Natural Gas Recovery from Hydrates in a Silica Sand Matrix

by

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ABSTRACT

This thesis studies methane hydrate crystal formation and decomposition at 1.0, 4.0 and 7.0°C in a new apparatus. Hydrate was formed in the interstitial space of a variable volume bed of silica sand particles with an average diameter equal to 329µm (150 to 630µm range). The initial pressure inside the reactor was 8.0MPa for all the formation experiments. Three bed sizes were employed in order to observe the effects of the silica sand bed size on the rate of methane consumption (formation) and release (decomposition). The temperature at various locations inside the silica sand bed was measured with thermocouples during formation and decomposition experiments. For the decomposition experiments, two different methods were employed to dissociate the hydrate: thermal stimulation and depressurization.

It was found that more than 74.0% of water conversion to hydrates was achieved in all hydrate formation experiments at 4.0°C and 1.0°C starting with a pressure of 8.0MPa. The dissociation of hydrate was found to occur in two stages when thermal stimulation was employed whereas three stages were found during depressurization. In both cases, the first stage was strongly affected by the changing bed size whereas it was not found to depend on the bed size afterwards.

TABLE OF CONTENTS

ABSTRACT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	V
LIST OF FIGURES	vi
NOMENCLATURE	ix
ACKNOWLEDGEMENTS	X
CHAPTER 1: INTRODUCTION	1
1.1 Introduction to gas hydrates	1
1.2 Gas hydrate structures	3
1.3 Classes of hydrate deposits	4
1.4 Significance of natural gas hydrates	5
1.4.1 Potential energy source	6
1.4.2 Environmental hazards and climate change	6
1.5 Gas hydrate decomposition techniques	8
CHAPTER 2: LITERATURE REVIEW & RESEARCH OBJECTIVE	ES10
2.1 Thermodynamic studies of clathrate or gas hydrates	10
2.2 Kinetics of gas hydrate formation	11
2.3 Kinetics of gas hydrate dissociation	13
2.4 Gas hydrates in porous media	14
2.4.1 Growth habit of gas hydrates in porous media	14
2.4.2 Kinetic studies of gas hydrate formation in porous media	
2.4.3 Kinetic studies of gas hydrate dissociation in porous media	20
2.5 Modelling of hydrate dissociation in porous media	27

2.5.	1 Ana	lytical models proposed	
2.5.	2 Nur	nerical models proposed	
2.6	Resear	rch objectives	34
CHAPT	ER 3:	MATERIALS AND METHODS	35
3.1	Experi	mental apparatus	35
3.2	Materi	als	
3.3	Experi	mental method	
3.3.	1 Exp	erimental procedure (formation)	40
3.3.	2 Exp	erimental procedure (decomposition)	41
3	.3.2.1	Thermal stimulation	42
3	.3.2.2	Depressurization	42
CHAPT	ER 4:	RESULTS AND DISCUSSION	45
4.1	Gas hy	drate formation for thermal stimulation experiments	45
4.2	Gas hy	vdrate decomposition by thermal stimulation	60
4.3	Gas hy	drate formation for depressurization experiments	69
4.4	Gas hy	vdrate decomposition by depressurization	70
4.5	Morph	ology studies on methane hydrate formation	77
4.5.	1 Hyd	lrate phase characterization	79
СНАРТ	ER 5:	CONCLUSIONS AND RECOMMENDATIONS	82
5.1	Conclu	usions	82
5.2	Recon	nmendations	84
REFER	ENCES	5	86
APPENI	DIX A:	THERMAL STIMULATION RESULTS	91
APPENI	DIX B:	DEPRESSURIZATION RESULTS	140

LIST OF TABLES

Table 1.1: Hydrate Unit Crystal Structural Properties
Table 4.1: Hydrate formation experimental conditions along with induction times and water
was 8.0MPa)
Table 4.2: Hydrate decomposition experimental conditions along with the rate of recovery and final percent of methane recovered
Table 4.3: Hydrate formation experimental conditions along with induction times and water conversion to hydrates (The initial experimental pressure for all the experiments was 8.0MPa)
Table 4.4: Hydrate decomposition experimental conditions along with the rate of recovery and final percent of methane recovered

LIST OF FIGURES

Figure 1.1: Map of discovered gas-hydrate deposits, reprinted from (Makogon et al., 2007), with permission from Elsevier
Figure 1.2: Schematic of a runaway greenhouse effect (Englezos, 1993)7
Figure 1.3: Thermal stimulation and Depressurization Methods9
Figure 2.1: Possible distribution of hydrates in porous media, reprinted from (Winters et al., 2004), with permission from MSA
Figure 2.2: Calibrated CT scans from a single central location at nine times over the depressurization/thermal stimulation, reprinted from (Kneafsey et al., 2005), with permission from the corresponding author Timothy J. Kneafsey
Figure 2.3: Average density change (heavy line), moles of gas collected and location-specific density along the vertical cross section over the depressurization and thermal stimulation. The apparent location of the dissociation front is indicated by the thin black line and the arrow. Reprinted from (Kneafsey et al., 2007), with permission from Elsevier
Figure 3.1: Experimental apparatus
Figure 3.2: Location of thermocouples in the crystallizer
Figure 3.3: Arrangement of copper cylinders in the crystallizer along with the location of thermocouples
Figure 3.4: PSA (particle size analysis) result for the silica sand used in our experiments39
Figure 4.1: Conceptual model of a capillary pressure gradient induced by the presence of hydrate in a porous medium. Reprinted from (Kneafsey et al., 2007), with permission from Elsevier
Figure 4.2: Rate of pressure drop due to hydrate growth during hydrate formation (time zero in the graph corresponds to the time of induction point given in Table 4.1). Number in the parenthesis indicates the experiment number in Table 4.1

Figure 4.3: Gas uptake measurement curve at 7.0°C (Experiment 1, Table 4.1)......50

Figure 4.4: Gas uptake measurement curve at 4.0°C (Experiment 3, Table 4.1)51
Figure 4.5: Temperature profiles as a function of time for Experiment 3 at 4.0°C53
Figure 4.6: Gas uptake measurement curves in the presence of one copper cylinder (Experiment 11) and two copper cylinders (Experiment 13)
Figure 4.7: Temperature profiles as a function of time for Experiment 11 with CC ₁ placed in the crystallizer at 4.0°C
Figure 4.8: Comparison of the mole fractions of gas in the liquid for hydrate formation and solubility experiments
Figure 4.9: Time vs. depth curves for different saturation percentages
Figure 4.10: Decomposition experiment carried out at 4.6MPa (Experiment 4, Table 4.2)62
Figure 4.11: Methane release measurement curve from hydrates showing two stages of recovery and the calculated rate of recovery (Experiment 6, Table 4.2)
Figure 4.12: Methane recovery from hydrates from the decomposition experiments carried out with the presence of CC ₁ at 4.6MPa and driving force (Δ T) of 4.0 & 10°C. Number in the parenthesis indicates the experiment number in Table 4.264
Figure 4.13: Methane recovery from hydrates from the decomposition experiments carried out with the presence of CC_1 and CC_2 at 4.6MPa and driving force (ΔT) of 4.0 & 10°C respectively. Number in the parenthesis indicates the experiment number in Table 4.2
Figure 4.14: Comparison of methane recovery from decomposition experiments for the three different silica bed sizes studied at constant pressure of 4.6MPa and a temperature driving force (Δ T) of 4.0°C. Number in the parenthesis indicates the experiment number in Table 4.2

Figure 1.10. The calculated faces along with the standard errors proteed against different oed
sizes for all the decompositions experiments carried out at a driving force of
4.0°C. (CR: experiment 5, CR+CC ₁ : experiment 9 & 10, CR+CC ₁ +CC ₂ :
experiment 13 & 14)68
Figure 4.17: T-profile and volume of gas released during decomposition by depressurization
carried out at 3.2MPa (Experiment 6, Table 4.4)71
Figure 4.18: Pre-decomposition gas release and projected pressure reduction for Experiment 9 in Table 4.4
Figure 4.19: Recovery percentage comparison between 20% and 40% depressurization
methods
Figure 4.20: Comparison of percent methane recovery from decomposition by
depressurization experiments for three different silica bed sizes (CR, CR+CC1,
$CR+CC_1+CC_2$). Number in the parenthesis indicates the experiment number in
Table 4.475
Figure 4.21: Methane release measurement curve from hydrates showing three stages of
Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
 Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
 Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
 Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
 Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
 Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
 Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
 Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)
 Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)

NOMENCLATURE

- n_{T} : Total number of moles
- n_{H} : Moles of the gas in Hydrate + Water phase of CR
- n_G : Moles of gas in gas phase of CR
- n_{R} : Moles of gas in R
- V_{G} : Volume of gas phase in CR
- V_R : Volume of R
- z : Compressibility factor
- $(\Delta n_{H,\downarrow})_{t_{end}}$: Number of moles consumed for hydrate formation at the end of a formation experiment.
- $(\Delta n_{_{\rm H,\uparrow}})_t$: Number of moles released from hydrates during hydrate decomposition at any given time

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CHAPTER 1: INTRODUCTION

1.1 Introduction to gas hydrates

Natural gas hydrates are crystalline substances which are comprised of natural gas molecules such as carbon dioxide, methane, ethane, propane, etc. trapped in cages formed by water molecules. Water molecules act as the host molecules and form the cages that will trap the guest molecules (gas) inside. It is also necessary to mention that there is no chemical interaction between the host water molecules and guest gas molecules. Hydrates occur and stay stable under favourable conditions of pressure and temperature. If the appropriate pressure conditions are provided, they can exist at temperatures significantly above the freezing point of water. Salinity is another property that affects the stability of hydrates.

Hydrates were first discovered by Davy (1811), who found out that a solid could be formed when an aqueous solution of chlorine (then known as oxymuriatic acid) was cooled below 9.0°C (Davidson, 1973). The first major studies arose in early 1930's from the discovery that hydrates formed during oil and gas transport, causing pipeline blockages (Hammerschmidt, 1934). This led to a strong focus on flow assurance, and methods to inhibit hydrate formation and manage the risk while running pipelines and equipment.

Recent studies have focused on exploiting methane stored in hydrates under the permafrost and the sea floor; these deposits are thought to contain as much as twice the carbon as in all of the other fossil fuel reserves combined, thus being a large potential energy source. It has been found that 1 m³ of hydrate can hold up to 184 m³ natural gas (Yousif and Sloan, 1991). Therefore, significant amounts of gas could be produced from these hydrate deposits. Based on various studies, the amount of the hydrates worldwide is estimated to be in a range between 10¹⁵ and 10¹⁷ m³, likely being closer to the lower part of this range (Kvenvolden, 1999). That number substantially exceeds the energy content of the current fuel fossil reserves recoverable by conventional methods. The dispersed nature of the hydrates, however, poses great technical challenges for its development.

Another aspect of hydrates is the environmental impact arising from the decomposition of hydrates. Geological evidence has been found showing that hydrate decomposition beneath the sea floor caused slumping, and with the deep water oil and gas exploration, the safety and stability of offshore platforms requires a good understanding of the behaviour of these hydrates. In addition to this, it is feared that rising sea temperatures due to global warming may lead to the decomposition of these hydrates, thus releasing more methane and causing further warming, leading to a runaway greenhouse effect (Dickens et al., 1997; Hatzikiriakos and Englezos, 1994).

