120 h experiments. The temperature remained at about 277 K during this period. After 24 h and 120 h of CO₂ injection 0.684 and 0.738 mol of CO₂ were stored in hydrate form respectively. It was also found that 86.3 % and 93.1 % of the original water was converted to hydrate with a CO₂ hydrate saturation values of 0.209 and 0.225, respectively. This indicates that almost all of the original water in the reservoir formed CO₂ hydrate after 120 h. Thus, under the same temperature and initial water saturation conditions the amount of CO₂ stored gas under constant flow rate followed by constant pressure injection increased by about 50 % compared to constant pressure injection. It may be the case that at constant pressure gas injection more hydrate formed within a small period of time at the beginning (higher temperature rise) and hindered the gas transfer to the reservoir thus significantly reducing hydrate formation in the reservoir.
Figure 2.12 Pressure and temperature profiles in the reservoir corresponding to experiment (h4) for the injection of CO$_2$ under constant flow rate (5 mL/min) followed by constant pressure (3200 kPa) into the crystallizer for 24 h, the first 360 min and 120 h.
Table 2.3 The number of moles of CO₂ stored in hydrate ($n_{CO₂, H}$), the percent of water formed hydrate ($R_{CO₂, W}$), the CO₂ hydrate saturation ($S_{CO₂, H}$), the CO₂ storage density as the form of hydrate ($\rho_{CR}^{CO₂, H}$) and the induction time for vertical tubing mode CO₂ injection experiments.

<table>
<thead>
<tr>
<th>Injection mode</th>
<th>Exp.</th>
<th>Duration (h)</th>
<th>$n_{CO₂, H}$ (mol)</th>
<th>$R_{CO₂, W}$ (%)</th>
<th>$S_{CO₂, H}$</th>
<th>$\rho_{CR}^{CO₂, H}$ (kg/m³)</th>
<th>Induction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g) Vertical tubing</td>
<td>g1</td>
<td>24</td>
<td>0.467</td>
<td>58.9</td>
<td>0.14</td>
<td>51.4</td>
<td>12</td>
</tr>
<tr>
<td>constant pressure gas injection</td>
<td>g2</td>
<td>24</td>
<td>0.467</td>
<td>58.9</td>
<td>0.14</td>
<td>51.4</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>g3</td>
<td>24</td>
<td>0.466</td>
<td>58.8</td>
<td>0.14</td>
<td>51.3</td>
<td>10</td>
</tr>
<tr>
<td>(h) Vertical tubing</td>
<td>h1</td>
<td>24</td>
<td>0.684</td>
<td>86.3</td>
<td>0.21</td>
<td>75.2</td>
<td>74</td>
</tr>
<tr>
<td>constant flow rate</td>
<td>h2</td>
<td>24</td>
<td>0.707</td>
<td>89.2</td>
<td>0.22</td>
<td>77.8</td>
<td>70</td>
</tr>
<tr>
<td>followed by constant pressure gas injection</td>
<td>h3</td>
<td>24</td>
<td>0.709</td>
<td>89.5</td>
<td>0.22</td>
<td>78.0</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>h4</td>
<td>120</td>
<td>0.738</td>
<td>93.1</td>
<td>0.23</td>
<td>81.2</td>
<td>74</td>
</tr>
</tbody>
</table>

2.5 Summary

In this lab study the injection of CO₂ into a partially water saturated sand bed was studied at conditions where hydrate formation is thermodynamically possible as seen in Figure 2.13 and the hydrate formation was observed. This demonstrates that CO₂ can be stored as hydrate when the gas is injected into a porous formation simulating a depleted natural gas reservoir. Multiple
positions gas injection resulted in more CO$_2$ gas uptake than the gas cap injection mode. It was also noted that injected CO$_2$ under a constant flow rate into the reservoir at the beginning promoted the hydrate formation and provided more CO$_2$ storage. It may be the case that at constant pressure gas injection more hydrate formed within a small period of time at the beginning (higher temperature rise) and hindered the gas transfer to the reservoir thus reducing hydrate formation.

Figure 2.13 CO$_2$ partial phase diagram with Alberta depleted natural gas reservoirs P-T condition region.
3 Injection of CO₂ into Reservoirs Containing PVP, Tapioca Starch and Saline Solution

Since the injection of CO₂ using vertical tubing under constant flow rate followed by constant pressure into a partially water saturated reservoir resulted in enhanced hydrate formation and corresponding CO₂ storage, this gas injection mode was used for the assessment of the CO₂ storage as hydrate in further experimental studies. In this chapter we explore the use of additives to further enhance hydrate formation and thus CO₂ storage. In addition, the fact that natural reservoirs have saline waters taken into account to determine the potential impact on CO₂ storage density.

3.1 Materials and methods

The CO₂ gas was obtained from Praxair and had 99.5 % purity. Sodium Chloride (NaCl, Fisher Scientific), Polyvinylpyrrolidone (PVP, average molecular mass of 3.5 kDa, Acros Organics) and tapioca starch (average molecular mass of 3 mDa, National Starch ULC) were used. Silica sand was obtained from Sigma-Aldrich with the average diameter of 329 μm and porosity of 0.35.

Different with (h) Vertical tubing constant flow rate followed by constant pressure gas injection experiments the water contained (i) 1 wt %, (j) 3 wt % of PVP, (k) 0.5 wt %, (l) 1 wt % and (m) 3 wt % of tapioca starch, (n) 2 wt % and (o) 4 wt % NaCl were used to prepare the sand bed. The CO₂ gas injection method was the same as experiments (h). PVP and NaCl solutions were directly made of the mixture of PVP and NaCl chemicals with deionized water, however the tapioca starch solution was prepared according to a method described elsewhere. Briefly the tapioca starch powder was mixed with water in a beaker to prepare a starch solution at 95 °C.
The starch solution was cooled down to the room temperature before using it for injection in the reservoir. The CO$_2$ injection operation and the metrics calculation were the same as described in experiments (h). Each experiment was run three times for 24 h and once for 120 h. In the absence of any literature data for the hydration number of CO$_2$ hydrate formed in 1 wt %, 3 wt % of PVP and 0.5 wt %, 1 wt % and 3 wt % of tapioca starch solutions the value for CO$_2$ hydrate formed in pure water of 6.17 was used. The values for the hydration number for CO$_2$ hydrate formed in 2 wt % and 4 wt % NaCl solutions were determined by CSMGem as 6.14 and 6.11 respectively$^{49}$.

3.2 Injection of CO$_2$ into a reservoir containing 1 and 3 wt % of PVP

Figure 3.1 shows the pressure and temperature profiles in the reservoir corresponding to experiment (i4) for the injection of CO$_2$ under constant flow rate followed by constant pressure into a reservoir containing 1 wt % PVP solution for 24 h, the first 360 min and 120 h. It is noted that 1 to 2 K temperature rises were observed in this case and compared to the pure water case the onset of hydrate nucleation was prolonged from 74 min to 118 min as expected. As seen in Table 3.1, the amount of CO$_2$ stored as hydrate was 0.642 mol and 81.0 % of the original water formed CO$_2$ hydrate after 24 h. It is also noted that after 120 h, 0.720 mol of CO$_2$ was stored in hydrate form and 90.9 % of water was converted to hydrate. Thus, the addition of 1 wt % of PVP in the reservoir reduced the hydrate formation and CO$_2$ storage in both 24 h and 120 h experiments. While the delay in the onset of nucleation is expected when additives like PVP are included in the water the fact that the hydrate conversion did not improve is contrary to our expectation based on observations of accelerated hydrate growth in static systems$^{64}$.
Figure 3.1 Pressure and temperature profiles in the reservoir corresponding to experiment (i4) for the injection of CO$_2$ under constant flow rate (5 mL/min) followed by constant pressure (3200 kPa) into the reservoir containing 1 wt % PVP aqueous solution for 24 h, the first 360 min and 120 h.
Table 3.1 The number of moles of CO\(_2\) stored in hydrate (\(n_{\text{CO}_2,H}\)), the percent of water formed hydrate (\(R_{\text{CO}_2,W}\)), the CO\(_2\) hydrate saturation (\(S_{\text{CO}_2,H}\)), the CO\(_2\) storage density as the form of hydrate (\(\rho_{\text{CR}}^{\text{CO}_2,H}\)) and the induction time for the experiments of CO\(_2\) injection into a reservoir containing 1 and 3 wt % PVP.

<table>
<thead>
<tr>
<th>Injection mode</th>
<th>Exp.</th>
<th>Duration (h)</th>
<th>(n_{\text{CO}_2,H}) (mol)</th>
<th>(R_{\text{CO}_2,W}) (%)</th>
<th>(S_{\text{CO}_2,H})</th>
<th>(\rho_{\text{CR}}^{\text{CO}_2,H}) (kg/m(^3))</th>
<th>Induction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Constant flow rate followed by constant pressure gas injection into a reservoir containing 1 wt % PVP</td>
<td>i1</td>
<td>24</td>
<td>0.642</td>
<td>81.0</td>
<td>0.196</td>
<td>70.6</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>i2</td>
<td>24</td>
<td>0.627</td>
<td>79.1</td>
<td>0.191</td>
<td>69.0</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>i3</td>
<td>24</td>
<td>0.635</td>
<td>80.1</td>
<td>0.194</td>
<td>69.9</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>i4</td>
<td>120</td>
<td>0.720</td>
<td>90.9</td>
<td>0.220</td>
<td>79.2</td>
<td>118</td>
</tr>
<tr>
<td>(j) Constant flow rate followed by constant pressure gas injection into a reservoir containing 3 wt % PVP</td>
<td>j1</td>
<td>24</td>
<td>0.542</td>
<td>68.4</td>
<td>0.166</td>
<td>59.6</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>j2</td>
<td>24</td>
<td>0.538</td>
<td>67.9</td>
<td>0.164</td>
<td>59.2</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>j3</td>
<td>24</td>
<td>0.532</td>
<td>67.1</td>
<td>0.162</td>
<td>58.5</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>j4</td>
<td>120</td>
<td>0.786</td>
<td>99.2</td>
<td>0.240</td>
<td>86.5</td>
<td>142</td>
</tr>
</tbody>
</table>

Figure 3.2 shows the pressure and temperature profiles in the reservoir corresponding to experiment (j4) for the injection of CO\(_2\) under constant flow rate followed by constant pressure into a reservoir containing 3 wt % PVP solution for 24 h, the first 360 min and 120 h. It is noted that 1 to 1.5 K temperature rises were observed when pressure increased to 3200 kPa at 142 min.
which is later than the pure water and the case with 1 wt % of PVP. Thus, the onset of hydrate formation is prolonged as expected. The pressure was maintained at 3200 kPa after 2.5 h and 0.542 and 0.786 mol of CO₂ stored in hydrate form after 24 and 120 h. The amount of water that was converted to hydrate was 68.4 % and 99.2 % after 24 h and 120 h, respectively. The corresponding CO₂ hydrate saturation was 0.166 and 0.240 respectively. The addition of 3 wt % of PVP in the reservoir delayed the onset of hydrate nucleation and reduced the amount of hydrate formed in the early stage but accelerated the crystal growth and almost all of the water formed hydrate after 120 h. Accelerated hydrate growth in the presence of PVP is consistent with recent findings⁶⁴. From a practical standpoint the delay in nucleation is welcome to avoid possible hydrate blockage in the injection system. The increase in hydrate formation is also beneficial since it increases the CO₂ storage density of the reservoir.
Figure 3.2 Pressure and temperature profiles in the reservoir corresponding to experiment (j4) for the injection of CO$_2$ under constant flow rate (5 mL/min) followed by constant pressure (3200 kPa) into the reservoir containing 3 wt % PVP aqueous solution for 24 h, the first 360 min and 120 h.
3.3 Injection of CO$_2$ into a reservoir containing 0.5, 1 and 3 wt % of tapioca starch

Figure 3.3, 3.4 and 3.5 shows the pressure and temperature profiles in the reservoir corresponding to experiment (k4), (l4) and (m4) for the injection of CO$_2$ under constant flow followed by constant pressure rate into reservoirs containing 0.5 wt %, 1 wt % and 3 wt % tapioca starch for 24 h, the first 360 min and 120 h. It is noted that 1 to 2 K temperature rises were observed in (k4) and (l4) at 70 to 80 min and 1.5 to 3 K temperature rises were observed in (m4) at 110 min. The increase of the concentration of tapioca starch delayed the onset of hydrate nucleation as expected but the growth showed interesting behaviour. As the starch concentration increases the period during which the temperature decays to its starting value after reaching its peak decreases. Also noted is a second temperature rise of 0.5 to 1 K, which was observed in experiment (l4) at about 195 min and is seen in Figure 3.4. This is the thermal signature of another intensive hydrate formation period. As seen in Table 3.2, the numbers of moles of CO$_2$ stored in hydrate were 0.715, 0.681 and 0.631 after 24 h in experiments (k4), (l4) and (m4) respectively. The amount of stored CO$_2$ increased to 0.747, 0.772 and 0.688 mol after 120 hours. It is then interesting that increasing tapioca starch does not have the same benefit as adding PVP i.e. to increase CO$_2$ storage.
Figure 3.3 Pressure and temperature profiles in the reservoir corresponding to experiment (k4) for the injection of CO₂ under constant flow rate (5 mL/min) followed by constant pressure (3200 kPa) into the reservoir containing 0.5 wt % tapioca starch aqueous solution for 24 h, the first 360 min and 120 h.
Figure 3.4 Pressure and temperature profiles in the reservoir corresponding to experiment (14) for the injection of CO₂ under constant flow rate (5 mL/min) followed by constant pressure (3200 kPa) into the reservoir containing 1 wt % tapioca starch aqueous solution for 24 h, the first 360 min and 120 h.
Figure 3.5 Pressure and temperature profiles in the reservoir corresponding to experiment (m4) for the injection of CO₂ under constant flow rate (5 mL/min) followed by constant pressure (3200 kPa) into the reservoir containing 3 wt % tapioca starch aqueous solution for 24 h, the first 360 min and 120 h.
Table 3.2 The number of moles of CO$_2$ stored in hydrate ($n_{CO2,H}$), the percent of water formed hydrate ($R_{CO2,W}$), the CO$_2$ hydrate saturation ($S_{CO2,H}$), the CO$_2$ storage density as the form of hydrate ($\rho_{CR}^{CO2,H}$) and the induction time for the experiments of CO$_2$ injection into a reservoir containing 0.5, 1 and 3 wt % tapioca starch.

<table>
<thead>
<tr>
<th>Injection mode</th>
<th>Exp.</th>
<th>Duration (h)</th>
<th>$n_{CO2,H}$ (mol)</th>
<th>$R_{CO2,W}$ (%)</th>
<th>$S_{CO2,H}$</th>
<th>$\rho_{CR}^{CO2,H}$ (kg/m$^3$)</th>
<th>Induction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k) Constant flow rate followed by constant pressure gas injection into a reservoir containing 0.5 wt % tapioca starch</td>
<td>k1</td>
<td>24</td>
<td>0.715</td>
<td>90.2</td>
<td>0.218</td>
<td>78.7</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>k2</td>
<td>24</td>
<td>0.718</td>
<td>90.6</td>
<td>0.219</td>
<td>79.0</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>k3</td>
<td>24</td>
<td>0.720</td>
<td>90.9</td>
<td>0.220</td>
<td>79.2</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>k4</td>
<td>120</td>
<td>0.747</td>
<td>94.3</td>
<td>0.228</td>
<td>82.2</td>
<td>76</td>
</tr>
<tr>
<td>(l) Constant flow rate followed by constant pressure gas injection into a reservoir containing 1 wt % tapioca starch</td>
<td>l1</td>
<td>24</td>
<td>0.681</td>
<td>85.9</td>
<td>0.208</td>
<td>74.9</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>l2</td>
<td>24</td>
<td>0.674</td>
<td>85.1</td>
<td>0.206</td>
<td>74.1</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>l3</td>
<td>24</td>
<td>0.684</td>
<td>86.3</td>
<td>0.209</td>
<td>75.2</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>l4</td>
<td>120</td>
<td>0.772</td>
<td>97.4</td>
<td>0.236</td>
<td>84.9</td>
<td>74</td>
</tr>
<tr>
<td>(m) Constant flow rate followed by constant pressure gas injection into a reservoir containing 3 wt % tapioca starch</td>
<td>m1</td>
<td>24</td>
<td>0.631</td>
<td>79.6</td>
<td>0.193</td>
<td>69.4</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>m2</td>
<td>24</td>
<td>0.620</td>
<td>78.2</td>
<td>0.189</td>
<td>68.2</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>m3</td>
<td>24</td>
<td>0.622</td>
<td>78.5</td>
<td>0.190</td>
<td>68.4</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>m4</td>
<td>120</td>
<td>0.688</td>
<td>86.8</td>
<td>0.210</td>
<td>75.7</td>
<td>110</td>
</tr>
</tbody>
</table>
3.4 Injection of CO$_2$ into a reservoir containing 2 and 4 wt % NaCl solution

Figure 3.6 shows the pressure and temperature profiles in the reservoir corresponding to experiment (n1) for the injection of CO$_2$ under constant flow rate followed by constant pressure into a reservoir containing 2 wt % NaCl solution for 24 h and the first 360 min. It is noted that 2 to 2.5 K temperature rises were observed at 121 min. Unlike the above mentioned cases the reservoir temperature in this case started to decrease just after the peaks. When hydrates form the electrolyte is excluded from the hydrate crystal. Since the amount of water decreases the electrolyte concentration increases and this causes the equilibrium hydrate formation pressure to increase. Consequently, the driving force for hydrate growth decreases under the isothermal conditions of the experiment. As seen in Table 3.3, 0.587 mol of CO$_2$ stored in hydrate form and 73.7 % of initial water converted to hydrate. The hydrate saturation was 0.178 after 24 h.
Figure 3.6 Pressure and temperature profiles in the reservoir corresponding to experiment (n1) for the injection of CO₂ under constant flow rate (5 mL/min) followed by constant pressure (3200 kPa) into the reservoir containing 2 wt % NaCl solution for 24 h and for the first 360 min.
Table 3.3 The number of moles of CO\(_2\) stored in hydrate (\(n_{CO2,H}\)), the percent of water formed hydrate (\(R_{CO2,W}\)), the CO\(_2\) hydrate saturation (\(S_{CO2,H}\)), the CO\(_2\) storage density as the form of hydrate (\(\rho_{CR}^{CO2,H}\)) and the induction time for the experiments of CO\(_2\) injection into a reservoir containing 2 and 4 wt % NaCl solutions.

<table>
<thead>
<tr>
<th>Injection mode</th>
<th>Exp.</th>
<th>Duration (h)</th>
<th>(n_{CO2,H}) (mol)</th>
<th>(R_{CO2,W}) (%)</th>
<th>(S_{CO2,H})</th>
<th>(\rho_{CR}^{CO2,H}) (kg/m(^3))</th>
<th>Induction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n) Constant flow rate followed by constant pressure gas injection into a reservoir containing 2 wt % NaCl solution</td>
<td>n1</td>
<td>24</td>
<td>0.587</td>
<td>73.7</td>
<td>0.178</td>
<td>64.6</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>n2</td>
<td>24</td>
<td>0.574</td>
<td>72.1</td>
<td>0.174</td>
<td>63.1</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>n3</td>
<td>24</td>
<td>0.583</td>
<td>73.2</td>
<td>0.177</td>
<td>64.1</td>
<td>113</td>
</tr>
<tr>
<td>(o) Constant flow rate followed by constant pressure gas injection into a reservoir containing 4 wt % NaCl solution</td>
<td>o1</td>
<td>24</td>
<td>0.451</td>
<td>56.4</td>
<td>0.136</td>
<td>49.6</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>o2</td>
<td>24</td>
<td>0.447</td>
<td>55.9</td>
<td>0.135</td>
<td>49.2</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>o3</td>
<td>24</td>
<td>0.450</td>
<td>56.2</td>
<td>0.136</td>
<td>49.5</td>
<td>102</td>
</tr>
</tbody>
</table>

Figure 3.7 shows the pressure and temperature profiles in the reservoir corresponding to experiment (o1) for the injection of CO\(_2\) under constant flow rate followed by constant pressure into a reservoir containing 4 wt % NaCl solution for 24 h and the first 360 min. It is noted that 1 to 1.5 K temperature rises were observed at 99 min. It is lower than the temperature rises in 2 wt % saline contained reservoir case. The pressure reached 3200 kPa at 3.2 h then remained constant.
It is also noted that 0.451 mol of CO$_2$ stored in hydrate form and 56.4% of initial water converted to hydrate. Hydrate saturation reached 0.136 after 24 h. These observations are consistent with the fact that increased salinity increases the equilibrium hydrate formation pressure and thus decreases the driving force for hydrate growth.

Figure 3.7 Pressure and temperature profiles in the reservoir corresponding to experiment (o1) for the injection of CO$_2$ under constant flow rate (5 mL/min) followed by constant pressure (3200 kPa) into the reservoir containing 4 wt % NaCl solution for 24 h and for the first 360 min.
3.5 Summary

In order to improve the CO$_2$ storage density in the reservoir as gas hydrate a small amount of PVP and tapioca starch were added in the sand bed. Figure 3.8 shows the number of moles of CO$_2$ stored in hydrate form in the reservoirs containing pure water, 3 wt % PVP and 1 wt % tapioca starch solutions in 120 h. The number of moles of CO$_2$ stored in 3 wt % of PVP and 1 wt % of tapioca starch contained reservoirs exceeded the one stored in pure water containing reservoir at 80 and 26 h, respectively. After 120 h the increase of the number of moles of CO$_2$ stored as hydrate in the reservoirs almost stopped due to decreasing amount of potential water for the CO$_2$ hydrate formation. Reservoirs with higher water saturation will have more capacity to store CO$_2$. The addition of PVP and tapioca starch solution in the reservoir played a role as hydrate inhibitors at the early stage of the experiments. It can be considered a positive factor for the CO$_2$ gas injection into the depleted reservoirs due to a decreased risk to plug the injection system arising from the formation of the hydrate.
Figure 3.8 The number of moles of CO$_2$ stored in hydrate in deionized water (h4), 3 wt % PVP (j4) and 1 wt % tapioca starch (l4) reservoirs in 120 h experiments.