As mentioned before, gas hydrates occur under low temperature and relatively high pressure conditions. In natural environments, these conditions can occur offshore in shallow depths below the ocean floor and onshore beneath the permafrost. There is a certain depth interval for each case where hydrates may be stable. In offshore sites, hydrates are mostly found stable at depths between 100 and 500 m below the ocean floor depending on bottom-water temperatures. In permafrost regions, if the surface temperature is below the freezing point of water, the stability interval of the hydrates changes from 150 to 2000 m depth (Pooladi-Darvish, 2004). Figure 1.1 shows the locations of gas-hydrate deposits on earth that are

known or inferred. The Mallik field in Northwest Territories, Canada, the Prudhoe Bay/Kuparuk River area in Alaska, U.S. and the Nankai trough, offshore Japan are some of the potential hydrate deposits around the world that are being observed. It should also be noted that the amount of energy in ocean hydrates is several orders of magnitude greater than that in permafrost hydrates.



Figure 1.1: Map of discovered gas-hydrate deposits, reprinted from (Makogon et al., 2007), with permission from Elsevier.

1.2 Gas hydrate structures

Naturally occurring hydrates can be categorized in three structure classes; Structure I (sI), structure II (sII), and structure H (sH). The structure of the hydrate is related to the ratio of the guest gas molecule size to the cavity size and also to the thermodynamic conditions such

as temperature, pressure. The structural properties of these classes are found using x-ray diffraction studies (Davidson, 1973; Ripmeester et al., 1987; Tulk et al., 2000).

sI and sII are both cubic crystals whereas sH is a hexagonal crystal,. The common cage that all three structures have is the small cage with 12 pentagonal faces (5^{12}). This cage accommodates small guest gas molecules. Another large cage is present in all structure types with 12 pentagonal faces plus 2, 4 and 6 hexagonal faces for sI, sII, and sH, respectively ($5^{12}6^2$, $5^{12}6^4$, $5^{12}6^6$). These cages accommodate relatively larger molecules. Different from sI and sII, sH has another medium-sized cage composed of 3-square faces, 6-pentagonal faces, and 3- hexagonal faces ($4^35^66^3$). These properties are summarized in Table 1.1.

Hydrate Crystal Structure]	[II		Н		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5 ¹²	$5^{12}6^2$	5 ¹²	$5^{12}6^4$	5 ¹²	$4^35^66^3$	$5^{12}6^8$
Number of cavities/unit cell	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91	4.06	5.71
Coordination number	20	24	20	28	20	20	36
No. of H ₂ O molecules/unit cell	46		136		34		

 Table 1.1: Hydrate Unit Crystal Structural Properties

1.3 Classes of hydrate deposits

Natural gas hydrate deposits are classified in three categories which are Class 1, 2, and 3. Class 1 accumulations are formed of two layers which are the hydrate interval and an underlying two-phase fluid zone with free gas. Class 1 can be observed in two different subcategories such as Class 1W, which involves water and hydrate in the hydrate zone, and Class 1G, which involves gas and hydrate in the hydrate zone. Class 2 consists of two zones,

a hydrate interval and an overlying mobile water zone. Class 3 is composed of only a single zone, a hydrate interval. There is no underlying zone of mobile fluids in Class 3. Most of the ongoing researches are being conducted on Class 1 deposits because this class appears to be the most promising target for gas production since the thermodynamic proximity to the hydrate equilibrium at the highest possible temperature requires only small changes in pressure and temperature to induce dissociation (Moridis et al., 2007).

Naturally-occurring methane hydrate stays stable within a specified pressure and temperature range, which is called the hydrate-stability zone. In order to extract gas from hydrates, three objectives must be achieved. Firstly, the pressure and temperature conditions around hydrate particles should be brought outside the hydrate-stability zone. Secondly, the decomposition of hydrates is an endothermic reaction and requires energy. Therefore, the necessary energy must be provided. And thirdly, the products of decomposition must be transferred to the production wells and a way to do that should be made available. All of these objectives must be accomplished economically and safely (Pooladi-Darvish, 2004). There are three different methods known to produce gas from hydrate deposits. These are depressurization, thermal stimulation and inhibitor injection. These methods are explained in Section 1.5.

1.4 Significance of natural gas hydrates

Based on the studies conducted in last couple decades, natural gas hydrates are now considered as a potential energy source, a factor in global climate change, and a potential submarine geohazard (Kvenvolden, 1999).

1.4.1 Potential energy source

There are different speculations about the estimated amount of methane hydrates occurring in nature. According to separate studies Kvenvolden (1999) and MacDonald (1990) conducted, they agreed on 2.1×10^{16} m³ as the methane hydrate content in oceanic sediments. The hydrate content in the permafrost region is considered to be significantly less compared to this number. According to the Potential Gas Committee (1981), this quantity ranges between 1.4×10^{13} m³ and 3.4×10^{16} m³ in permafrost regions. Despite the fact that there is a margin of error associated with these estimates, even the most conservative estimates suggest that the amount of energy in hydrates is equivalent to twice that of all other fossil fuels combined. Besides, according to MacDonald (1990), the energy density (volume of methane at standard conditions per volume of sediment) of methane hydrate is 2- to 5-fold greater than the energy density of conventional natural gas. A recent estimate of the amount of methane trapped in hydrates is as much as 300 times that in conventional U.S. reserves (Sloan, 1998).

1.4.2 Environmental hazards and climate change

Methane is an important contributor to global warming. Even though it accounts for only 15% of the current global warming effect, it has a 21 times larger global warming potential compared to CO₂ (Taylor, 1991). Therefore, the extensive release of methane gas from naturally-occurred methane hydrates due to their decomposition can enhance global warming and may lead to a 'run-away green house effect' (Hatzikiriakos and Englezos, 1993). It is feared that rising sea temperatures, especially bottom water temperatures, due to current global warming may lead to the dissociation of the hydrates underneath the ocean floor, thus releasing more methane and causing further warming, therefore leading to a runaway greenhouse effect. This loop is displayed visually in Figure 1.2.



Figure 1.2: Schematic of a runaway greenhouse effect (Englezos, 1993)

It should be mentioned, however, that there are obstacles to methane reaching the atmosphere. Thus, Kvenvolden (1999) claims that most of the methane gas released will be oxidized to CO_2 , which can dissolve in the water, therefore will not reach to the atmosphere where it acts as a strong greenhouse gas. On the other hand it should be mentioned that CO_2 will then intensify the acidification of the ocean.

In addition to the run-away greenhouse effect, decomposing hydrate sediments may cause disruptions on the seafloor and lead to slumping. These submarine disruptions of the seafloor impact human welfare if human-made structures are located in regions of potential failure. As humankind expands its interest in the seafloor at increasing water depth, such as in the petroleum industry's search for oil and gas, stability of the seafloor becomes increasingly important for any engineering structures. The potential vulnerability of engineering structures

to gas-hydrate dissociation in oceanic sediments has been recently recognized and described (Kvenvolden, 1999).

1.5 Gas hydrate decomposition techniques

In order to efficiently produce natural gas from hydrate reservoirs, an understanding of how hydrate and porous media behave upon dissociation is necessary. So far, several studies have been made to simulate the hydrates in porous media and their dissociation by one of the three concepts proposed to decompose hydrates. Highlights of these studies are summarized in the literature review section. The first concept proposed is increasing the temperature until the decomposition zone is reached and this method is called thermal stimulation. Another way to decompose hydrates is decreasing the pressure until the decomposition zone is reached, a technique which is called depressurization. The final concept proposed is altering the equilibrium condition by injecting inhibitors (methanol, glycol, salt). This option though, inhibitors are very costly and huge amounts are necessary, thus this method is not very practical. The studies here are mostly focused on the first two options. In my experiments, thermal stimulation and depressurization methods are used to decompose hydrates. The two concepts followed are displayed in Figure 1.3.



Figure 1.3: Thermal stimulation and Depressurization Methods

CHAPTER 2: LITERATURE REVIEW & RESEARCH OBJECTIVES

2.1 Thermodynamic studies of clathrate or gas hydrates

Because of the importance of hydrate formation in oil and gas pipelines and its consequences, experimental studies on clathrate hydrates were conducted to find the incipient equilibrium hydrate formation properties. Incipient equilibrium refers to the condition under which an infinitesimal amount of the hydrate phase is present in equilibrium with fluid phases. The next stage was formulating predictive methods for calculating the phase equilibrium and thus being able to calculate the hydrate formation conditions.

The first thermodynamic model was developed by Van der Waals and Platteeuw (1959). According to that model, it was assumed that a cavity can only hold one guest molecule and the motion of a guest molecule in its cage is independent of the number and types of guest molecules present. It was also assumed that the interactions between host and guest molecules are weak van der Waals forces and extend only to the first shell of water molecules around each guest molecule. Finally, it was assumed that the hydrate lattice is not distorted by the guest molecule. Despite its limitations and simple assumptions, this first model has provided the basis of all subsequent models developed to predict the phase equilibrium properties of gas hydrates (Koh, 2002). Parrish and Prausnitz (1972) extended the Van der Waals and Platteeuw model in order to make it applicable to multi-component mixtures. Later, Holder and Grigoriou (1980) simplified that extension. Recently, Klauda and Sandler (2000) developed a classical thermodynamic approach to predict hydrate phase

behaviour which removes the need for reference energy parameters, as used in the Van der Waals and Platteeuw type models, and thereby increases the accuracy of the predictions of equilibrium pressures for gas hydrate formation. Published equilibrium properties of hydrates of several different hydrocarbons were compiled and made available for the public by Sloan (1998).

2.2 Kinetics of gas hydrate formation

Hydrate formation is viewed as a crystallization process that includes the nucleation and growth processes. Hydrate nucleation is an intrinsically stochastic process that involves the formation and growth of gas-water clusters to critical sized, stable hydrate nuclei. Hydrate growth processes involves the growth of stable hydrate nuclei as solid hydrates (Bishnoi and Natarajan, 1996).

So far, numerous kinetic data sets during hydrate formation have been collected by different hydrate researchers such as Bishnoi (Bishnoi and Natarajan, 1996; Bishnoi et al., 1993; Bishnoi and Vsyniauskas, 1980), Englezos (Englezos et al., 1987a; Englezos et al., 1987b), Sloan (Sloan, 1998). Although tremendous progress has been achieved, there is still need for continued kinetic studies in order to improve the kinetic models developed for hydrate formation and dissociation.

One of the main difficulties in obtaining kinetic data is the stochastic nature of hydrate nucleation (Kumar, 2005). The stochastic nature of crystallization processes at low driving force conditions is a well-known phenomenon of heterogeneous nucleation, where induction

times generally have large variations, and can range from a few seconds to hours (Koh, 2002).

Natarajan et.al (1994) presented some induction data measurements for formation of methane, ethane and carbon dioxide hydrates. They used the crystallization theory to formulate a model for the hydrate induction time required for formation of stable hydrate nuclei. Parent and Bishnoi (1996) conducted a series of investigations to identify nucleation process variables to verify the existence of an aqueous phase thermal history. Bishnoi and Natarajan (1996) presented various perspectives on the kinetic processes at a conceptual level and identified key issues for research in the area of gas hydrate kinetics.

Vysniauskus and Bishnoi (1983) made the first measurements of the rate of methane hydrate formation. This study was also the first attempt to model the formation kinetics of gas hydrates and laid the ground work for several studies that followed it. According to this work, the hydrate growth is dependant on the interfacial area, temperature, the degree of supercooling, and pressure. Besides, the nucleation induction is affected by the history of the water used; however, no visible effect on the growth of nuclei was observed.

Englezos et al. (1987a; 1987b) introduced the first model that accounts for the fact that hydrate formation is a crystallization process. The difference between the fugacity of the dissolved gas and the three-phase equilibrium fugacity is used as the driving force for particle growth. The formation kinetics of hydrate formed from methane, ethane, and their mixtures are investigated and described by coupling the crystallization theory and mass transfer phenomena at the gas-liquid interface. Lekvam and Ruoff (1993) presented a reaction kinetics model for methane hydrate formation with five pseudo-elementary reaction steps based on experimental results. These pseudoelementary steps consist of three dynamic elements; the dissolution of methane gas into the water phase, the build-up of an oligomeric precursor of methane hydrate and the growth of methane hydrate by an autocatalytic process. The length of the induction period and reaction rates for each of the 5 reactions steps were estimated via this model.

Malegaonkar et al. (1997) determined the intrinsic kinetic rate constants of carbon dioxide and methane hydrate formation. The model is based on the crystallization theory coupled with the two-film theory for gas absorption in the liquid phase.

2.3 Kinetics of gas hydrate dissociation

Kim et al. (1987) performed the first quantitative study of methane hydrate decomposition kinetics using a semi-batch stirred reactor. They kept track of the amount of methane collected during decomposition, while maintaining a constant temperature and pressure. An estimate of the hydrate particle diameters in the experiments and the assumption of having hydrate particles with same diameter before decomposition allowed them to obtain the intrinsic rate constant in their model. A conclusion drawn out of the data indicated that the decomposition rate was proportional to the particle surface area and to the difference in the fugacity of methane at the equilibrium pressure and the decomposition pressure.

Clarke and Bishnoi (2001) overcame the shortcoming of the model developed by Kim et al. (1987) via modifying the apparatus used in their study by including an inline particle size

analyzer. They recalculated the activation energy and intrinsic rate constant for methane, ethane and their mixtures. The activation energy from their study was similar to that calculated from Kim et al. (1987). While, the intrinsic rate constant was approximately 10 times smaller.

2.4 Gas hydrates in porous media

Natural gas hydrates are found underneath the permafrost region onshore or buried in the oceanic sediments offshore. These hydrates are often found dispersed in pores of coarse grained sediments or fractures in the earth's crust, or as 'massive hydrates' containing less than 6% sediment (Sloan, 1998). Therefore, the understanding of the kinetics and thermodynamics of hydrates in porous media is extremely crucial. Typical natural materials known as hydrate bearing sediments include silica sand, sandstone and clays (Kumar, 2005). In lab-scale studies, commercially available uniformly sized glass beads or silica sand are used to simulate the naturally occurring hydrate environment.

2.4.1 Growth habit of gas hydrates in porous media

Once the studies of hydrate formation in porous media were started, it brought up several questions about hydrate formation and its growth habit in porous media (Clennell et al., 1999; Kleinberg et al., 2003). It was highly debated whether the grain surfaces or pore space were the host area for hydrate formation. The degree of effect of the pore size and surface properties of the host sediment grain on the hydrate formation and distribution was another questioned topic. In response to these issues, a capillary-thermodynamic model is proposed by Henry et al. (1999) and Clennell et al. (1999). One of the conclusions they drew is that in

fine-grained sediments such as clays and silts, the hydrate phase may be destabilized thermodynamically, and perhaps inhibited from nucleating.

Experiments conducted by Yousif and Sloan (1991) revealed that it should be expected that the capillary forces, as well as the adsorption of water molecules on the solid surface, would impose an additional energy requirement for the hydrates to start forming. This is also confirmed by Clennell et al. (1999) where they predicted that hydrate formation in fine grained and more clay rich sediments will be inhibited by water adsorption particularly when gas saturation is high. The formation of hydrate is also inhibited by the capillary effects, and an extra thermodynamic drive is required to promote the reaction.

Other experiments show that porous medium with a maximum pore size of 100nm and a minimum pore size of 3nm decreases the stability range of hydrates (Handa and Stupin, 1992; Henry et al., 1999). In determining the upper limit for which no pore effects occur, the maximum pore size, d_{max} , is estimated such that the value of ΔT is less than the accuracy of the temperature measurements (i.e. the ΔT is so small that it is not measurable by current measurement apparatus). The lower limit of the effective pore diameter, d_{min} , for a given hydrate structure must exceed the unit cell size of the bulk hydrate structure. A greater pressure or a lower temperature is necessary to form the hydrate, and lower dissociation temperature is observed on warming, than in the case of hydrate in bulk aqueous conditions (Sloan, 1990). It is also concluded by Handa and Stupin (1992) that the hydrate in a porous network behaves in much the same way as ice. Also, that the enthalpy of formation of gas hydrate is decreased in porous media and the induction time for hydrate formation in porous

media is reduced with respect to formation in free solution, and agitation is not required to induce nucleation of hydrate. This is attributed to the large gas-water surface area in porous media.

Another factor that has an effect on hydrate formation in porous media is the fluid saturation. The space available for gas is limited by the increase in the water saturation and that leads to a reduction of the contact between two phases. On the other hand, such an increase in the water saturation decreases the capillary forces which are believed to obstruct the initiation of hydrate formation. Overall, the experimental results showed that the increase in water saturation causes an increase in the gas-to-hydrate conversion (Yousif and Sloan, 1991).

Another study about the effects of sediment properties was conducted by Evgeny et al. (2002). According to the findings, pore water is partially transformed to hydrate in methane saturated sediments. The maximum water-to-hydrate conversion achieved in sandy sediments is 80%. The minimum conversion is reported as 15% in montmorillonite clay. Another conclusion drawn is the decrease in water-to-hydrate conversion with the increase of salinity.

As mentioned before in this section, the formation habit of hydrates in porous media is poorly understood. Winters et al. (2004) developed a model for formation of hydrate in porous media and concluded that hydrate can occur as pore filling, frame building or may act as a cementing agent between grains. However, it is not known whether hydrate tends to form at grain contacts and cement the frame even when its quantities are small or it uniformly coats the grains, so that the cementing effect increases progressively with the hydrate volume. Another option is the formation of hydrates in the centre of pores acting as a partial support to the frame. The schematic possible distribution of hydrates in porous media is shown in Figure 2.1 (Winters et al., 2004).



Figure 2.1: Possible distribution of hydrates in porous media, reprinted from (Winters et al., 2004), with permission from MSA.

According to the experimental studies with synthetic porous media (glass micro-models) conducted by Tohidi et al. (2001), all THF, CH_4 , and CO_2 hydrates formed within the center of the pore spaces, rather than at the grain surfaces. Cementation of grains occurred in

regions of small grain size or where a large proportion of pore space was filled with hydrate. However, even at high clathrate saturation, a thin film of free water persisted on grain surfaces. The existence of film water on grains and the preference for growth in the center of pores demonstrated that clathrates would have restricted cementing effect on grains, unless the majority of pore space was filled with hydrate. If these results are extrapolated to natural systems, it could have major inferences for the cementation of sediments by hydrates, particularly with respect to seismic properties and slope stability.

The experiments that I am going to present in this thesis are conducted with silica sand that has a pore size of 0.9nm which is not large enough to host hydrate formation within. Therefore, it is assumed that hydrate is formed within the interstitial space between particles.

2.4.2 Kinetic studies of gas hydrate formation in porous media

Yousif et al.(1990) conducted experiments in order to measure the dissociation rate of hydrates, taking advantage of electrical resistivity measurements to monitor the position of the hydrate front. Of course, to observe dissociation, first, hydrates were formed in a cylindrical Berea Sandstone core enclosed within a heat shrunk plastic tube which was contained within a stainless steel pressure sample bomb. Throughout the process the temperature was kept constant at 273.7 K with the help of a temperature-controlled bath. The procedure started with the evacuation of the sandstone core and followed by the injection of a 1.5 wt% sodium chloride solution until the full saturation of the core was achieved. Next, methane gas was injected into the core at a pressure higher than the equilibrium pressure, thus leading to hydrate formation, resulting in water and pressure reduction in the system. Hydrate formation proceeded until there was no further pressure reduction in the system and

it stopped at a pressure greater than the equilibrium three-phase pressure of 2.84MPa. After that, the pressure was decreased below this pressure to start dissociation. Although it is mentioned that during hydrate formation both the gas and water volumes injected and produced were closely monitored, water-to-hydrate conversion or the amount of hydrates formed were not reported.

The same experiment was repeated with two different sandstone cores with permeability values of 8.388×10^{-14} and 40×10^{-14} m², respectively. The hydrate formation process was completed in 20-30 hours in the less permeable core whereas it took only 4-5 hours to complete the same process in the high-permeability core. There was a greater pressure drop observed at the gas inlet compared to the outlet point. This occurrence is due to greater hydrate formation being formed at the inlet, thus leading to the blockage of the gas passageway and preventing the outlet pressure from equilibrating with the inlet. Although the core was re-pressurized, inlet pressure drop was still greater than that of the outlet.

The work mentioned above was improved using the same apparatus but applying some changes in the procedure (Yousif et al., 1991; Yousif and Sloan, 1991). This time, electrical resistance was measured at four equally-distanced locations along the core length and that provided another method after pressure drop measurements to check both the amount and the uniformity of hydrate formation. A big change in the formation procedure was the annealing process introduced which helped to decrease the pressure drop encountered across the core after the hydrate formation. In the annealing process, the hydrate is dissociated and reformed by subsequent heating and cooling of the core. After four annealing processes, the pressure drop was eliminated and more uniform hydrate formation was achieved in the core. These

results indicated that more hydrate could be formed in consolidated porous medium through an annealing process simulating the thermodynamic and geological conditions accompanying hydrate formation in nature (Yousif and Sloan, 1991).

2.4.3 Kinetic studies of gas hydrate dissociation in porous media

Two reports from the Los Alamos National laboratory presented the first state of the art and pointed out the difficulties associated with natural gas recovery techniques (Barraclough, 1980; McGuire, 1981; McGuire, 1982). Holder et al. (1982) concluded that reservoir porosity and the thermal properties of the hydrates and the reservoir are determining factors that would enable a gas hydrate reservoir to produce gas in an energy efficient manner. It was also realized during these early studies that knowledge of the rate of hydrate decomposition is required. A reliable assessment of the feasibility of producing natural gas from hydrates requires several pieces of key information (Kneafsey et al., 2007). While some are reservoirspecific others such as dissociation kinetics have general applicability and can be evaluated in the laboratory (Kneafsey et al., 2007). Although significant progress has been made regarding modeling and numerical simulation of natural gas hydrate reservoirs, (Gerami and Pooladi-Darvish, 2007; Kneafsey et al., 2007; Kowalsky and Moridis, 2007; Moridis et al., 2002; Moridis, 2003; Moridis, 2004; Moridis et al., 2004) very few papers are available in the literature on experimental data on hydrate kinetics investigated in porous media (Handa and Stupin, 1992; Katsuki et al., 2007; Kneafsey et al., 2007; Sakamoto et al., 2007; Stern et al., 1996; Tang et al., 2005).