Figure 3.9 shows how the salinity shifts the hydrate formation equilibrium to a higher pressure (at constant temperature) or lower temperature (at constant pressure). The equilibria are calculated using a CSMGem software. During hydrate formation the salinity increases and in the experiments with 2 and 4 wt % salinity the water was consumed to form hydrate and the resulting salinity was 7.4 and 9.1 wt % (average of the three experiments in each case), respectively. The equilibrium curves for these salinities are also shown. Thus, it is easy to see how the driving force expressed as P-P$_{eq}$ changes during hydrate formation due to the change in the salinity from 2 to 7.4 or 4 to 9.1 wt %, respectively. There is 1218 kPa pressure driving force.
for the CO₂ to form hydrate in the pure water reservoir ever after 24 h. However, the driving force in the 2 wt % saline contained reservoir reduced to 196 kPa after 24 h. Thus reduction in the value of the driving force causes the decrease in the hydrate growth. In the case of the 4 wt % saline containing reservoir, the salinity increases and approaches a point where the equilibrium pressure approaches the experimental value of 3200 kPa. This means that hydrate growth ceases when the driving force approaches zero and the salinity does not increase any further.

Figure 3.9 CO₂ hydrate phase diagram in pure water, 2, 4, 7.4 and 9.1 wt % saline solutions.

ΔP₀ = 1218 kPa, ΔP₂ = 1013 kPa, ΔP₄ = 768 kPa, ΔP₇.₄ = 196 kPa and ΔP₉.₁ = -211 kPa.
4 Injection of CO₂ and CO₂/N₂ into CH₄ Rich and CH₄ Free Reservoirs

In order to advance further our understanding of the parameters affecting CO₂ storage we need to take into account the fact that CO₂ gas captured from large stationary sources are mixed with impurities like N₂ and O₂. In order to render the CO₂ capture (separation) process economically viable the CO₂ concentration in the treated flue gas is about 90 mol %. Another practical consideration is the fact that depleted gas reservoirs still contain residual gas at a pressure of about 500 kPa. Because natural gas forms gas hydrate as well it is important that this is taken into account in any consideration for the injection of CO₂ into depleted gas reservoirs.

4.1 Materials

The material to create the porous medium was the same silica sand (SiO₂) used in previous experiments. CO₂, CH₄ and N₂ gas were obtained from Praxair and the purities were 99.5, 99.97 and 99.999 %, respectively. Tapioca starch (average molecular mass of 3 mDa, National Starch ULC) was also used as a hydrate kinetic additive. The gas injection apparatus was the same as Figure 2.9 and the vertical tubing shown in Figure 2.10 was applied. The list of experiments is given in Table 4.1. The CO₂/N₂ (90/10 mol %) gas mixture was injected at constant flow rate followed by constant pressure injection at 277 K. In addition, three experiments were conducted with CO₂ gas. The reservoir conditions at the beginning of the injection (residual gas and water phase) are also shown in Table 4.1 along with the duration of the experiment and the relevant results. In all experiments 1836 g of silica sand and 88 mL of water were used in the reservoir and resulted in water saturation value of 0.22.
Table 4.1. The hydrate formation induction time, the number of moles of CO\(_2\) stored in hydrate form (\(n_{CO_2,H}\)), the percentage of reservoir water formed CO\(_2\) hydrate (\(R_{CO_2,W}\)), the CO\(_2\) hydrate saturation (\(S_{CO_2,H}\)), CO\(_2\) storage density in hydrate form (\(\rho_{CR}^{CO_2,H}\)). All experiments at 277 K.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Injected gas or gas mixture</th>
<th>Gas and solution in the reservoir (at the start of experiment)</th>
<th>Induction time (min)</th>
<th>Sampling point (h)</th>
<th>(n_{CO_2,H}) (mol)</th>
<th>(R_{CO_2,W}) (%)</th>
<th>(S_{CO_2,H})</th>
<th>(\rho_{CR}^{CO_2,H}) (kg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p1)</td>
<td>CO(_2)</td>
<td>500 kPa CH(_4) Deionized water</td>
<td>109</td>
<td>24</td>
<td>0.637</td>
<td>80.3</td>
<td>0.194</td>
<td>70.1</td>
</tr>
<tr>
<td>(p2)</td>
<td></td>
<td></td>
<td>97</td>
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<td>0.632</td>
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<td></td>
<td></td>
<td>113</td>
<td>24</td>
<td>0.640</td>
<td>80.6</td>
<td>0.195</td>
<td>70.4</td>
</tr>
<tr>
<td>(q1)</td>
<td>CO(_2)/N(_2) (90/10 mol %)</td>
<td>Deionized water</td>
<td>154</td>
<td>24</td>
<td>0.620</td>
<td>78.1</td>
<td>0.189</td>
<td>68.2</td>
</tr>
<tr>
<td>(q2)</td>
<td></td>
<td></td>
<td>138</td>
<td>24</td>
<td>0.617</td>
<td>77.7</td>
<td>0.188</td>
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<tr>
<td>(q3)</td>
<td></td>
<td></td>
<td>262</td>
<td>24</td>
<td>0.622</td>
<td>78.4</td>
<td>0.190</td>
<td>68.4</td>
</tr>
<tr>
<td>(r1)</td>
<td>CO(_2)/N(_2) (90/10 mol %)</td>
<td>500 kPa CH(_4) Deionized water</td>
<td>216</td>
<td>24</td>
<td>0.576</td>
<td>72.5</td>
<td>0.175</td>
<td>63.4</td>
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<td>24</td>
<td>0.558</td>
<td>70.2</td>
<td>0.170</td>
<td>61.4</td>
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<td>24</td>
<td>0.566</td>
<td>71.2</td>
<td>0.172</td>
<td>62.3</td>
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<tr>
<td>(s1)</td>
<td>CO(_2)/N(_2) (90/10 mol %)</td>
<td>500 kPa CH(_4) 1 wt % aqueous tapioca starch solution</td>
<td>337</td>
<td>24</td>
<td>0.557</td>
<td>70.1</td>
<td>0.170</td>
<td>61.3</td>
</tr>
<tr>
<td>(s2)</td>
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<td>24</td>
<td>0.551</td>
<td>69.3</td>
<td>0.168</td>
<td>60.6</td>
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<tr>
<td>(s3)</td>
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<td>331</td>
<td>24</td>
<td>0.546</td>
<td>68.7</td>
<td>0.166</td>
<td>60.1</td>
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</table>
4.2 Injection of CO$_2$ into a reservoir containing 500 kPa CH$_4$

The CO$_2$ was injected into the crystallizer from the supply vessel through the Quizix Q5000 pump under 5 cm$^3$/min constant flow rate. When the reservoir pressure reached 3200 kPa the gas injection method was switched from constant flow rate to that at constant pressure of 3200 kPa through the use of a PID controller. Three experiments were conducted and each lasted 120 h. Gas samples in the crystallizer were taken every 24 hours by a 0.15 cm$^3$ inner volume stainless steel gas sampling tubing and analyzed with a GC. Considering the crystallizer volume of 1236 cm$^3$, the amount of the sampling gas was assumed that it did not affect the gas phase composition in the crystallizer. Before each analysis the column of the GC and the gas sampling tubing were purged with He gas for three times.

The number of moles of CO$_2$ stored in hydrate is given by the following formula

\[
n_{CO_2,H} = \left( n_{SV-CO_2,0} - n_{SV-CO_2,t} \right) - \left( n_{CR-CO_2,t} - n_{CR-CO_2,0} \right) - n_{D,t} \\
= \left[ \frac{P_{SV}V_{SV}}{zRT} \right]_{SV,0} - \left[ \frac{P_{SV}V_{SV}}{zRT} \right]_{SV,t} - \left[ \frac{y_{CO_2,t}P_{CR}V_{CR}}{zRT} \right]_{CR,t} - 0 - n_{D,t} \tag{4.1}
\]

In equation, $y_{CO_2,t}$ indicates the mole fraction of CO$_2$ gas in the crystallizer at time $t$ determined by GC analysis. The other metrics calculations were the same as (c) *Constant pressure gas injection in a gas cap*. The hydration number of CO$_2$/CH$_4$ hydrate was considered to be 6.16$^{49}$. 
Figure 4.1 Progress of the pressure and temperature profiles in the reservoir corresponding to experiment (p1) for 24 h, the first 360 min and 120 h.

Figure 4.1 shows the pressure and temperature profiles in the reservoir for experiment (p1) during which the injection of CO₂ into a reservoir containing 500 kPa CH₄ for 120 h was
conducted. The profiles for the first 24 h and 360 min are also shown in the figure. CO₂ gas was injected into the reservoir under 5 cm³/min and a rapid 3 K temperature rise was observed at 100 to 110 min which indicates hydrate crystal formation. The time elapsed from the beginning of gas injection into the reservoir to the onset of hydrate formation is called induction time. The reservoir pressure reached 3200 kPa at about 300 min and was maintained at that level for the rest of the experiment through the use of the PID controller. During the constant pressure phase of the experiment the temperature profile indicates slow hydrate formation. Figure 4.2 shows the calculated CO₂/CH₄ hydrate partial phase diagram using CSMGem software⁴⁹. The presence of CH₄ changes the hydrate equilibrium and shifts the CO₂ hydrate phase boundary to a higher pressure at constant temperature. At the nucleation point (3100 kPa) the gas phase composition resulting from the injection of pure CO₂ into the reservoir containing pure CH₄ at 500 kPa is 84 mol % CO₂. The equilibrium hydrate formation for this CO₂/CH₄ mixture is 2118 kPa (see Figure 4.2) and hence the pressure driving force to form hydrate is 3100-2118=982 kPa. This driving force is responsible for the hydrate formation and the corresponding temperature rise. The CO₂/CH₄ gas phase composition after 120 h is approximately 95/5 mol % CO₂ (experiment p1). As seen in Figure 4.2 there is a small change in the minimum pressure required to form hydrates from the CO₂/CH₄ (95/5 mol %) gas mixture compared to having pure CO₂ at a given temperature. In general, a shift in the phase boundary impacts the driving force for hydrate formation⁷⁴. As seen in Figure 4.2 there exists a 1178 kPa pressure driving force to form hydrate in the reservoir at 277 K. This is because the crystallizer pressure is 3200 kPa and the equilibrium pressure for the CO₂/CH₄ (95/5 mol %) hydrate is 2022 kPa. Thus, there still exists a pressure driving force to form hydrates. However, as shown in Figure 4.1 the hydrate formation process almost stopped after 24 h as seen from the pressure and temperature profiles.
Considering that there still exists 15% of water in place available to form hydrates (as discussed in the section below) the reason why hydrate formation reduces drastically is the fact that the hydrate crystals that already formed have created a barrier to the mass transfer of hydrate forming gas to the residual pore water.