Selim and Sloan (1990) used thermal stimulation to decompose hydrates formed in porous media in the laboratory. The dissociation rate was found to depend on the thermal properties

and the porosity of the reservoir. Another work was conducted by Yousif and Sloan (1991) where they formed and dissociated methane hydrate in Berea sandstone core samples. Then they determined the dissociation rate of such hydrates at constant pressure and temperature by using depressurization as the dissociation method. Another value determined was electric resistance which was measured with the help of four pairs of electrodes embedded at equal distances along the core length. That way the uniformity of the hydrate was measured. Also, the dissociation front was tracked. Three different sand core samples with different porosities and permeability values have been used. After the formation of hydrate, the dissociation began and the gas production rate was calculated by measuring the amount of water that has been transferred into a graduated cylinder over 1-minute intervals.

The dissociation process is dependant on a number of factors such as the amount of hydrate formed, the uniformity of hydrates along the core, and the difference between the dissociation pressure and the equilibrium pressure, which is the main driving force that controls the kinetics of hydrate dissociation. The amount of hydrate formed can be obtained from the gas and water saturation results from the decomposition of the hydrate.

From the results, it was concluded that some of the runs lead to a linear gas production rate whereas the rest resulted in a decreasing nonlinear rate. The reason for that is given as the pressure conditions that the experiment was conducted at. The experiments that were run at a dissociation pressure lower than the equilibrium pressure results in a linear gas production rate. However, if the dissociation pressure was close to the equilibrium pressure, gas production rate was found to be nonlinear. Another conclusion of this experiment was that the experiments with more hydrate formation exhibits nonlinear dissociation rates.

21

Since the hydrate dissociation process is an endothermic process, heat is necessary to decompose the hydrate. This heat can come from various sources such as fluid, rock or the hydrate itself. However, at high dissociation rates, sudden release of heat could cause a local temperature drop large enough to stop the dissociation process and allow hydrates to re-form or ice to freeze. This phenomenon occurs especially when the dissociation is conducted near the three-phase (water-vapour-hydrate) equilibrium conditions (Yousif and Sloan, 1991). This incident occurred in the reported experiments once. Gas recovery stopped after a certain time and hydrate started to dissociate again after a slight increase in temperature that was done by the experimentalist. Next, the gas production rate decreased again. Therefore, during this gas recovery process, the temperature was raised whenever needed. The studies that were done on the Messoyakha field showed the same trend and as reported by Makogon (1974). The study also showed that a considerable amount of water will be produced as hydrate dissociation occurs.

Handa and Stupin (1992) reported thermodynamic properties and dissociation characteristics of methane and propane in silica gel pores. Stern et al. (1996) observed the peculiarities of methane clathrate hydrate formation and solid state deformation. However the conditions under which the observations (Handa and Stupin, 1992; Stern et al., 1996) were made are < 105 K and 10^{-3} Pa, whereas the natural environment for the samples is moderate pressures (approximately 3 to 10MPa) and above-freezing temperatures (Kneafsey et al., 2007).

Another study focusing on that topic was conducted by Kneafsey et al. (2005). The experiment included forming and dissociating hydrates, in the meantime performing

temperature and pressure measurements along with x-ray computed tomography (CT). The purpose of using CT technology was to determine the detailed locations where processes were occurring. As a result, the measurements could be ascribed to local changes rather than those of the bulk sample. Natural gas production from hydrates is mainly affected by heat transfer, dissociation kinetics, and mass transfer. This paper focuses on the first two aspects.

Methane hydrate was firstly formed and then dissociated in partially water-saturated sand contained in an x-ray transparent aluminum pressure vessel. The vessel was packed with moistened silica sand and it was placed in a heat exchanger where the temperature was controlled by flowing water/propylene glycol solution through the exchanger. The temperature in the vessel was measured at four different points by four different thermocouples.

Firstly, methane hydrate was formed by increasing the pressure while keeping the temperature constant at 1.1°C. According to the temperature and pressure measurements, water-to-hydrate conversion achieved was 63% assuming full cage occupancy. Then an increase of the temperature was applied to observe the response of the system with and without hydrate. The results showed that the temperature in the sample increased faster when there is hydrate present in the system. This outcome implies that a hydrate/water system provides an environment with a higher thermal conductivity than a single water-phase system. Next, another two temperature increases were carried out to induce dissociation of hydrate and consequently the pressure in the system increased. The change in the pressure was used to quantify the amount of gas obtained from hydrate dissociation. While dissociation occurs, CT scans were taken at a single central location over time. These scans

indicate the changes in the density and the locations where these changes occur during the dissociation process.

After that, hydrate was reformed by connecting the vessel to a pressurized methane reservoir and reducing the temperature to the stability zone. Subsequently, the system pressure was set to a point right above the stability zone and the system was allowed to equilibrate. Next, the depressurization test began and the gas produced from the hydrates were collected and quantified. Since the gas recovery process is an endothermic reaction, the temperature of the entire sample had dropped, but the bath temperature was held constant. Therefore, it can be stated that the resulting dissociation was thermally induced (thermal stimulation). Again, the density changes were examined by CT and it was observed that the dissociation front moved radially inwards from the vessel wall as displayed in Figure 2.2.



Figure 2.2: Calibrated CT scans from a single central location at nine times over the depressurization/thermal stimulation, reprinted from (Kneafsey et al., 2005), with permission from the corresponding author Timothy J. Kneafsey. CT scans were taken every 20 minutes and represent a time frame of \sim 3 hours. From the readings and the scans, it is found out that the average density decreased as the hydrate dissociated. An average density change and number of moles of gas collected during depressurization and thermal stimulation of this experiment are modified and published in the next paper of Kneafsey et al. (2007) (Figure 2.3).



Figure 2.3: Average density change (heavy line), moles of gas collected and locationspecific density along the vertical cross section over the depressurization and thermal stimulation. The apparent location of the dissociation front is indicated by the thin black line and the arrow. Reprinted from (Kneafsey et al., 2007), with permission from Elsevier.

As it can be seen from the figures above, the local density changes a lot during the dissociation process. The terms that affect the local density can be listed as saturation changes, mechanical deformation, and gas pressure. Out of these three, the saturation changes have the greatest effect. Basically, it was found out that the thermally induced

dissociation proceeds from the outside towards the sample center. As the dissociation occurred and water was produced along with the natural gas, the water moved towards the area, where hydrate was present, due to a lower capillary pressure in that region. Thus, the outer zone has become drier. When, the second hydrate formation process began, it advanced towards the center, where water saturation was lower. The final dissociation which was caused by depressurization and thermal stimulation gave the same distribution of water as in the first dissociation process.

Kneafsey et al. (2007) further studied hydrate formation in the methane-water system in the presence of silica sand with particle sizes primarily between 100 to 200 μ m. Again, they employed an X-ray-transparent pressure vessel in which they monitored pressure, temperature and the local density changes through X-ray computed topography. They observed that the rate of hydrate formation is not always proportional to the driving force (i.e. pressure, temperature) in the porous medium. They also conclude that there is a need for multiple means of measurement which is critical for understanding hydrate behaviour during hydrate formation.

In another paper, Sun and Mohanty (2006) investigated the study that Yousif et al. (1991) had conducted. Other than the conclusions that have been drawn by Yousif et al. (1991), they found out that the gas saturation has both positive and negative effects on the dissociation rate. The positive effect is accredited to the effect of gas saturation on the relative permeability of the gas phase, which was defined as 1.0 for the base case. As the gas saturation goes up, an increase of gas mobility is observed, which in turn leads to the increase of the overall mobility of fluid flow. That is because the gas phase has much lower viscosity
than the aqueous-phase and the overall mobility of fluid flow in the gas–aqueous phase system is dominated by the gas phase. The increase of overall mobility improves the dissociation rate by increasing the fluid velocity to the outlet and lowering the pressure within the hydrate region faster. An increase in the initial gas saturation can also have negative effects on hydrate dissociation such as leading to a decrease in the overall heat capacity of the system, which will lead to temperature drops in the system and this is a barrier for the overall hydrate dissociation rate since the hydrate dissociation process is an endothermic reaction and it needs an increase in temperature rather than a decrease. The overall tendency of hydrate dissociation rate to increase indicates that the positive effect of the gas saturation dominates the negative one.

Katsuki et al.(2007) reported that the morphology of methane hydrate crystals formed in the porous medium filled with the methane–saturated liquid water depends on the magnitude of the mass transfer of the methane molecules in the liquid water. Tang et al. (2005) studied the production behaviour of gas hydrate under thermal stimulation in unconsolidated sediment. They reported that the gas production rate increased with time until it reached a maximum and then it began to decrease. The hydrate content for all the experiments that were reported was less than 18.0 volume %.

2.5 Modelling of hydrate dissociation in porous media

There have been a number of studies on simulating the gas hydrate dissociation process. Thermodynamic techniques as well as kinetic approaches have been developed in these studies and several types of predictive models for gas hydrate dissociation have been published in the literature. These models are discussed in two subtopics, analytical and numerical models proposed.

2.5.1 Analytical models proposed

An analytical model of hydrate dissociation employing thermal stimulation as the recovery method is developed by Selim and Sloan (1990; Yousif et al., 1990) which incorporated fluid flow through porous media. The gas flow in the dissociated zone and convective and conductive heat transfer in the dissociated and undissociated zones are also accounted for. It was assumed that the water resulting from dissociation remained stationary and the dissociating interface remained at thermodynamic equilibrium. However, intrinsic kinetics of hydrate dissociation was not incorporated in this study. Makogon (1997) included the Joule-Thompson effect in the energy-balance equation in addition to the heat transfer and fluid flow mechanisms.

The decomposition process by depressurization can be defined as a combination of multiphase fluid flow, conductive and convective heat flow, and kinetic decomposition of hydrates (Kumar, 2005). Any of the three mechanisms can be the controlling mechanism in the overall production of gas from the gas hydrates depending upon the conditions. However, there is a large uncertainty involved in the accuracy of physical properties and parameters like permeability variation in the presence of hydrates, thermal conductivity of the porous media etc. These are crucial parameters that have to be known in order to develop a mathematical/numerical model for predicting gas production from hydrates in porous media.

Tsypkin (2000) proposed a new mathematical model to describe the dissociation of gas hydrate in strata. This model allows formation of an extended dissociation zone or formation of an ice–gas region located between hydrate dissociation and ice melting fronts. The results obtained were that for media with high permeability, the amount of gas hydrate dissociated in the extended zone exceeds the amount of hydrate decomposed in the total dissociation zone by several orders. The formation of ice during gas hydrate dissociation leads to a reduction in gas permeability that significantly affects the gas production volume. The presence of ice also changes the properties of the stratum, as in a multiphase system.

Hong et al. (2003) investigated three different mechanisms that can control the rate of decomposition; heat transfer to the decomposing zone, intrinsic hydrate decomposition, and gas-water two-phase flow. Based on that study, it was concluded that fluid flow has the smallest effect on the overall decomposition via depressurization. Thus, an analytical model was developed accounting for heat transfer and the intrinsic kinetics of hydrate decomposition. This was the first model that was incorporating the intrinsic kinetic equation into an analytical solution. The model was able to predict the temperature distribution in the hydrate zone, the decomposition interface location at any time, and the rate of the decomposition. There were a few assumptions incorporated into the model such as ignoring the resistance caused by fluid flow, neglecting the effect of heat transfer in the decomposed zone. It is also noted that the effect of the fluid flow can be important in reservoirs where fluids have to travel a very long distance from the decomposing surface to the wellbore. Therefore, all three mechanisms must be thoroughly examined before any assumptions are made.

Ahmadi et al. (2004) modified Makogon's radial model by including heat conduction in the hydrate zone and presented a one-dimensional model for natural gas production form hydrate dissociation by depressurization. Numerical solutions for time evolution of pressure and temperature profiles in the hydrate reservoir, as well as the location of the dissociation front were obtained for several well pressures and reservoir temperatures. The simulation results were compared with those obtained earlier by a linearization approach and were found to be more accurate. The linearization methods used earlier neglects the balance of energy at the dissociation front, which is included in this presented numerical model. It was shown that the natural gas production rate is a sensitive function of well pressure, reservoir pressure, reservoir temperature and permeability.

2.5.2 Numerical models proposed

In some complex cases, analytical modeling can be inadequate to simulate the hydrate dissociation mechanism properly. However, numerical solutions, in general, can handle those complexities and are more capable of solving more complicated equations than analytical models. So far, several numerical models have been proposed for analyzing gas production from gas hydrate deposits (Masuda et al., 1997; Masuda et al., 1999; Moridis et al., 1998; Yousif et al., 1991)

Holder and Angert (1982) modelled a gas reservoir overlaid by an impermeable methane hydrate layer. In this model, gas was being produced through a well leading to the reduced reservoir pressure (depressurization). The energy needed for decomposition is provided by the sensible heat of the reservoir itself. Also in this model, the influence of the water produced due to decomposition on the flow of gas is ignored and not taken into consideration. Later on, Burshears et al. (1986) extended this model by including the effect of the water movement. However, neither of these models accounted for convective heat transfer of the gas and water.

Jamaluddin et al. (1989) combined the equations of heat transfer and intrinsic kinetics to simulate the decomposition of a methane hydrate core. It was the first numerical model which incorporated the kinetics of hydrate decomposition in modeling dissociation of hydrates in sediments.

Yousif et al. (1991) proposed a 1D, three-phase numerical finite difference simulator to model the process of gas production from hydrate in Berea sandstone samples. Depressurization was used as the recovery method and the driving mechanism. This model coupled kinetics equation with fluid flow equations. It was assumed that the hydrate dissociation process took place under isothermal conditions. Results obtained both experimentally and numerically demonstrated a significant amount of water production along with the gas production as a result of hydrate dissociation. The model provided a fitting match to the experimental data.

Masuda et al. (1997) developed a 1-D numerical model accounting for the kinetics of hydrate decomposition and two phase fluid flow for simulating gas production behavior from cores containing hydrates. However, temperature changes during the dissociation process were ignored. One of the conclusions drawn was that the permeability is reduced significantly in the presence of hydrates and suggested a correlation for permeability variation in presence of hydrates. This model was modified by Masuda et al. (1999) by including the Kim-Bishnoi

equation (1987) for kinetics of hydrate decomposition along with the flow and energy equations.

Moridis et al. (1998) developed a module named EOSHYDR for the TOUGH2 generalpurpose simulator for 3D, multi-component, multiphase fluid and heat flow and transport in the subsurface. It includes both an equilibrium model and kinetic model of hydrate formation and dissociation. EOSHYDR is particularly designed to model the non-isothermal CH₄ release, phase behaviour and flow under the conditions of the common methane hydrate deposits (i.e., in the permafrost and in deep ocean sediments) via solving the coupled equations of heat and mass balance. Other than water (liquid phase) and methane (gaseous phase), two more solid phases are introduced; methane hydrate and ice. This model incorporated phase changes and corresponding heat transfers during formation and dissociation. It also takes into account the effect of salt in pore waters on CH₄ solubility and on the growth and decomposition of gas hydrates. Later on, Moridis et al. (2002) conducted a numerical study on the gas production from several CH₄ hydrate zones at the Mallik site.

Moridis and Collett (2003) also classified the type of hydrate reservoirs (Class 1, 2, 3) and conducted simulation studies using EOSHYDR2 to analyze production strategies from these types of deposits. Several studies were carried out by using the same module in the past years (Moridis et al., 2002; Moridis, 2003; Moridis, 2004; Moridis et al., 2004).

Recently, Moridis et al. (2005) determined the parameters of the kinetic reaction of hydrate dissociation in porous media, based on the laboratory data gathered by Kneafsey et al. (2005). They employed TOUGH-Fx/HYDRATE, improved version of EOSHYDR2, which

can model the nonisothermal hydration reaction, phase behaviour, and flow of fluids and heat in complex geological media at any scale (from laboratory to reservoir). It includes both equilibrium and kinetic models of hydrate formation and dissociation and accounts for heat and up to three mass components (i.e., water, CH4, and water-soluble inhibitors such as salts or alcohols) partitioned among four possible phases: gas, aqueous, ice and hydrate. The model can describe any combination of the possible hydrate dissociation mechanisms, (i.e., depressurization, thermal stimulation, and inhibitor injection).

Hong and Pooladi-Darvish (2005) presented a 2D cylindrical simulator for gas production from hydrate reservoirs. The model accounts for gas-water two-phase flow, conductive and convective heat transfer, and the intrinsic kinetics of hydrate decomposition. Through this model, the importance of the different mechanisms involved in gas hydrate decomposition was also examined and demonstrated. It was concluded that by using depressurization technique significant gas production could be achieved from hydrates in contact with an underlying free gas zone. The other important parameters affecting the production rate and amount were thermal conductivity, rock permeability, presence of a mobile phase to transmit the low pressures caused by production, and wellbore pressure.

Kurihara et al. (2008) developed a numerical simulator (MH21-HYDRES) for rigorous prediction of MH dissociation and production behaviours both at core and field scales. This simulator has a capability to deal with 3-D, 5-phase and 4-component problems associated with MH dissociation kinetics. This model was used in predicting the performance of a subsequent planned production test, scheduled for March 2008.

2.6 Research objectives

The objective of this work is to study the kinetics of hydrate formation and decomposition in a new apparatus which was specifically designed to investigate how gas hydrate formation and decomposition depends on the size of the silica sand bed. Key information like the gas consumption rate during hydrate formation, gas recovery rate during decomposition, along with the temperature profiles at various locations of the bed are also presented. This information allows the calculation of the percent conversion of water to hydrate and the gas recovery rate during hydrate decomposition.

CHAPTER 3: MATERIALS AND METHODS

3.1 Experimental apparatus

A detailed description of the silica sand apparatus is given below. Figure 3.1 shows the schematic of the experimental apparatus. It consists of a crystallizer (CR) which is a cylindrical vessel (ID = 10.16cm, Height = 15.24cm) made of 316 stainless steel. It has a volume of 1236.05 cm³. There is a reservoir (R) with a volume of 1000 cm³ that collects gas released during the decomposition experiments. The crystallizer and the reservoir are immersed in a temperature controlled water bath. The temperature of the water bath is controlled by an external refrigerator (VWR Scientific). Two Rosemount smart pressure transducers, model 3051 (Norpac controls, Vancouver, BC) are employed for pressure measurement with a maximum uncertainty of 0.12% of the span (0-15,000 kPa) i.e. 18 kPa. The temperature of the hydrate phase and the gas phase of the crystallizer is measured using Omega copper-constantan thermocouples with an uncertainty of 0.1 K. Eight thermocouples are located in the crystallizer with two in the gas phase and six in the silica sand bed. A control valve (Fisher Bauman) coupled with a PID controller enables carrying out the decomposition experiment at constant pressure. The data acquisition system (National Instruments) is coupled with a computer to record the data as well as to communicate with the control valve during the experiment and the software used for this purpose is LabView 8.0 (National Instruments). The apparatus is also equipped with a safety pressure valve.



Figure 3.1: Experimental apparatus

The various locations of the eight thermocouples placed in the crystallizer are shown in Figure 3.2. In order to study the effect of the variable volume of the silica sand bed on hydrate formation and decomposition, two copper cylinders are placed inside the crystallizer as shown in Figure 3.3. The first copper cylinder (CC_1) has a diameter of 3 inches and the

second one (CC_2) 2 inches. The wall thickness of both cylinders is 0.5 inches. It is noted that only four thermocouples could be accommodated in the silica bed with both CC_1 and CC_2 present in the crystallizer.



Figure 3.2: Location of thermocouples in the crystallizer





3.2 Materials

UHP grade methane (Praxair Technology Inc), silica sand with an average diameter of 329µm (diameter ranges from 150 to 630µm) supplied by Sigma-Aldrich and distilled and

deionised water was used. The average diameter of the particles is determined using the Malvern Mastersizer and the result of this analysis is presented in Figure 3.4. BET surface area analysis of the sand showed that the BET surface area of the sand used in this work is $0.3499 \text{cm}^2/\text{g}$ and that the sand is micro porous with a pore volume of $0.000152 \text{cm}^3/\text{g}$ and a pore diameter of 0.90 nm.



Figure 3.4: PSA (particle size analysis) result for the silica sand used in our experiments

3.3 Experimental method

In this section, the experimental procedure followed for formation and decomposition is explained separately.

3.3.1 Experimental procedure (formation)

The amount of silica sand put in the crystallizer is 914.1 g (Height of silica bed = 7 cm). The volume of water required to fill the void space with water was found to be 35.0 ml for 161.0 g of sand or $0.217 \text{cm}^3/\text{g}$ which is the interstitial or pore volume of the bed of sand particles. Accordingly, 198.5 ml of water is added into the sand. The procedure for the formation experiment is the same when one (CC₁) or two copper cylinders (CC₁+CC₂) are placed in the crystallizer. The height of the silica sand bed was fixed the same as 7.0cm. Hence, the amount of the sand placed in the crystallizer is reduced to 513.7 g when there is one (CC₁) copper cylinder is present inside the crystallizer. Accordingly, the amount of water added to fill the void space of the sand is 111.7 ml. When two (CC₁+CC₂) copper cylinders are present the amounts of sand and water added were 228.5 g and 49.7 ml, respectively.

Once the crystallizer bed is setup the thermocouples are positioned and then the crystallizer is closed. The crystallizer is pressurized with methane and depressurized at a pressure below the equilibrium hydrate formation pressure three times in order to eliminate the presence of any air bubbles in the system. The pressure in the crystallizer is then set to the desired experimental pressure (8.0MPa) and the temperature is allowed to reach the target temperature (approximately 5 min). This is time zero for the formation experiment. Data is then logged in the computer for every 20 seconds. All hydrate formation experiments are carried out with a fixed amount of water and gas (closed system). The temperature in the crystallizer is maintained constant by an external refrigerator. When hydrate formation occurs, gas will be consumed and hence the pressure in the closed system drops. The experiment is allowed to continue until there is no significant change in the crystallizer pressure.