As seen in Table 4.1 0.636 mol of CO\textsubscript{2} gas was stored in hydrate form (average of experiments p1, p2, and p3) and 80.2% (average of experiments p1, p2 and p3) of the reservoir water formed CO\textsubscript{2} hydrate in 24 h. After 120 hours 0.674 mol of CO\textsubscript{2} formed hydrate with 84.9% of the original water in place (average). The CO\textsubscript{2} storage density in hydrate form reached the value of 74.1 kg/m\textsuperscript{3} (average) which is about 8% less than the storage density in the experiment of CO\textsubscript{2} injection into CH\textsubscript{4} free reservoir reported in 2.4.2. Thus, the presence of CH\textsubscript{4} in the reservoir reduced the amount of CO\textsubscript{2} stored in hydrate mainly due to the fact that some cages are now filled with CH\textsubscript{4} molecules.
Figure 4.2 CO₂/CH₄-H₂O partial phase diagram. The dark circle represents the equilibrium pressure of hydrate formed by the CO₂/CH₄ (84/16 mol %) mixture at 277 K at the hydrate nucleation point, where driving force ΔPₚ = 3100 kPa-2118 kPa = 982 kPa. The dark spot represents the equilibrium pressure of hydrate formed by the CO₂/CH₄ (95/5 mol %) mixture at 277 K after 120 h, where driving force ΔPₚ = 3200 kPa-2022 kPa = 1178 kPa.

4.3 Injection of CO₂/N₂ (90/10 mol %) into a reservoir without CH₄

In experiments (q) CO₂/N₂ (90/10 mol %) was injected to the reservoir following the same injection procedure in experiments (p). The number of moles of CO₂ stored in hydrate in the reservoir is given by the next equation
\[ n_{\text{CO}_2,H} = (n_{SV-CO_2,0} - n_{SV-CO_2,t}) - (n_{CR-CO_2,t} - n_{CR-CO_2,0}) - n_{D,t} \]

\[
= \left[ \left( \frac{0.9P_{SVV_{SV}}}{zRT} \right)_{SV,0} - \left( \frac{0.9P_{SVV_{SV}}}{zRT} \right)_{SV,t} \right] - \left[ \left( \frac{y_{CO_2,t}P_{CRV_{CR}}}{zRT} \right)_{CR,t} - \left( \frac{y_{CO_2,0}P_{CRV_{CR}}}{zRT} \right)_{CR,0} \right] - n_{D,t} \quad (4.2)
\]

Calculations of the percentage of water conversion, CO\(_2\) hydrate saturation and CO\(_2\) storage density were the same as in the experiments (p). The hydration number of CO\(_2\)/N\(_2\) hydrate formed was considered to be 6.16\(^{40}\).

Figure 4.3 shows the pressure and temperature profiles in the reservoir for experiment (q1) during which a CO\(_2\)/N\(_2\) (90/10 mol \%) gas mixture was injected into a reservoir that did not contain any CH\(_4\). The CO\(_2\)/N\(_2\) gas mixture was injected into the reservoir at 277 K and at the rate of 5 cm\(^3\)/min (0.0072 m\(^3\)/day). Hydrate did not form until the reservoir pressure reached 3200 kPa. A 3.5 K rapid temperature rise was observed at about 160 min. This temperature rise is larger than the temperature rise of 1.5 K observed at about 74 min and the reservoir pressure of 2456 kPa in the experiments of CO\(_2\) injection into a reservoir without CH\(_4\) reported in 2.4.2, which shows less hydrate formed at lower pressure driving force (2456-1982=454 kPa) conditions. Thus the presence of N\(_2\) in the reservoir resulted in a higher pressure required to form hydrate and prolonged the onset of hydrate formation under the same method of CO\(_2\) gas injection into the reservoir. A delay in the onset of hydrate formation reduces the risk of hydrate plug formation in the injection system. The reservoir temperatures slowly decreased to 277 K after the peak and no significant temperature change appeared indicating a decreased rate of hydrate formation due to mass transfer limitations noted above. Figure 4.4 shows the calculated CO\(_2\)/N\(_2\) hydrate partial phase diagram using CSMGem software\(^{47}\). The presence of N\(_2\) changes the hydrate equilibrium and shifts the CO\(_2\) hydrate phase boundary to a higher pressure at constant temperature. The CO\(_2\)/N\(_2\) hydrate equilibrium shifted from CO\(_2\)/N\(_2\) (90/10 mol \%) to
that of a CO\textsubscript{2}/N\textsubscript{2} (85/15 mol %) mixture after 120 h reflecting the gas phase composition change while hydrate was forming. The pressure driving force for experiment (q1) at the nucleation point is 981 kPa (3200 kPa-2219 kPa) because the equilibrium hydrate formation pressure of the CO\textsubscript{2}/N\textsubscript{2} (90/10 mol %) mixture is 2219 kPa. The pressure driving force after 120 h is 841 kPa (3200 kPa-2359 kPa) because the equilibrium pressure of the CO\textsubscript{2}/N\textsubscript{2} (85/15 mol %) mixture is 2359 kPa. There still exists a pressure driving force of about 841 kPa to form hydrate in the reservoir since the experimental pressure is 3200 kPa and there is still water in the reservoir (12 % of the original water in place). As seen in Table 1 the number of moles of CO\textsubscript{2} stored in hydrate form after 24 h and 120 h was 0.620 (average for experiments q1, q2 and q3) and 0.703 (average), respectively. The CO\textsubscript{2} storage density in hydrate form reached 77.3 kg/m\textsuperscript{3} after 120 h (average). This is more than the 74.1 kg/m\textsuperscript{3} (average for experiments p1, p2 and p3) and indicates that more hydrate formed in experiments with CO\textsubscript{2}/N\textsubscript{2} injection in CH\textsubscript{4}-free reservoir compared to CO\textsubscript{2} injection in a CH\textsubscript{4} reservoir.
Figure 4.3 Progress of the pressure and temperature profiles in the reservoir corresponding to experiment (q1) for 24 h, the first 360 min and 120 h.
Figure 4.4 CO\textsubscript{2}/N\textsubscript{2}-H\textsubscript{2}O partial phase diagrams. The dark circle represents the equilibrium pressure of hydrate formed by the CO\textsubscript{2}/N\textsubscript{2} (90/10 mol %) mixture at 277 K at the hydrate nucleation point, where driving force $\Delta P_q = 3200$ kPa - 2219 kPa = 981 kPa. The dark spot represents the equilibrium pressure of hydrate formed by the CO\textsubscript{2}/N\textsubscript{2} (85/15 mol %) mixture at 277 K after 120 h, where $\Delta P_q = 3200$ kPa - 2359 kPa = 841 kPa.

4.4 Injection of CO\textsubscript{2}/N\textsubscript{2} (90/10 mol %) into a reservoir containing 500 kPa CH\textsubscript{4}

The injection procedure in experiments (r) is the same as in experiments (q) but it is noted that $(n_{CR-CO2,0}) = 0$ because at the beginning of the experiment there was no CO\textsubscript{2} in the reservoir. The number of moles of CO\textsubscript{2} stored in hydrate in the reservoir is calculated as follows
Calculations of the percentage of water conversion, CO₂ hydrate saturation and CO₂ storage density were the same as those for experiments (p). The hydration number of CO₂/N₂/CH₄ hydrate formed in this experimental work was found to be 6.15⁴⁹.

Figure 4.5 shows the pressure and temperature profiles for experiment (r₁) during which a CO₂/N₂ (90/10 mol %) gas mixture was injected into a reservoir containing 500 kPa CH₄. Like experiment (q₁) no hydrate formation in the reservoir was observed during the constant flow rate CO₂/N₂ injection period. A 3 K rapid temperature rise was observed at about 220 min. The temperature rise in experiment (r₁) is lower than that in experiment (q₁) perhaps because the presence of CH₄ in the gas mixture reduced the pressure driving force and this in turn results in a lower hydrate crystal growth and less hydrate formed overtime. Figure 4.6 shows the calculated CO₂/N₂/CH₄ hydrate partial phase diagram⁴⁹. The driving force for experiment (r₁) at the nucleation point is 871 kPa (3200 kPa-2329 kPa) because the gas phase composition is CO₂/N₂/CH₄ (76/8/16 mol %). The equilibrium hydrate formation pressure for this mixture is 2329 kPa. The driving force for (r₁) is less than the 981 kPa for experiment (q₁) indicating a delay in nucleation and less hydrate being formed. Indeed, the average nucleation time in experiments (r) is 223 min whereas for experiments (q) is 185 min as seen from Table 4.1. The driving force after 120 h for experiment (r₁) is 743 kPa (3200 kPa-2457 kPa) because the gas phase composition after 120 hours is CO₂/N₂/CH₄ (78/16/6 mol %). The amount of CO₂ stored also reflects the fact that less hydrate formed. As seen in Table 4.1, 0.567 and 0.654 mol (average for r₁, r₂ and r₃) of CO₂ stored in hydrate form after 24 h and 120 h, respectively.
These amounts are less than the corresponding amounts reported for experiment (q1). The CO$_2$ storage density in hydrate form in the reservoir is 71.9 kg/m$^3$ (average) after 120 h.

Figure 4.5 Progress of the pressure and temperature profiles in the reservoir corresponding to experiment (r1) for 24 h, the first 360 min and 120 h.
Figure 4.6 CO₂/N₂/CH₄-H₂O partial phase diagrams. The dark circle represents the equilibrium pressure of hydrate formed by the CO₂/N₂/CH₄ (76/8/16 mol %) mixture at 277 K at the hydrate nucleation point, where driving force ΔPᵣ = 3200 kPa-2329 kPa = 871 kPa. The dark spot represents the equilibrium pressure of hydrate formed by the CO₂/N₂/CH₄ (78/16/6 mol %) mixture at 277 K after 120 h, where driving force ΔPᵣ = 3200 kPa-2457 kPa = 743 kPa.
4.5 Injection of CO$_2$/N$_2$ (90/10 mol %) into a reservoir containing 500 kPa CH$_4$

and 1 wt % tapioca starch

It is noted that a 1 wt % tapioca starch aqueous solution was used in experiments (s). The tapioca starch solution was prepared according to the method mentioned in 3.3. The reservoir preparation, gas injection procedures and metrics calculations are the same as in experiments (r). No literature data has been found for the hydration number of CO$_2$/N$_2$/CH$_4$ hydrate formed 1 wt % tapioca starch solutions. Because tapioca starch is known not to enter the hydrate crystal lattice it is assumed that the hydration number remains unchanged 6.15.
Figure 4.7 Progress of the pressure and temperature profiles in the reservoir corresponding to experiment (s1) for 24 h, the first 600 min and 120 h.
Figure 4.7 shows the pressure and temperature profiles in the reservoir for experiment (s1) during which a CO$_2$/N$_2$ (90/10 mol %) gas mixture was injected into a reservoir containing 500 kPa CH$_4$ and 1 wt % tapioca starch. Rapid hydrate formation was observed at 350 min according to a 3 K temperature rise. The reservoir temperatures decreased gradually to 277 K in the following two hours and no significant temperature change was observed in the rest of the experiment. The gas composition shows no difference with the experiment (r1). As shown in Table 4.1 0.551 mol of CO$_2$ stored in hydrate and CO$_2$ storage density in hydrate form reached 61.3 kg/m$^3$ after 24 h which is less than the CO$_2$ storage in experiment (r1). However, the CO$_2$ storage density reached 74.7 kg/m$^3$ (average for s1, s2 and s3) after 120 h, which is more than the 71.9 kg/m$^3$ (average for experiments r1, r2 and r3). The addition of 1 wt % tapioca starch postponed the onset of hydrate formation because the starch is a hydrate kinetic inhibitor. Moreover, the presence of starch was found to reduce the amount of CO$_2$ stored in hydrate in the first 38 h but then accelerated the hydrate formation during the rest of the experiment period. This observation was also reported in 3.3 and denotes the fact that tapioca starch acts as a kinetic hydrate inhibitor like Polyvinylcaprolactam (PVCap). About 85.4 % (average for experiments s1, s2 and s3) of initial reservoir water formed CO$_2$ hydrate and the CO$_2$ hydrate saturation in the reservoir was 0.207 after 120 h (average).