Calculation of the amount of gas consumed during hydrate formation:

Pressure and temperature data are used to calculate the moles of methane consumed in the crystallizer (gas uptake). At any given time, the total number of moles of methane in the system (crystallizer (CR) and the connecting tubing) remains constant and equal to that at time zero.

$$\mathbf{n}_{\rm G,0} + \mathbf{n}_{\rm H,0} = \mathbf{n}_{\rm G,t} + \mathbf{n}_{\rm H,t} \tag{3.1}$$

where n_G is the number of moles in the gas phase and n_H the number of moles consumed to form hydrate formation or dissolved in water. Thus, the number of moles of the gas that has been consumed for hydrate formation at time t = t is given by the equation.

$$\mathbf{n}_{\rm H,t} - \mathbf{n}_{\rm H,0} = \mathbf{n}_{\rm G,0} - \mathbf{n}_{\rm G,t} \tag{3.2}$$

or

$$\Delta \mathbf{n}_{\mathrm{H},\downarrow} = \mathbf{n}_{\mathrm{H},\mathrm{t}} - \mathbf{n}_{\mathrm{H},0} = \left(\frac{\mathrm{PV}}{\mathrm{zRT}}\right)_{\mathrm{G},0} - \left(\frac{\mathrm{PV}}{\mathrm{zRT}}\right)_{\mathrm{G},\mathrm{t}}$$
(3.3)

where z is the compressibility factor calculated by Pitzer's correlation (Smith et al., 2001).

3.3.2 Experimental procedure (decomposition)

Two different decomposition techniques, namely thermal stimulation and depressurization, are conducted and the results from both techniques are compared in the results and discussion section.

3.3.2.1 Thermal stimulation

After the completion of each hydrate formation experiment, the hydrates are decomposed at a constant pressure as follows. The pressure in the crystallizer is decreased to the desired pressure (20% above the equilibrium hydrate formation pressure). The temperature in the crystallizer is then allowed to become stable. This takes less then about 10 min. At that point, hydrates will not decompose as the pressure in the system is above equilibrium for the given temperature. Next, the temperature of the crystallizer is increased to the desired value by heating the water bath with an external refrigerator/heater. This is time zero for the decomposition experiment. During the experiment, when the temperature of the crystallizer crosses the equilibrium phase boundary, the hydrate starts to decompose and since the pressure in the crystallizer is maintained constant by the PID controller, the excess gas is released from the crystallizer and collected in the reservoir (R). The experiment proceeds until there is no further release of methane gas from the silica sand.

3.3.2.2 Depressurization

After the completion of each hydrate formation experiment, first, the pressure is brought down to about 10% above the equilibrium pressure, which is 4.2MPa at the current experimental conditions. The temperature in the crystallizer is then allowed to become stable. It is noted that at this pressure the hydrates do not decompose as the experimental pressure is still above the equilibrium pressure. This is time zero for the decomposition experiment. After that, the pressure in the crystallizer is reduced to 20% below the equilibrium, which is 3.1MPa at 4°C. During this step, the gas is released at a rate of ~20kPa/sec. As a result of this depressurization process, we move into the no hydrate zone and as the pressure crosses the equilibrium phase boundary, the hydrates start to decompose. Since the pressure in the crystallizer is maintained constant at 3.1MPa by a PID controller coupled with a control valve, the excess gas released from the crystallizer is collected in the reservoir (R). The experiment proceeds until there is no further release of methane gas from the silica sand. In experiment #10 in the depressurization section (Table 4.4), 40% depressurization was applied to compare the effects of the degree of depressurization and to select one method for the subsequent experiments. This selection process is discussed in Chapter 4 in more detail.

Calculation of the amount of gas released during hydrate decomposition:

At any given time, the total number of moles $(n_{T,t})$ in the system remains constant and equal to that at time zero $(n_{T,0})$. The system in this case includes the crystallizer (CR), the reservoir (R) and the connecting tubing. During the decomposition experiment the pressure in the crystallizer is kept constant. Hence the gas released from the hydrates during the experiment is collected in the reservoir using a PID controller coupled with a control value. The total number of moles at any given time is the sum of the number of moles (n_G) in gas phase (G) of the crystallizer, the number of moles (n_R) collected in the reservoir and the number of moles (n_H) in the hydrate phase.

$$\mathbf{n}_{\rm G,0} + \mathbf{n}_{\rm R,0} + \mathbf{n}_{\rm H,0} = \mathbf{n}_{\rm G,t} + \mathbf{n}_{\rm R,t} + \mathbf{n}_{\rm H,t}$$
(3.4)

The number of moles of gas released from the hydrate at any time during hydrate decomposition can then be calculated as follows,

$$n_{H,0} - n_{H,t} = n_{G,t} - n_{G,0} + n_{R,t} - n_{R,0}$$
(3.5)

or

$$\Delta n_{\mathrm{H},\uparrow} = n_{\mathrm{H},0} - n_{\mathrm{H},t} = \left(\frac{\mathrm{PV}}{\mathrm{zRT}}\right)_{\mathrm{G},t} - \left(\frac{\mathrm{PV}}{\mathrm{zRT}}\right)_{\mathrm{G},0} + \left(\frac{\mathrm{PV}}{\mathrm{zRT}}\right)_{\mathrm{R},t} - \left(\frac{\mathrm{PV}}{\mathrm{zRT}}\right)_{\mathrm{R},0}$$
(3.6)

where z is the compressibility factor calculated by Pitzer's correlation (Smith et al., 2001).

The percent methane recovery is calculated as a function of time for any given decomposition experiment based on information obtained from its formation experiment and is calculated by the following equation:

% methane recovery =
$$\frac{(\Delta n_{\rm H,\uparrow})_{\rm t}}{(\Delta n_{\rm H,\downarrow})_{\rm t_{end}}} \times 100$$
 (3.7)

where $(\Delta n_{H,\downarrow})_{t_{end}}$ is the number of moles consumed for hydrate formation at the end of a typical formation experiment and $(\Delta n_{H,\uparrow})_t$ is the number of moles released from hydrates during hydrate decomposition at any given time.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Gas hydrate formation for thermal stimulation experiments

Table 4.1 summarizes the hydrate formation experimental conditions and results indicating induction time and water conversion achieved.

 Table 4.1: Hydrate formation experimental conditions along with induction times and water conversion to hydrates (The initial experimental pressure for all the experiments was 8.0MPa).

System	Exp. No.	T _{exp} [C]	Induction Time [min]	Enc	d of experiment	Water
				Time [hr]	CH ₄ consumed [mol/mol of H ₂ 0]	conversion to hydrates [mol%]
CH4/Silica sand/water [CR]	1	7.0	130.0	92.5	0.0172	10.5
	2	7.0	206.7	100.6	0.0180	11.0
	3	4.0	18.3	71.6	0.1287	78.5
	4	4.0	69.7	48.6	0.1261	77.0
	5	4.0	61.3	29.0	0.1266	77.2
	6	4.0	644.3	29.0	0.1215	74.1
	7	1.0	123.7	65.3	0.1308	79.8
	8	1.0	87.7	95.4	0.1350	82.4
CH ₄ /Silica sand/water [CR + CC ₁]	9	4.0	546.3	61.2	0.1288	78.5
	10	4.0	8.7	24.0	0.1244	75.9
	11	4.0	40.3	24.0	0.1315	80.2
	12	4.0	63.7	40.0	0.1381	84.3
$CH_4/Silica \\ sand/water \\ [CR + CC_1 + CC_2]$	13	4.0	11.0	46.9	0.1261	76.9
	14	4.0	7.3	41.7	0.1410	85.9
	15	4.0	8.0	46.7	0.1238	75.5
	16	4.0	7.3	34.8	0.1603	97.8

The conversion of water to hydrate during the formation experiment was determined for all the formation experiments using the gas uptake information. The hydration number for methane/water system was assumed as 6.1 for our calculations (Ripmeester and Ratcliffe, 1988). The experiments at 4.0°C and 1.0°C achieved the same level of water to hydrate conversion. However, there is a distinct difference in water to hydrate conversion percentages between 7.0°C and 4.0°C (i.e.10% vs. 78%). Based on these observations and since conducting our experiments at 1.0°C would require more energy, a temperature of 4.0°C was found satisfactory and selected as the experimental temperature for the experiments that were carried out with the variable sand bed size (CC_1 and CC_1+CC_2). Kneafsey et al. (2007) have also achieved a 65% water-to-hydrate conversion in their experiments based on a hydration number of 5.75. The grain size of the silica sand that they used was 100-200 µm whereas in our experiments it was ranging between 150-630 µm. According to the conceptual model proposed in that study, a portion of the water present in the pore space (interstitial space between sand particles) was consumed and converted to hydrate. The porous medium containing the hydrate would act like a porous medium having smaller pores, because hydrate now partially fills the pores. And just as water would flow from a wide capillary tube into a narrow one, water would flow towards the location containing hydrate as a result of the improved capillarity there. This model is schematically represented in Figure 4.1. The same model might as well be the reason for getting such a high water-to-hydrate conversion in our experiments but further experiments such as observing the density changes within the sand must be conducted in order to confirm the hydrate formation mechanism inside the silica sand bed.



Figure 4.1: Conceptual model of a capillary pressure gradient induced by the presence of hydrate in a porous medium. Reprinted from (Kneafsey et al., 2007), with permission from Elsevier.

The initial experimental pressure for all the formation experiments was 8.0MPa. The experiment was allowed to continue until there was no further gas consumption for hydrate formation. This is indicated by a near-zero rate of pressure drop as seen in Figure 4.2 for a typical formation experiment.



Figure 4.2: Rate of pressure drop due to hydrate growth during hydrate formation (time zero in the graph corresponds to the time of induction point given in Table 4.1). Number in the parenthesis indicates the experiment number in Table 4.1.

Figure 4.3 shows the gas uptake measurement curve (moles of methane consumed per mole of water in the system) of a formation experiment carried out at 7.0°C along with the temperature profiles of the thermocouples located inside the bed. The data during the first five hours are also shown in the expanded graph. The uncertainties in the mole numbers due to the uncertainties in the measurement of pressure and temperature were calculated. For example, for Experiment 1 in Table 4.1, the uncertainty was found to be 1.4 % at the induction time, 1.1 % at 1 hour after induction time and 0.6 % at the end of the experiment. Since these uncertainties do not include other potential factors they are considered minimum values. The uncertainty at the induction time was determined to be less than 4.0% for all the experiments and to decrease as the number of moles consumed increases.

Hydrate formation is an exothermic crystallization process. Hence during hydrate formation, heat is released which can be seen in the figure at 130 min. This point during hydrate formation is called the nucleation point or turbidity point. The temperature of the system is gradually restored to its set point because the crystallizer is immersed in the constant temperature bath regulated with a control system.



Figure 4.3: Gas uptake measurement curve at 7.0°C (Experiment 1, Table 4.1)

While all six thermocouples during the experiment at 7.0°C indicate one nucleation point (at 130 min) there are several nucleation regions observed in the results at 4.0°C (Figure 4.4). The first temperature increase at the nucleation point can be seen in section A in the figure. In section B, the temperature increase is not localized and there is a larger consumption of gas for hydrate formation during that region, while there are several temperature spikes in other regions which indicate the nucleation sites are localized as can be seen in sections E, D and F in the figure. Similar observations were made for the other experiment carried out at 4.0°C and also the experiments carried out at 1.0°C. Overall, as can be seen in Figure 4.4, hydrate growth does not proceed at a constant rate. Similar observations were made for the other experiments were made for the other experiments as well as by Kneafsey et al. (2007) when hydrates were formed at 6.2MPa and 1.1°C in the presence of silica sand with a particle size of 100 to 200 µm.



Figure 4.4: Gas uptake measurement curve at 4.0°C (Experiment 3, Table 4.1)

The temperature profiles shown in Figure 4.4 are not clear enough to visualize well due to overlap and hence are shown in Figure 4.5 as individual graphs plotted as a function of time. It can be seen in the figure that hydrate formation occurs at different locations at different time which can be the reason why the methane uptake does not proceed at constant rate. This also resulted in achieving a higher percent conversion of water to hydrate for the experiments carried out at 4.0 and 1.0°C respectively, compared to the experiments carried out at 7.0°C as shown in Table 4.1.



Figure 4.5: Temperature profiles as a function of time for Experiment 3 at 4.0°C

Two formation experiments carried out at 4.0° C, one with the presence of one copper cylinder (CR+CC₁) and the other with the presence of both copper cylinders (CR+CC₁+CC₂) are shown in Figure 4.6. For experiment 11, one can see several temperature spikes during the hydrate formation experiment similar to the experiments conducted with no copper cylinders at 4.0°C. Comparison of Figures 4.4 and 4.6 indicates that as the bed size gets narrowed, the extent of temperature increases due to multiple nucleation and hydrate formation get smaller. In our opinion, as we narrow the silica sand bed with copper cylinders, heat is removed faster from the crystallizer to the water bath and as a result the spikes are getting smaller. The same trend was observed for all the other formation experiments.



Figure 4.6: Gas uptake measurement curves in the presence of one copper cylinder (Experiment 11) and two copper cylinders (Experiment 13)

It is noted that the thermocouple location in the crystallizer in the presence of copper cylinders are located at the same distance from the cylindrical wall, T_3 and T_4 at the top and T_1 and T_2 at the bottom as indicated in Figure 3.3. Figure 4.7 shows the temperature profiles plotted individually as a function of time for experiment 11. As can be seen from the profiles of T_3 and T_4 , the activity of hydrate formation is different in these two regions in the crystallizer although they are at the same distance from the cylinder wall. The same observation applies to T_1 and T_2 as well. Similar observations were made for all the other experiments as well. The final water conversion achieved at the end of the experiments are shown in Table 4.1 and it can be seen that for all the formation experiments carried out at 4.0°C with the presence of copper cylinders, more than 74% of water conversion to methane hydrate was achieved at the end of the experiment.



Figure 4.7: Temperature profiles as a function of time for Experiment 11 with CC₁ placed in the crystallizer at 4.0°C

Besides the hydrate formation and decomposition experiments, a solubility experiment is conducted for simply comparing the mole fraction of gas in a liquid after a mixing process and the experimental mole fraction values obtained at the induction point in the formation experiments. The solubility experiment is conducted in a stirred tank reactor. A detailed description of the apparatus is available in the literature (Lee et al., 2005; Linga et al., 2007).

The experiment was conducted at the same temperature as the hydrate formation experiments (4.0°C) and at a pressure of 3.4MPa (equilibrium pressure is 3.85MPa at 4.0°C). The mole fraction of gas in the liquid at the end of that experiment was found to be 0.001773 and this number is compared with the mole fractions obtained at induction time from each hydrate formation experiments conducted and are shown in Figure 4.8.



Figure 4.8: Comparison of the mole fractions of gas in the liquid for hydrate formation and solubility experiments

As observed in the graph, all the experimental values are below the mole fraction calculated after solubility experiment. This is not surprising because there was no mixing in our hydrate formation system whereas the system was continuously mixed in the solubility experiment (uniform concentration in the liquid phase). In addition to the mole fractions, theoretical saturation of gas in the liquid was calculated. It was assumed there was no silica sand in the system and the calculations were made based on the diffusion of gas into liquid. The calculation procedure that Servio and Englezos (2003) used was employed in order to create the plot below. Figure 4.9 shows the time needed to reach to certain saturation percentages at different depths. The average saturation percentage for the formation experiments was found to be 0.34% and lies within 0.2% and 0.4% curves in the figure.



Figure 4.9: Time vs. depth curves for different saturation percentages

4.2 Gas hydrate decomposition by thermal stimulation

The number of moles released during a decomposition experiment is calculated from equation 3.6 in Chapter 3. The decomposition experiments are summarized in Table 4.2.

System	Exp. No	P _{exp} [MPa]	$\Delta T = T_{end} - T_{start}$		$T_d at P_{exp}^a$	Rate of methane release/mol of water ^b [hr ⁻¹]		Methane Recovery
			T _{start} [C]	ΔT [C]	[C]	Stage 1	Stage 2	[mol%]
CH4/Silica sand/water [CR]	1	6.2	7.0	3.0	8.8	0.0037	0.0015	96.0
	2	6.2	7.0	3.0	8.8	0.0047	0.0011	96.0
	3	4.6	4.0	3.8	5.8	0.0140	0.0046	99.0
	4	4.6	4.0	4.8	5.7	0.0274	0.0084	97.6
	5	4.6	4.0	4.0	5.7	0.0186	0.0056	99.4
	6	4.6	4.0	10.0	5.8	0.0481	0.0216	97.7
	7	3.5	1.0	4.0	2.9	0.0138	0.0033	97.1
	8	3.5	1.0	4.0	2.9	0.0127	0.0029	98.1
CH ₄ /Silica sand/water [CR + CC ₁]	9	4.6	4.0	4.0	5.7	0.0221	0.0052	97.4
	10	4.6	4.0	4.0	5.7	0.0211	0.0055	99.6
	11	4.6	4.0	10.0	5.8	0.0544	0.0214	98.5
	12	4.6	4.0	10.0	5.7	0.0582	0.0207	98.9
CH ₄ /Silica sand/water [CR+CC ₁ +CC ₂]	13	4.6	4.0	4.0	5.7	0.0300	0.0065	96.2
	14	4.6	4.0	4.0	5.7	0.0303	0.0072	94.7
	15	4.6	4.0	10.0	5.7	0.0774	0.0234	96.1
	16	4.6	4.0	10.0	5.7	0.0805	0.0284	95.0

 Table 4.2: Hydrate decomposition experimental conditions along with the rate of recovery and final percent of methane recovered

a – T_d is the decomposition temperature at which methane release occurs from the hydrates for the experimental pressure, P_{exp} .

b – The rate of methane recovery was calculated for the first 2 hours of methane release by fitting the data to a straight line.

Figure 4.10 shows the typical gas recovery curve obtained from the decomposition experiment with temperature as the driving force at a pressure of 4.6MPa (Experiment 4 in Table 4.2). As can be seen in the figure, there is no gas release until the temperature crosses the phase boundary. For this experiment, when the temperature crosses 5.7°C, hydrate starts to decompose and since the pressure in the crystallizer is maintained constant, the gas released is collected in the reservoir (R). When the temperature exceeds 5.7°C, the temperature profile of T₁ (thermocouple located at the bottom of the crystallizer and also near the cylindrical wall, Figure 3.2) follows a gradual increase due to driving force (heating). The other thermocouple profiles follow different paths and finally catch up with T₁. This is due to the fact that gas from hydrate decomposition is released in the upward direction within the reactor (towards the gas phase region) thereby resulting in a decrease in the temperature along this direction. This temperature decrease is in turn compensated by the heating applied for the decomposition experiment through the water bath. All the other temperature profiles catch up slowly with T_1 . The decomposition temperatures at which methane release occurred for the other decomposition experiments carried out at 6.2MPa and 3.5MPa are given in Table 4.2.



Figure 4.10: Decomposition experiment carried out at 4.6MPa (Experiment 4, Table 4.2)

Figure 4.11 shows the methane recovery curve for the experiment (Experiment 6, Table 4.2) carried out at 4.6MPa and a driving force (Δ T) of 4.0 °C. Time zero in the figure is the time when methane release occurs from the hydrates. As can be seen in the figure, methane recovery occurred in two stages (Stage 1 and Stage 2). The same trend was observed for all the decomposition experiments. The rate of methane release per mole of water for each stage was calculated by fitting the data to a straight line. The methane recovery rates calculated for the two stages are given in Table 4.2. The percentage recovery of methane from hydrates for the decomposition experiments was determined using equation 3.7 and is also presented in Table 4.2. As can be seen, a percentage recovery in the range of 95 to 99% was obtained for all of the decomposition experiments performed at 6.2, 4.6 and 3.5MPa, respectively.


Figure 4.11: Methane release measurement curve from hydrates showing two stages of recovery and the calculated rate of recovery (Experiment 6, Table 4.2)

In order to study the effect of silica sand bed on methane recovery from hydrates, decomposition experiments were carried out for the formation experiments with the presence of copper cylinder 1 (CC₁) in the crystallizer. The decomposition experiments were carried out at two driving forces of 4.0°C and 10.0°C respectively and at a pressure of 4.6MPa. The same study was carried out with the presence of both CC₁ and CC₂ in the crystallizer. Since all the formation experiments with the presence of copper cylinders were carried out at 4.0°C, all of the decomposition experiments were carried out at 4.6MPa. Table 4.2 summarizes the experimental conditions, the decomposition temperatures when the release of methane gas started from hydrates and the methane recovery rates.

The percent recovery of methane for the set of experiments carried out in the presence of copper cylinder CC_1 and in the presence of both CC_1 and CC_2 is calculated using equation 3.7 and shown in Figures 4.12 and 4.13. As can be seen from the figures, the recovery of methane from hydrates was faster for a higher driving force of 10.0°C for both cases. Moreover, complete recovery was achieved in just over 200 min for the higher driving force whereas it took around 750 min for the experiments carried out at a driving force of 4.0°C with the presence of CC_1 and around 500 min with the presence of both CC_1 and CC_2 at the driving force of 4.0°C.



Figure 4.12: Methane recovery from hydrates from the decomposition experiments carried out with the presence of CC₁ at 4.6MPa and driving force (ΔT) of 4.0 & 10°C. Number in the parenthesis indicates the experiment number in Table 4.2.



Figure 4.13: Methane recovery from hydrates from the decomposition experiments carried out with the presence of CC_1 and CC_2 at 4.6MPa and driving force (ΔT) of 4.0 & 10°C respectively. Number in the parenthesis indicates the experiment number in Table 4.2.

Figure 4.14 shows a comparison of methane recovery curves for all the decomposition experiments carried out at a constant pressure of 4.6MPa and with a temperature driving force of 4.0°C and for all the three cases; one with the silica bed at its largest size, one with the silica bed with CC_1 inside the crystallizer and one with the silica bed with both CC_1 and CC_2 placed in the crystallizer. We can see from the figure that the evolution of the recovery of methane versus time is qualitatively the same (follows the same trend), irrespective of the sample size. Quantitatively, however, one can see an initial difference in the slope of the

curve. The final methane conversions are all within a few percent. It is not clear how significant this difference is in the methane recovery versus time as we narrow down the bed size by installing copper cylinders inside the crystallizer.



Figure 4.14: Comparison of methane recovery from decomposition experiments for the three different silica bed sizes studied at constant pressure of 4.6MPa and a temperature driving force (ΔT) of 4.0°C. Number in the parenthesis indicates the experiment number in Table 4.2.

Similar trends can be seen in Figure 4.15, which show the methane recovery curves obtained for the decomposition experiments carried out at a constant pressure of 4.6MPa and with a temperature driving force of 10.0°C.