4.6 Summary

Figure 4.8 shows the average ratio of moles of CO$_2$ stored in hydrate over the moles of water in place in the reservoir. Data from 2.4.2 are also included for comparison purposes. It is noted that after the first 24 h, more CO$_2$ stored in the experiments (p1) than (q1). However, the opposite results were observed in the experiments during the rest four days. The addition of 1 wt %
tapioca starch affects the hydrate formation and the CO$_2$ storage. In the first 24 h more CO$_2$ stored in the experiments (r1) than (s1). However, the amount of CO$_2$ stored in experiments (s1) is more than experiments (r1) in the rest four days. This phenomenon has been also observed in 3.3. The presence of 1 wt % tapioca starch in the reservoir prevented the hydrate formation in the early stage and then enhanced the hydrate formation. This may be considered a positive factor in the process of CO$_2$ gas injection into the depleted reservoirs in two ways. First, it decreases the risk of plug formation near the injection wellbore due to the delay in the onset of nucleation. Secondly, the hydrate formation is enhanced at later stage of the injection process and this in turn increases the amount of stored CO$_2$ as hydrate.

![Figure 4.8](image.png)

**Figure 4.8** The ratio of moles of CO$_2$ stored in hydrate form over the moles of water in place in the reservoir after every 24 h in experiments (h1) and (p1) to (s1).
5 Measurement of Hydrate Phase Equilibria in the CO$_2$/CH$_4$/N$_2$/H$_2$O system in a Stirred High Pressure Crystallizer and High Pressure Micro Differential Scanning Calorimetry (HP-$\mu$DSC)

In this chapter the equilibria of hydrate formed in high pressure crystallizer as well as with calorimetry at the typical depleted natural gas reservoir conditions were measured and the measured values were compared with calculated values using CSMGem software were also discussed.

5.1 Materials

The CO$_2$, CH$_4$ and N$_2$ gas with 99.5 %, 97.97 % and 99.999 % purities respectively were obtained from Praxair. Sodium Chloride (NaCl) was obtained from Fisher Scientific. The silica sand was obtained from Sigma-Aldrich with the porosity of 0.35 and the average diameter of 329 $\mu$m. Tapioca starch (average molecular mass of 3 mDa) was obtained from National Starch ULC.

5.2 Hydrate formation and dissociation in a stirred high pressure crystallizer containing water, 2 and 4 wt % saline solution

5.2.1 Experimental setup and methods

Binary mixtures containing a target concentration of 95 and 85 mol % CO$_2$ with CH$_4$ and N$_2$, respectively, prepared from the above gases and were employed in the experiments. The exact concentrations of the gas mixtures obtained by Gas Chromatography are shown in Table 5.1,
which lists all the experiments. A ternary CO$_2$/N$_2$/CH$_4$ mixture with a target composition of 78/16/6 mol % was also prepared and the real concentrations are shown in Table 5.1. The incipient hydrate equilibrium formation pressures were determined by the well-known isothermal pressure search method$^{62,96}$. The hydrate formation and dissociation apparatus is shown in Figure 5.1 and was described elsewhere$^{63}$ (the literature reported apparatus is shown in Appendix B). Briefly, a 211 mL high pressure crystallizer was employed to conduct the hydrate equilibria measurement experiments. There were two circle windows on the crystallizer to provide visual observation of the hydrate formation and dissociation process. An amount of 80 mL of deionized water or 2 and 4 wt % NaCl solutions prepared by weighting the salt was located into the crystallizer. The crystallizer was then immersed into the temperature controlled bath. Three thermocouples (Omega) with 0.1 K uncertainties were employed to measure the gas, liquid and gas/water interface temperatures. Pressure transducers (Rosemount, model 3051) with maximum uncertainty of 0.075 % of the 0 to 15000 kPa span were used to measure the crystallizer and supply vessel pressures. The temperature and pressure data were logged by a data acquisition system every 5 sec to a computer using LabView software. The crystallizer was pressurized with CO$_2$ gas or the gas mixtures to 1500 kPa and then was depressurized three times to eliminate the presence of the air. When all the three temperatures arrived at the desired value the CO$_2$ gas or the gas mixtures was injected into the crystallizer to approximately 1000 kPa higher than the hydrate equilibrium pressure at the given temperature and started stirring at 500 rpm in the crystallizer. The temperature rises and pressure decreases indicated the formation of gas hydrate. The nucleation of hydrate also can be verified by the visual observation through the window on the crystallizer. Flocculent crystals were initially formed at the interface of the gas and liquid, then grew toward to the liquid phase.
Table 5.1 Hydrate equilibrium pressures measured in high pressure crystallizer at fixed temperature.

<table>
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<th>$P$ (kPa)</th>
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<tbody>
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<td></td>
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<td>in 4 wt % NaCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$P$</td>
<td>This work</td>
<td>CSM</td>
<td>Gem</td>
<td>This work</td>
<td>CSM</td>
<td>Gem</td>
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<td>2009</td>
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Figure 5.1 Schematic of the apparatus for hydrate formation and dissociation in bulk system.
As shown in Table 5.1 the gas hydrate dissociation pressures were measured at 276.15, 277.15 and 278.15 K, which represent the typical Alberta hydrocarbon reservoirs temperatures. The calculation values using CSMGem software are also shown in Table 5.1. Once the hydrate formed the crystallizer was depressurized to decompose the hydrate. The induction of hydrate nucleation and the hydrate decomposition was repeated twice more to enhance the degree of the liquid phase structuralization and to eliminate the hysteresis phenomenon. Then the crystallizer was pressurized again with specific gases 10 kPa above the calculated hydrate equilibrium pressures to induce the hydrate formation. After 3 to 4 h if a small amount of hydrate formation was observed while temperatures and pressure remained steady then the crystallizer pressure was considered to be the equilibrium pressure at the setting temperature. If no hydrate formation was detected the crystallizer was pressurized 20 kPa higher than the previous value and the crystallizer was left at these conditions for 3 to 4 h. The operation was repeated until temperature and pressure conditions remained steady while there is a small amount of hydrate present. If hydrate already formed, then the crystallizer was depressurized by 20 kPa to decomposed the hydrate. Then the above mentioned procedure was repeated to increase the pressure 20 kPa once until hydrate equilibrium pressure was obtained. The equilibrium pressure measurement was conducted from 278.15 K then lower temperatures of 277.15 and 276.15 K were subsequently set to measure the following hydrate equilibrium pressures. All the equilibria measurement experiments were conducted three times.

### 5.2.2 Results and discussion

The measured CO$_2$, CO$_2$/CH$_4$ (95/5 mol %), CO$_2$/N$_2$ (85/15 mol %) and CO$_2$/N$_2$/CH$_4$ (78/16/6 mol %) hydrate equilibrium pressures at 276.15, 277.15 and 278.15 K in water, 2 and 4 wt % NaCl solutions are shown in Table 1. The measured equilibrium pressures and the calculated
values using the CSMGem software are shown in Figure 5.2 to 5.5. The NaCl as expected shifts the hydrate equilibrium to a higher pressure region at constant temperature. The measured hydrate equilibrium pressures are in a good agreement with the calculated values (within ± 40 kPa).

Figure 5.2 CO₂ hydrate equilibrium pressures measured in the stirred high pressure crystallizer and by high pressure micro differential scanning calorimetry in water, 2 and 4 wt % NaCl solutions.
Figure 5.3 CO$_2$/CH$_4$ (95/5 mol %) hydrate equilibrium pressures measured in the stirred high pressure crystallizer and by high pressure micro differential scanning calorimetry in water, 2 and 4 wt % NaCl solutions.
Figure 5.4 CO$_2$/N$_2$ (85/15 mol%) hydrate equilibrium pressures measured in the stirred high pressure crystallizer and by high pressure micro differential scanning calorimetry in water, 2 and 4 wt% NaCl solutions.
Figure 5.5 CO₂/N₂/CH₄ (78/16/6 mol %) hydrate equilibrium pressures measured in the stirred high pressure crystallizer and by high pressure micro differential scanning calorimetry in water, 2 and 4 wt % NaCl solutions.

5.3 Hydrate dissociation in a high pressure micro differential scanning calorimetry containing water, 2 and 4 wt % saline solution

5.3.1 Experimental setup and methods

The use of the calorimeter to obtain equilibrium data is briefly described. The HP-μDSC 7 Evo, Setaram high pressure calorimeter was used to detect and measure the heat transfer when gas hydrate formed and dissociated. Double-stage temperature control with Peltier coolers was used...
in the HP-μDSC to provide a programmable temperature scanning between 228.15 and 393.15 K under the heating or cooling rate of 0.001 to 2 K/min. The uncertainties of the temperature and heat flow measurement are known to be 0.1 K and 0.05 mJ. The HP-μDSC has two 1 mL cells, sample cell and reference cell, which both can sustain up to 40 MPa. Two types of sample holder were used and are shown in Figure 5.6. One is called droplet sample holder and its description can be found elsewhere. Briefly, it is a customized stainless steel holder with four 1.5 mm diameter, 2.6 mm depth pits and a 1.6 mm diameter, 7 mm length rod. The volume for each pit is 1 mL and 1 μL deionized water or 2 or 4 wt % NaCl solution was injected into the pits using a micro-syringe carefully. Thus the total volume of the injected water or solutions was 4 μL. The other one is a reservoir sample holder and was developed in this work. It consists of a high-pressure Nylo-Seal Nylon tubing with an inside diameter of 2.3 mm and inside height of 8 mm. The cylindrical tubing was sealed at the bottom to make it a sample holder. 40 mg silica sand was placed into the holder and 8.7 μL of aqueous solution was injected into the sand using a micro-syringe to render it fully water saturated. The list of the experiments using HP-μDSC is shown in Table 5.2. The sample holder was then placed in the high-pressure sample cell. The sample cell and the reference cell were pressurized to 1500 kPa with the gas hydrate forming gas. This was followed by depressurization. This operation was repeated two times to eliminate the air in the cells. Subsequently, the cells were pressurized to 3200 kPa and the temperature ramping program was started. The cells were cooled from 288.15 K to 248.15 K at the rate of 0.1 K/min to form gas hydrate and were heated from 248.15 K to 288.15 K at the same rate to decompose the hydrate. Gas hydrate nucleation and dissociation are represented by exothermic and endothermic peaks respectively. It is noted that all the experiments with the HP-μDSC were conducted three times.
5.3.2 Results and discussion

The measured hydrate equilibrium dissociation temperatures and endothermic heat under constant 3200 kPa in a HP-μDSC in the water droplet and water, 2 and 4 wt % NaCl solutions fully saturated reservoir are shown in Table 5.2 and Figure 5.2 to 5.5. Figure 5.7 shows the hydrate dissociation peaks for CO₂, CO₂/CH₄ (95/5 mol %), CO₂/N₂ (85/15 mol %) and CO₂/N₂/CH₄ (78/16/6 mol %) gas or gas mixture hydrate forming systems observed with HP-μDSC in the water droplet sample holder under a 0.1 K/min heating protocol. The presence of 5 mol % of CH₄ in the CO₂/CH₄ shows a very small effect on the hydrate dissociation temperatures compared to the case of pure CO₂. It is calculated by using CSMGem software that at a given temperature the hydrate equilibrium pressure of CO₂ increases by about 35 kPa when hydrates form from a CH₄/CO₂ mixture with 5 mol % CH₄⁴⁹.
Table 5.2 Hydrate dissociation temperatures and endothermic heat measured under constant 3200 kPa in a HP-μDSC in the water droplet and water, 2 and 4 wt % NaCl solutions fully saturated reservoir.

| Sample gas/gas mixtures | Droplet in water | | Reservoir in 2 wt % NaCl | | Reservoir in 4 wt % NaCl |
|-------------------------|------------------|------------------|------------------|------------------|
|                         | $T$ (K) | $H$ (mJ) | $T$ (K) | $H$ (mJ) | $T$ (K) | $H$ (mJ) | $T$ (K) | $H$ (mJ) |
| CO$_2$                  | 280.8 | 280.7 | 482.3 | 280.6 | 3636.0 | 279.8 | 279.8 | 3050.3 | 278.9 | 279.0 | 2204.5 |
|                         | 280.9 | 492.4 | | 280.6 | 3696.7 | 279.8 | 3098.4 | | 278.8 | 2185.9 | |
|                         | 280.8 | 488.1 | | 280.6 | 3643.5 | 279.7 | 3110.8 | | 278.9 | 2238.6 | |
| CO$_2$/CH$_4$ (95/5 mol %) | 280.6 | 280.7 | 469.1 | 280.5 | 3404.0 | 279.8 | 279.9 | 2798.0 | 278.9 | 279.0 | 1920.3 |
| #1: (95.10/4.90 mol %)   | 280.6 | 447.7 | | 280.6 | 3379.3 | 279.9 | 2805.1 | | 279.0 | 1895.4 | |
| #2: (95.03/4.97 mol %)   | 280.7 | 453.9 | | 280.6 | 3309.1 | 279.8 | 2765.2 | | 278.9 | 1919.0 | |
| #3: (94.95/5.05 mol %)   | 279.6 | 279.5 | 497.5 | 279.4 | 2908.4 | 278.6 | 278.7 | 2490.6 | 277.7 | 277.8 | 1537.7 |
| CO$_2$/N$_2$ (85/15 mol %) | 279.5 | 439.0 | | 279.4 | 3008.8 | 278.7 | 2491.3 | | 277.8 | 1572.8 | |
| #1: (85.03/14.97 mol %)  | 279.6 | 446.2 | | 279.6 | 2973.3 | 278.5 | 2439.7 | | 277.7 | 1598.5 | |
| #3: (84.94/15.06 mol %)  | 279.3 | 279.4 | 433.0 | 279.3 | 2898.9 | 278.5 | 278.6 | 2426.9 | 277.7 | 277.7 | 1522.7 |
| CO$_2$/N$_2$/CH$_4$ (78/16/6 mol %) | 279.3 | 279.4 | 433.0 | 279.3 | 2898.9 | 278.5 | 278.6 | 2426.9 | 277.7 | 277.7 | 1522.7 |
| #1: (78.02/15.89/6.09 mol %) | 279.3 | 435.1 | | 279.4 | 2878.1 | 278.4 | 2419.8 | | 277.6 | 1530.9 | |
| #2: (77.98/15.98/6.04 mol %) | 279.3 | 427.8 | | 279.4 | 2937.4 | 278.5 | 2400.5 | | 277.6 | 1519.4 | |
Figure 5.7 Hydrate dissociation peaks for four hydrate forming systems (#1) observed with HP-μDSC in the droplet sample holder under a 0.1 K/min heating protocol.

The hydrate dissociation temperature shifts to a lower region when N₂ or N₂ and CH₄ are added to CO₂. The endothermic heat measured during the dissociation of hydrate in the HP-μDSC is also shown in Table 5.2. It is also noted that during the CO₂/N₂ (85/15 mol %) hydrate dissociation process, a second and much smaller endothermic peak is observed at about 280 K and it is not known why. The measured hydrate dissociation temperatures show - 0.1 to 0.2 K differences from the calculated values. As shown in Figure 5.7, peaks with shoulder or tail were observed. It may be related to the different subcooling for the different droplets and this could result in slightly different dissociations for the four droplets and therefore the dissociation peaks.
Figure 5.8 to 11 show the hydrate dissociation peaks for hydrates formed by the CO$_2$, CO$_2$/CH$_4$ (95/5 mol %), CO$_2$/N$_2$ (85/15 mol %) and CO$_2$/N$_2$/CH$_4$ (78/16/6 mol %) in deionized water, 2 and 4 wt % NaCl solutions. The measured hydrate dissociation temperatures and the calculation data are shown in Table 5.2. Similar to the measurements with the water droplet sample holder, the presence of N$_2$, CH$_4$ or N$_2$/CH$_4$ in the CO$_2$ shifted the hydrate dissociation temperature to a lower region. The increase of salinity in the reservoir resulted in lower hydrate dissociation temperatures at the constant pressure of 3200 kPa. The hydrate dissociation endothermic heat also showed a decreasing trend with the increasing of the salinities in the reservoir, which indicates less hydrate formed. It is noted that the hydrate dissociation process in 2 and 4 wt % NaCl reservoirs lasted longer period compared to the hydrate dissociation in the water reservoir. Because NaCl does not participate in the hydrate lattice, the salinity of the aqueous solution increases as hydrate formation proceeds. Similarly, when the hydrate decomposes the salinity is restored as water is being released. The incipient equilibrium hydrate formation points correspond to the presence of an infinitesimal amount of hydrate (onset of hydrate formation) or when an infinitesimal amount of hydrate remains undissociated$^{62,63,96}$. It is also noted that the measured hydrate dissociation temperatures in the reservoir sample holders show ± 0.2 K difference with the calculated values$^{49}$. 
Figure 5.8 CO$_2$ hydrate dissociation peaks for hydrate formed in deionized water, 2 and 4 wt % NaCl solutions observed with the HP-$\mu$DSC in the reservoir sample holder under a 0.1 K/min heating protocol.
Figure 5.9 Hydrate dissociation peaks for hydrate formed by the CO$_2$/CH$_4$ (95.10/4.90 mol %) gas mixture in deionized water, 2 and 4 wt % NaCl solutions observed with the HP-$\mu$DSC in the reservoir sample holder under a 0.1 K/min heating protocol.
Figure 5.10 Hydrate dissociation peaks for hydrate formed by the CO$_2$/N$_2$ (85.03/14.97 mol %) gas mixture in deionized water, 2 and 4 wt % NaCl solutions observed with the HP-$\mu$DSC in the reservoir sample holder under a 0.1 K/min heating protocol.
Figure 5.11 Hydrate dissociation peaks for the hydrate formed by the CO$_2$/N$_2$/CH$_4$ (78.02/15.89/6.09 mol %) gas mixture in deionized water, 2 and 4 wt % NaCl solutions observed with the HP-μDSC in the reservoir sample holder under a 0.1 K/min heating protocol.

The percentage of water converted to hydrate was calculated based on the endothermic heat measured when hydrate dissociated in the HP-μDSC. It is known that the enthalpy change is 65 kJ/mol and the hydration number is 6.17 for the CO$_2$ hydrate$^{49,97}$. Results showed that about 21 % of the initial water in the droplet sample holders formed hydrate, which is much less than 72 % of the water conversion in the reservoir sample holder. This observation is consistent with experimental findings reported in the literature for sand beds$^{98}$. It is noted that the enhanced rate in the presence of a porous medium created by sand prompted further work with other media in
an effort to optimize the clathrate hydrate processes for CO₂ capture. The water conversion in the reservoir samples containing 2 and 4 wt % NaCl solutions was found to be 61 and 43 %, respectively, indicating less hydrate formed at higher salinity, which is expected as the pressure was constant.

5.4 Summary

The incipient hydrate equilibrium pressures measured in the stirred autoclave are in a good agreement with the calculated values (within ± 40 kPa). The hydrate dissociation temperatures determined by the calorimeter using a droplet and a porous media (reservoir) sample holder also show good agreement with the calculated values (within ± 0.2 K). The salinity shifts hydrate equilibrium to higher pressure region at constant temperature or lower dissociation temperature region at constant pressure as expected. Correspondingly, the amount of formed hydrate is reduced. Results indicate that 40 to 60 % of the original water formed hydrate when CO₂ was injected into a typical saline reservoir sample.
6 CO₂ Storage Density

In this chapter the CO₂ storage density in kg/m³ (mass of CO₂ per pore volume in the laboratory reservoir) based on our experimental data is calculated. In addition, the amount that can be stored in a typical Alberta reservoir is estimated as well as the total storage capacity of the 121 Alberta reservoirs.

6.1 CO₂ storage density with and without hydrate technology

The stored CO₂ consists of CO₂ as hydrate, CO₂ gas in the remaining pore volume not occupied by hydrate and also the amount of CO₂ dissolved in the remaining water. Table 6.1 shows the experimental conditions from experiments (a) to (s). Figure 6.1 shows the total CO₂ storage densities (kg/m³, mass of CO₂ per pore volume in the laboratory reservoir) that was determined in the experiments (a) to (s) mentioned in Chapter 2, 3 and 4 (average for the three runs of experiments under each method). The standard deviations of the total CO₂ storage density for the experiments which were run for three times are given as (a) 0.374, (b) 0.698, (c) 0.262, (d) 0.189, (e) 0.125, (f) 0.125, (g) 0.047, (h) 1.275, (i) 0.655, (j) 0.455, (k) 0.205, (l) 0.464, (m) 0.525, (n) 0.624, (o) 0.170, (p-24 h) 0.374, (p-120 h) 0.262, (q-24 h) 1.134, (q-120 h) 0.283, (r-24 h) 0.818, (r-120 h) 1.236, (s-24 h) 0.492 and (s-120 h) 0.125. The conditions for CO₂ stored in gas form in experiments (a), (b) and (c) are 1850 kPa, 274 K, 3180 kPa, 274 K and 3200 kPa, 274 K, respectively. 3200 kPa, 277 K are the conditions for CO₂ storage as gas in all the other experiments. More CO₂ stored in multiple gas injection cases (gas injection through spiral and vertical tubing) than the experiments of gas injection in a gas cap. Gas injection under constant flow rate and constant pressure experiment results in more CO₂ storage compared to constant pressure injection case. Higher initial pressure driving force in constant pressure injection
experiment likely leads to rapid hydrate formation in the porous bed. This may hinder mass transfer of gas into the unconverted water in other interstitial spaces. Even though the rate of hydrate growth decreases after the first few hours it continues beyond the 24 h period. Experiments conducted after 120 h showed that more total CO₂ storage density in the reservoirs containing 1 wt % of tapioca starch (experiments l, 145.2 kg/m³) and 3 wt % of PVP (experiments j, 146.6 kg/m³) compared to in a pure water reservoir (experiments h, 142.9 kg/m³). The effect of the addition of 3 wt % of PVP and 1 wt % of tapioca starch on hydrate formation is in accordance with a previous work⁵⁸. However, if the tapioca starch concentration increases to 3 wt % both 24 h and 120 h experiments results less CO₂ storage density than pure water experiment. It is also seen that the presence of 2 wt % (experiments n, 126.7 kg/m³) and 4 wt % (experiments o, 114.0 kg/m³) of salinity in the reservoir reduces the CO₂ storage density compared to a reservoir containing pure water (experiments h, 138.2 kg/m³) after 24 h. When a CO₂/N₂ gas mixture is injected in a reservoir containing CH₄ the total CO₂ storage density (experiments r, 118.6 kg/m³) decreases by 17 % compared to the CO₂ injection into a CH₄ free reservoir (experiments h, 142.9 kg/m³) after 120 h. The addition of 1 wt % of tapioca starch in the reservoir containing CO₂/N₂/CH₄ (experiments s) results in 121.0 kg/m³ total CO₂ storage density which is 2 % higher than the CO₂ storage density in the reservoir without starch (experiments r, 118.6 kg/m³) after 120 h.
Table 6.1 Experimental conditions of experiments (a) to (s)

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<th>Exp.</th>
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<th>Injection method</th>
<th>Initial reservoir temperature [k]</th>
<th>Additives in reservoir</th>
<th>Residual gas in reservoir</th>
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<tr>
<td>(b)</td>
<td>CO₂</td>
<td>Series-batch injection in a gas cap</td>
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<td>-</td>
</tr>
<tr>
<td>(c)</td>
<td>CO₂</td>
<td>Constant pressure injection in a gas cap (3200 kPa)</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>(d)</td>
<td>CO₂</td>
<td>Constant pressure injection through a spiral tubing at top (3200 kPa)</td>
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<td>-</td>
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<tr>
<td>(e)</td>
<td>CO₂</td>
<td>Constant pressure injection through a spiral tubing at bottom (3200 kPa)</td>
<td>277.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(f)</td>
<td>CO₂</td>
<td>Constant pressure injection through spiral tubing at both top and bottom (3200 kPa)</td>
<td>277.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(g)</td>
<td>CO₂</td>
<td>Constant pressure injection through a vertical tubing (3200 kPa)</td>
<td>277.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(h)</td>
<td>CO₂</td>
<td>Constant flow rate (5 mL/min) followed by constant pressure (3200 kPa) injection through a vertical tubing</td>
<td>277.15</td>
<td>1 wt % PVP</td>
<td>-</td>
</tr>
<tr>
<td>(i)</td>
<td>CO₂</td>
<td>Same as above</td>
<td>277.15</td>
<td>3 wt % PVP</td>
<td>-</td>
</tr>
<tr>
<td>(j)</td>
<td>CO₂</td>
<td>Same as above</td>
<td>277.15</td>
<td>0.5 wt % starch</td>
<td>-</td>
</tr>
<tr>
<td>(k)</td>
<td>CO₂</td>
<td>Same as above</td>
<td>277.15</td>
<td>1 wt % starch</td>
<td>-</td>
</tr>
<tr>
<td>(l)</td>
<td>CO₂</td>
<td>Same as above</td>
<td>277.15</td>
<td>3 wt % starch</td>
<td>-</td>
</tr>
<tr>
<td>(m)</td>
<td>CO₂</td>
<td>Same as above</td>
<td>277.15</td>
<td>1 wt % starch</td>
<td>-</td>
</tr>
<tr>
<td>(n)</td>
<td>CO₂</td>
<td>Same as above</td>
<td>277.15</td>
<td>2 wt % NaCl</td>
<td>-</td>
</tr>
<tr>
<td>(o)</td>
<td>CO₂</td>
<td>Same as above</td>
<td>277.15</td>
<td>4 wt % NaCl</td>
<td>-</td>
</tr>
<tr>
<td>(p)</td>
<td>CO₂</td>
<td>Same as above</td>
<td>277.15</td>
<td>-</td>
<td>500 kPa CH₄</td>
</tr>
<tr>
<td>(q)</td>
<td>CO₂/N₂ (90/10 mol %)</td>
<td>Same as above</td>
<td>277.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(r)</td>
<td>CO₂/N₂ (90/10 mol %)</td>
<td>Same as above</td>
<td>277.15</td>
<td>-</td>
<td>500 kPa CH₄</td>
</tr>
<tr>
<td>(s)</td>
<td>CO₂/N₂ (90/10 mol %)</td>
<td>Same as above</td>
<td>277.15</td>
<td>1 wt % starch</td>
<td>500 kPa CH₄</td>
</tr>
</tbody>
</table>
Figure 6.1 Total CO$_2$ storage densities (Average for the three runs of experiments under each method).
Figure 6.2 shows the average of total CO₂ storage densities in experiments (s) for 120 h, CO₂ storage as low pressure gas form at 2110 kPa, 277 K and high pressure gas form at 5220 kPa, 285 K under the injection of CO₂/N₂ (90/10 mol %) gas mixture into a reservoir without water and CH₄. The CO₂/N₂ (90/10 mol %) gas mixture is assumed to occupy all of the free space in the reservoir for the gas and liquid form storage, respectively. The average of total CO₂ storage density in the experiments (s) is 121.0 kg/m³, which is about 190 % greater compared to the low pressure gas storage (41.3 kg/m³) and is almost the same as the high pressure gas storage (120.2 kg/m³). If CO₂ is stored as liquid at conditions near the bubble point of CO₂/N₂ (90/10 mol %) at 8500 kPa and 285 K, the CO₂ storage density as liquid is 890 kg/m³ i.e. approximately 6 times higher than the average CO₂ storage density in experiments (s) in this work. However, CO₂ storage in that liquid CO₂ state requires significantly more power for gas compression and is not safe.
6.2 CO₂ storage density in an Alberta reservoir

To assess the CO₂ storage potential in a depleted hydrocarbon reservoir in the field the CO₂ storage density obtained in this experimental work is applied to a reservoir selected from the borehole database provided by Alberta Energy and Utilities Board (AEUB)¹⁰¹ as a case study. The reservoir (Pool code 328098) with the porosity of 0.28 located 204 m underground in the LIEGE field has a reservoir volume of $1.1 \times 10^7 \text{ m}^3$ and the initial pressure/temperature
conditions are 840 kPa and 277 K. The initial water saturation was 0.25. Assuming that the CO₂ storage density is the same as that found in experiments which indicate the CO₂/N₂ (90/10 mol %) injection into a reservoir containing 500 kPa CH₄ and 1 wt % starch then the potential to store CO₂ as hydrate + gas + dissolved in water form is calculated as 373 kt in the real field reservoir. Considering the total volume of 2.1 × 10¹² m³ of Alberta depleted natural gas reservoir was investigated, about 71.2 Gt (43.9 Gt as hydrate form) of CO₂ can potentially be stored in these reservoirs if hydrate technology applied. Thus, storage of CO₂ using hydrate technology in depleted natural gas reservoirs in Alberta would be able to potentially store local CO₂ for more than 250 years.

6.3 Economic analysis of CO₂ storage

The motivation to store CO₂ in depleted natural gas reservoirs is of course driven by climate change concerns but also from the economic considerations. There is a profit or economic advantage from the CO₂ storage arising from savings (avoidance) of CO₂ emission levies. Current CO₂ levies in Alberta are $ 30 USD/tonne of CO₂ emitted and it shows an increasing trend in the next few years. The costs of the CO₂ storage are mainly from the CO₂ capture from the flue gas, transportation, compression and the right to use the depleted natural gas reservoirs. The estimated costs are $ 11 to 57 USD/t for the CO₂ capture, $ 3 to 4 USD/t for the transportation and $ 6 to 7 USD for the compression and injection (disposal). The land use, air and water emission permits cost $ 100 k USD/site. The cost of the addition of tapioca starch is $ 300 to 350 USD/100 tonnes and amount of starch required in one reservoir is about 1000 tonnes. Thus the cost of the starch can be ignored compared to other costs. The economic analysis of CO₂ storage is shown in Figure 6.3. The profit and cost estimation are given based on
the US dollar per tonne of CO₂. The costs are given as a range of the source value and three estimations of CO₂ storage profit are given by applying different CO₂ emission levies. One sees the interplay between carbon price and capture cost.

![Figure 6.3 Economic analysis of CO₂ storage.](image)

Applying the CO₂ storage economic estimation (total cost, 20 USD/t; storage profit, 30 USD/t) to the LIEGE field reservoir mentioned in 6.1, the net profit of the CO₂ storage using hydrate technology is calculated as follows
Net profit of CO₂ storage in the reservoir

\[
\text{Net profit of CO}_2 \text{ storage in the reservoir} = \left( \frac{\text{Net profit of CO}_2 \text{ storage}}{1 \text{ tonne of CO}_2} \times \text{CO}_2 \text{ capacity in reservoir} \right)
- \left( \frac{\text{Land use, air and water emission permits cost}}{\text{site}} \times 1 \text{ site} \right)
\]

\[
= $10 \text{ USD/t} \times 373 \text{ kt} - $100 \text{ k USD} = $3.63 \text{ m USD} \quad (6.1)
\]

In addition, the net profit of the CO₂ storage using hydrate technology in the investigated 121 depleted natural gas reservoirs in Alberta is as follows

Net profit of CO₂ storage in Alberta depleted natural gas reservoir

\[
= \left( \frac{\text{Net profit of CO}_2 \text{ storage}}{1 \text{ tonne of CO}_2} \times \text{Toal CO}_2 \text{ capacity in reservoirs} \right)
- \left( \frac{\text{Land use, air and water emission permits cost}}{\text{site}} \times 121 \text{ site} \right)
\]

\[
= $10 \text{ USD/t} \times 71.2 \text{ Gt} - \frac{\$100 \text{ k USD}}{\text{site}} \times 121 \text{ site}
\]

\[
= $7.12 \times 10^2 \text{ b USD} \quad (6.2)
\]
7 Conclusions and Recommendations

7.1 Conclusions

CO₂ hydrate formation and corresponding estimation of CO₂ storage were conducted in a laboratory scale partially water saturated reservoir simulating a typical Alberta depleted natural gas reservoir. The effect of gas injection method, the presence of additives (PVP, tapioca starch), salinity (NaCl) and residual natural gas (CH₄) in the reservoir were investigated. In addition, the presence of N₂ in the injection gas mixture on CO₂ storage density was also assessed.

It was found that multiple (spiral tubing) gas injection experiments result in more CO₂ gas uptake than gas cap mode gas injection experiments. More hydrate formed in the experiments under constant flow rate followed by constant pressure gas injection compared to the experiments under constant pressure gas injection. The addition of 3 wt % of PVP (molecular weight = 3.5 kDa) and 1 wt % of tapioca starch (molecular weight = 3 mDa) solution in the reservoir prolonged the hydrate nucleation at early stage then improved hydrate formation and resulted in 6.5 % and 4.6 % more CO₂ stored in hydrate form respectively compared to the CO₂ stored in pure water reservoir in the experiment period of 120 h. It can be considered a positive factor for the CO₂ gas injection into the reservoirs due to a decreased risk to plug the injection system arising from the formation of the hydrate. After 120 h, 90 % of the amount of water initially added in the reservoir formed hydrate and the combination of CO₂ stored in hydrate, gas and dissolved in water arrived 147 kg/m³. The presence of NaCl in the reservoir reduced the amount of hydrate formation as less hydrate formed in the reservoir containing higher salinity.
CO₂/N₂ (90/10 mol %) gas mixture and 500 kPa CH₄ were also utilized to simulate the injection gas and the residual gas in the reservoir to determine the CO₂ storage density taking into account the fact that the captured flue gas is about 90 mol % of CO₂ and also that the reservoir has residual natural gas. The presence of 10 mol % N₂ in the CO₂/N₂ injection gas mixture into a CH₄ free reservoir postponed the hydrate formation and reduced the stored amount of CO₂ as gas hydrate by 5 % compared to the pure CO₂ injection into a CH₄ free reservoir. The injection of CO₂ into a 500 kPa CH₄ reservoir also found to postpone the hydrate formation and reduced the stored amount of CO₂ as gas hydrate by 9 % compared to the pure CO₂ injection into a CH₄ free reservoir. The presence of 10 mol % N₂ in the CO₂/N₂ injection gas mixture into a 500 kPa CH₄ reservoir postponed the hydrate formation and reduced the stored amount of CO₂ as gas hydrate by 10 % compared to the pure CO₂ injection into a CH₄ free reservoir. The addition of 1 wt % tapioca starch in the reservoir delayed the onset of hydrate nucleation then improved the hydrate formation process and resulted in higher total CO₂ storage density (in hydrate, gas and dissolved in water). It was found the total CO₂ storage density reached 121 kg/m³ after 120 h experiment.

The equilibria of hydrate forming systems [CO₂, CO₂/CH₄ (95/5 mol %), CO₂/N₂ (85/15 mol %) and CO₂/N₂/CH₄ (78/16/6 mol %)] relevant to storage of CO₂ in depleted natural gas reservoirs was determined by following the isothermal pressure search method in a stirred autoclave and high pressure calorimetry containing deionized water and saline water. The incipient hydrate equilibrium pressures measured in the stirred autoclave are in a good agreement with the calculated values (within ± 40 kPa). The hydrate dissociation temperatures determined by the calorimeter using a droplet and a porous media (reservoir) sample holder also show good agreement with the calculated values (within ± 0.2 K). The salinity shifts hydrate equilibrium to
higher pressure at constant temperature or lower dissociation temperature region at constant pressure as expected. Correspondingly the amount of formed hydrate is reduced.

### 7.2 Recommendations for future work

Based on the study and understanding obtained from this thesis, the following recommendations are made for future work.

1. The number of depleted natural gas reservoirs in Alberta with suitable conditions for CO$_2$ storage in hydrate form increased from 61 in 2010 to 121 in 2013. It is necessary to ascertain the substances in the reservoir in addition to natural gas and salinity and assess the effect of these substances on the hydrate formation and corresponding CO$_2$ storage.

2. The effect of porosity and pore size of the sand or stone on hydrate formation has been reported recently$^{104-106}$. Further study of these parameters similar to the depleted natural gas reservoirs on hydrate formation kinetics is required.

3. In this study the CO$_2$/N$_2$ (90/10 mol %) was simulated as the flue gas captured for the gas injection experiments. However, there is more than N$_2$ in the flue gas emitted from the fossil fuel combustion sources like, O$_2$, SO$_2$ and H$_2$S. The effect of these impurities in the injection gas on hydrate formation is required to be assessed.

4. Beside the tapioca starch and PVP, other additives like sodium ethyl sulfate (SES), sodium dodecyl sulfate (SDS) which promote hydrate formation$^{107,108}$ could be added in the reservoir to test the performance of hydrate formation.
5. In order to properly account for the mass transfer and heat transfer in the reservoir in the process of gas injection and hydrate formation, numerical work should be conducted to study the gas and water phase movement and the energy change according to hydrate formation in the reservoir.
Bibliography


[44] Li, X. S., Xu, C. G., Chen, Z. Y., Cai, J. Synergic effect of cyclopentane and tetra-n-butyl ammonium bromide on hydrate-based carbon dioxide separation from fuel gas mixture by


Appendices

Appendix A: Mass balance and energy balance

To establish a simulation of the CO\textsubscript{2} hydrate formation in the reservoir the mass balance and energy balance were discussed. The following assumptions were made for formulating the equations in the process of CO\textsubscript{2} gas injection and hydrate formation in the reservoir.

1. Four components were considered as CO\textsubscript{2}, water, hydrate and silica sand.
2. Three phases were considered as gas, aqueous and solid.
3. The porosity of the sand is constant.
4. The density of the CO\textsubscript{2} hydrate is constant.
5. The boundary temperature is constant.
6. The intrinsic permeability is isotropy.
7. The gas and aqueous viscosity is isotropy.

During the CO\textsubscript{2} injection the mass change of the CO\textsubscript{2} with time is equal to the injection rate of CO\textsubscript{2} to the reservoir – the consumption rate of CO\textsubscript{2} in the reservoir + the CO\textsubscript{2} flow from the surrounding volumes. Thus the governing equation of CO\textsubscript{2} mass balance in block $n$ is in the form

$$\frac{dM_n^{CO_2}}{dt} = (q_n^{CO_2,inj} - q_n^{CO_2,con}) + A_n^{G-L} F_n^{CO_2}$$  \hspace{1cm} (A.1)

where $M_n^{CO_2}$ is the mass change of CO\textsubscript{2} per unit volume of block $n$, $q_n^{CO_2,inj}$ and $q_n^{CO_2,con}$ indicates the injection rate and consumption rate of CO\textsubscript{2} per unit volume of block $n$, $A_n^{G-L}$ is the gas-liquid surface area per unit volume in the block $n$ and $F_n^{CO_2}$ is the mass flux of CO\textsubscript{2} transported through the gas-water surface in block $n$. 
During the CO$_2$ injection the mass change of the water with time is equal to the consumption rate of water + the water flow from the surrounding volumes. Thus the mass balance of water in the reservoir is in the form

$$\frac{dM_n^W}{dt} = -q_{n,\text{con}}^W + A_{n,G}^L F_n^W$$  \hspace{1cm} (A.2)

where $M_n^W$ is the mass change of water and $q_{n,\text{con}}^W$ is the consumption rate of water per unit volume of block $n$, $F_n^W$ is the mass flux of water transported through the gas-liquid surface in block $n$.

During the CO$_2$ injection the mass change of the hydrate with time is equal to the hydrate formation rate. Thus the mass balance of hydrate in the reservoir is in the form

$$\frac{dM_n^H}{dt} = q_{n,\text{for}}^H$$  \hspace{1cm} (A.3)

where $M_n^H$ is the mass change of hydrate and $q_{n,\text{for}}^H$ is the formation rate of hydrate per unit volume in the block $n$.

Englezos et al.\textsuperscript{109} and Uddin et al.\textsuperscript{110} wrote the rate of hydrate growth per particle as

$$\left(\frac{dN}{dt}\right)_n = K_f A_n^H (f_n - f_{eq})$$  \hspace{1cm} (A.4)

where $N$ is the number of moles of hydrate per volume of block $n$, $K_f$ is the hydrate formation rate constant, $A_n^H$ is the hydrate surface area per volume of block $n$, $f_n$ and $f_{eq}$ indicate the fugacity of CO$_2$ at the pressure of block $n$ and the hydrate equilibrium pressure.
According to the equitation for $K_f$ wrote by Clark and Bishnoi\textsuperscript{111} to describe the hydrate decomposition, the equitation for $K_f$ in the hydrate formation process is in the form

$$K_f = K_f^0 \exp \left( \frac{\Delta E}{RT} \right)$$ \hspace{1cm} (A.5)

where $K_f^0$ is the intrinsic formation rate constant, $\Delta E$ is the activation energy, $R$ is the universal gas constant and $T$ is the temperature. Thus the mass balance of hydrate in the reservoir can be described as the form combing equations (A.3), (A.4) and (A.5)

$$\frac{dM_H}{dt} = K_f^0 \exp \left( \frac{\Delta E}{RT} \right) A_n (f_n - f_{eq}) M_H$$ \hspace{1cm} (A.6)

where $M_H$ is the molecular weight of the hydrate.

Hydrate formation is an exothermic reaction. In the energy balance equation, the conduction, convection and heat flow to the surrounding is considered. During the hydrate formation the energy change of the CO\textsubscript{2}, water, hydrate and silica sand is equal to - the source of heat (hydrate formation) - the heat transferred to the surrounding volume. Thus the energy balance is in the form

$$\frac{dU_n}{dt} = -Q_n^H - A_n^H F_n^h$$ \hspace{1cm} (A.7)

where $U_n$ is the total internal energy per unit volume of block n, $Q_n^H$ is the enthalpy of hydrate per unit volume of block n, $F_n^h$ is the heat flux flowed to the surrounding. Assuming there is no heat resistance between gas, water, hydrate and sand, the equation (A.7) can be written in terms of enthalpy as

$$\frac{d}{dt} \left[ \varnothing S_{CO_2} \rho_{CO_2} H_{CO_2} + \varnothing S_W \rho_W H_W + \varnothing S_H \rho_H H_H + (1 - \varnothing) S_S \rho_S H_S \right] = -Q_n^H - A_n^H F_n^h$$ \hspace{1cm} (A.8)
where $\emptyset$ is the porosity of the reservoir, $S_{CO_2}, S_W, S_H$ and $S_S$ indicate the saturation of CO$_2$ gas, water, hydrate and silica sand, $\rho_{CO_2}, \rho_W, \rho_H$ and $\rho_S$ indicate the density of CO$_2$ gas, water, hydrate and silica sand, $H_{CO_2}, H_W, H_H$ and $H_S$ indicate the enthalpy of CO$_2$ gas, water, hydrate and silica sand.
Appendix B: Apparatus of the experiments of hydrate equilibria measurement using high pressure crystallizers

Figure B.1 shows the high pressure crystallizer, which was reported in a previous work and also applied in the experiments of hydrate equilibria measurement in Chapter 5. In details, two stainless steel vessels (crystallizers) for two sets of apparatus with the inner volume of 211 mL were fitted with two circular polycarbonate winders for each on the front and back side to have a visual observation. Baffles were located in the vessels to control vortex formation during the stirring operation. The vessels were submerged in an insulated temperature controlled circulating bath to have desired temperature. The bath was filled with a propylene glycol solution, which contained propylene glycol and water as the volume ratio of 1:1. Two stainless steel supply vessels with the inner volume of 300 mL were also immersed in the bath to provide the gas to the crystallizers. The temperature of the bath was regulated by using an external refrigerating/heating programmable circulator obtained from VWR Scientific. A gas induce impeller coupled with a hollow shaft was located in each crystallizer and was controlled by a universal motor controller obtained from Autoclave Engineers. The pressure of the crystallizers and supply vessels were measured by using Rosemount smart pressure transmitters (model 3051, maximum uncertainty of 0.075 percent of the span of 1-15000 kPa). Three copper-constantan thermocouples obtained from Omega Engineering (uncertainty of 0.1 K) were used to measure the temperatures in gas, liquid and the liquid-gas interface. A high pressure and low flow control valve obtained from Fisher (Baumann 5100, NPS 1/4) coupled to a proportional, integral, derivative controller was installed between the crystallizer and supply vessel to regulate the crystallizer pressure for each set of the apparatus. The data acquisition system obtained from National Instruments was connected to a computer to record the pressure and temperature data.
A LabView software obtained from National Instruments was installed in the computer to communicate with the control valves and log the data into a Microsoft Excel file.

Figure B.1 Apparatus of the experiments of hydrate equilibria measurement using high pressure crystallizers. (Adapted from Sharifi et al., 2014)