Figure 4.15: Comparison of percent methane recovery from decomposition experiments for three different silica bed sizes (CR, CR+CC1, CR+CC1+ CC2) studied at a constant pressure of 4.6MPa and a temperature driving force (ΔT) of 10.0°C. Number in the parenthesis indicates the experiment number in Table 4.2.

If we compare the calculated rates of methane release from hydrate due to thermal stimulation as given in Table 4.2, there is a significant difference in the rates for any given driving force for the three bed sizes studied. Figure 4.16 shows the calculated rates along with the standard errors plotted against different bed volumes for the temperature driving force of 4.0°C. There is an decreasing trend in the calculated rate of methane release for the first stage as the bed volume is increased, whereas the rates are more or less the same for the

second stage. A similar trend was observed for the other experiments carried out with a temperature driving force of 10.0°C (Figure A.70) clearly suggesting that there is a strong dependence of methane recovery rate on the bed volume for the first stage while the calculated rates are more or less same for the second stage. Figures A.71 and A.72 present the relationship between the rate of recovery and the surface area for different driving forces (i.e. 4.0°C and 10.0°C, respectively). And finally, figures A.73 and A.74 display the dependence of the rate of recovery on the radius of the bed size.



Figure 4.16: The calculated rates along with the standard errors plotted against different bed sizes for all the decompositions experiments carried out at a driving force of 4.0°C. (CR: experiment 5, CR+CC₁: experiment 9 & 10, CR+CC₁+CC₂: experiment 13 & 14).

4.3 Gas hydrate formation for depressurization experiments

The formation experiments conducted prior to depressurization experiments followed the same procedure explained in Section 4.1. The main goal was to achieve a water-to-hydrate conversion of \sim 73% and above, so that there is enough hydrate to decompose and observe the rate of recovery. Due to the stochastic nature of hydrate formation, induction times were random. The conversion of water to hydrate during the formation experiment was determined for all the formation experiments using the gas uptake information. The hydration number for methane/water system was assumed as 6.1 for our calculations (Ripmeester and Ratcliffe, 1988).

Table 4.3 summarizes the hydrate formation experimental conditions and results indicating induction time and water-to-hydrate conversion achieved.

 Table 4.3: Hydrate formation experimental conditions along with induction times and water conversion to hydrates (The initial experimental pressure for all the experiments was 8.0MPa)

9.4	Exp. No.	T _{exp} [C]	Induction Time [min]	Enc	Water conversion	
System				Time [hr]	CH ₄ consumed [mol/mol of H ₂ 0]	to hydrates [mol%]
CH ₄ /Silica	1	4.0	363.0	56.1 0.1256		76.6
sand/water [CR]	2	4.0	39.7	49.8	0.1228	74.9
	3	4.0	332.7	72.6	0.1199	73.2
CH ₄ /Silica sand/water	4	4.0	17.0	89.1	0.1203	73.4
	5	4.0	2.7	77.2	0.1256	76.6
$[CR + CC_1]$	6	4.0	15.7	74.7	0.1255	76.6
$CH_4/Silica$ sand/water $[CR + CC_1 + CC_2]$	7	4.0	206.7	208.5	0.1368	83.5
	8	4.0	92.3	161.2	0.1307	79.7
	9	4.0	4.0	185.4	0.1391	84.8
	10*	4.0	246.0	119.1	0.1332	81.2

* In the decomposition section of this experiment, the system is depressurized 40% below P_{eq} .

4.4 Gas hydrate decomposition by depressurization

The number of moles released during a decomposition experiment is calculated from equation 3.6 in Chapter 3. The decomposition experiments are summarized in Table 4.4.

System	Exp. No.	P _{exp} [MPa]	T _{start} [C]	Rate of methane release/mol of water ^b [hr ⁻¹]			Methane Recovery
				Stage 1	Stage 2	Stage 3	[mol%]
CH ₄ /Silica sand/water [CR]	1	3.1	4.0	0.0445	0.0157	0.0037	97.8
	2	3.1	4.0	0.0416	0.0105	0.0028	95.6
	3	3.1	4.0	0.0354	0.0113	0.0035	95.8
CH ₄ /Silica sand/water [CR + CC ₁]	4	3.1	4.0	0.0714	0.0198	0.0053	95.3
	5	3.1	4.0	0.0669	0.0243	0.0043	96.4
	6	3.1	4.0	0.0758	0.0238	0.0036	93.1
CH ₄ /Silica sand/water [CR+CC ₁ +CC ₂]	7	3.1	4.0	0.0956	0.0230	0.0065	94.8
	8	3.1	4.0	0.1072	0.0268	0.0057	89.1
	9	3.1	4.0	0.1014	0.0259	0.0063	83.2
	10*	2.3	4.0	0.4586	0.1535	0.0103	75.7

 Table 4.4: Hydrate decomposition experimental conditions along with the rate of recovery and final percent of methane recovered

* In this experiment, the system is depressurized 40% below P_{eq} for comparison.

Figure 4.17 shows the typical gas recovery curve obtained from the decomposition experiment with pressure as the driving force (Experiment 6 in Table 4.4). For this experiment, when the pressure drops below 3.85MPa, hydrate started to decompose. The pressure in the crystallizer was maintained constant and the gas released was collected in the reservoir (R). The temperature inside the system during the depressurization process drops dramatically due to the sudden pressure release from the constant volume-reactor. The

behaviour of the temperature profiles at different locations within the silica sand bed is random and unlike the decomposition via thermal stimulation method there is no control of the temperature after depressurization. However, the external temperature was kept constant at 4.0°C, therefore the temperature profiles inside the crystallizer eventually reached to 4.0°C. As is explained in section 3.3.2.2, the pressure of the system is kept constant after dropping the pressure to 20% below the equilibrium pressure. The excess gas from decomposition is transferred to a separate reservoir and this transfer process takes place in the gas phase. Hence, the temperature profiles of the thermocouples closer to the gas-solid interface increase more slowly. Once the decomposition is over, they catch up those of T_1 and T_2 .



Figure 4.17: T-profile and volume of gas released during decomposition by depressurization carried out at 3.2MPa (Experiment 6, Table 4.4)

We have tried two scenarios for the depressurization experiments in the presence of two copper cylinders inside the crystallizer (CR+CC₁+CC₂) and picked one of them to apply in the subsequent experiments. These scenarios involved bringing the pressure down to 20% or 40% below the equilibrium pressure. It was observed that the recovery of methane was higher for depressurization experiments where the pressure was reduced 20% below the equilibrium pressure as compared to 40%. This was because of the gas release due to hydrate decomposition occurring while the system was being depressurized and the system leaves the hydrate stability zone. Therefore, there is some gas released that couldn't be captured in the reservoir. This situation is explained better in Figure 4.18.



Figure 4.18: Pre-decomposition gas release and projected pressure reduction for Experiment 9 in Table 4.4

In this figure, projected pressure values are shown with the dash line. The solid lines are the actual pressure readings inside the crystallizer. As can be observed, if the hydrates did not

start to decompose at the moment the phase boundary is crossed during the depressurization process, the pressure line would have followed the dotted line shown in the figure. However, as the pressure in the system is reduced below the equilibrium pressure (3.85MPa) and crosses the phase boundary, the decomposition starts and hence the pressure reduction rate slows down by the time we reach the desired experimental pressure. That is why the actual pressure readings are higher than the predicted values. The amount of gas lost during depressurization process is calculated for this particular experiment (experiment 9 in Table 4.4) and when this amount is incorporated into our recovery percentage calculations, the final recovery percentage rises from 83.2% to 98.1%. The reason for not getting a full recovery (100%) is the experimental error which is expected to be 1% for both formation and depressurization experiments. There is also a possibility that at the experimental pressure and temperature conditions during decomposition, some of the methane gas that has been diffused into water during the formation experiment will stay diffused in the water. According to our calculations this amount is less than 0.2% for all the formation experiments. As the pressure is reduced for a longer period of time to reach to 40% below the equilibrium, the amount of gas lost is higher. Hence, it is not surprising that the recovery percentage for 40% depressurization is lower compared to 20% depressurization (75.7% vs. 89.1%). These two experiments are compared in terms of recovery percentages and displayed in Figure 4.19. Based on the foregoing discussion we decided to apply the 20% depressurization method so that the amount of gas lost during depressurization is kept at a minimum although the rate of recovery is significantly faster for the 40% depressurization experiments.



Figure 4.19: Recovery percentage comparison between 20% and 40% depressurization methods

Figure 4.20 shows a comparison of methane recovery curves for all the decomposition experiments carried out by depressurization method and with all the three cases; one with the silica bed at its largest size, one with the silica bed with CC_1 inside the crystallizer and one with the silica bed with both CC_1 and CC_2 placed in the crystallizer. We can see from the figure that the methane recovery percentages are more or less the same. It is also visible in the same figure that the duration of methane recovery gets shorter as the bed size is narrowed down because when the bed size is narrower, less water and methane are consumed. Thus, less hydrate is formed prior to decomposition experiments leading to less methane release, consequently completing methane recovery process faster. The percentage recovery of methane from hydrates was determined using equation 3.7 and is also presented in Table 4.4.



Figure 4.20: Comparison of percent methane recovery from decomposition by depressurization experiments for three different silica bed sizes (CR, CR+CC1, CR+CC1+CC2). Number in the parenthesis indicates the experiment number in Table 4.4.

Unlike the thermal stimulation method, in decomposition by depressurization method the rate of methane recovery occurred in three stages. Figure 4.21 shows the methane recovery curve for the experiment (Experiment 1, Table 4.4) carried out at 3.1MPa and a driving force of 20% depressurization. Time zero in the figure is the time when methane release occurs from the hydrates. The same trend was observed for all the decomposition experiments. The rate of methane release per mole of water for each stage was calculated by fitting the data to a

straight line. Depressurization experiments could also be presented with a two-stage model but a three-stage model defined the rate of recovery better and increased the accuracy of the calculated rate of recovery. The methane recovery rate calculated for all three stages are given in Table 4.4.



Figure 4.21: Methane release measurement curve from hydrates showing three stages of recovery and the calculated rate of recovery (Experiment 1, Table 4.4)

The effect of the changing bed volume on the rate of methane recovery is examined in Figure 4.22. In that graph, the average rates of recovery for all the experiments conducted for each bed size (CR, CR+CC₁, CR+CC₁+CC₂) are presented along with the errors associated with them. As one can see, rates of recovery at stage 1 are strongly affected by the changing bed size. As we increase the bed volume, the rate of recovery decreases significantly. However, we can not observe the same trend at stage 2 and 3. At stage 2, there isn't any specific

relationship found between the bed size and the rate of recovery. The rates of recovery at stage 3 are approximately the same and are not being affected by the silica sand bed size either. In figures B.44 and B.45, the effect of the changing surface areas and radiuses of the bed on the rate of recovery is examined and the same trend is observed.



Figure 4.22: The average calculated rates along with the standard errors plotted against different bed volumes for all the decompositions experiments carried out by depressurization method.

4.5 Morphology studies on methane hydrate formation

A smaller-scale morphology experiment was conducted in order to visualize the uniform methane hydrate formation within the sediment. This experiment was carried out in another apparatus which is explained in detail by Lee et al. (2005) and Linga et al. (2007). 26.0 g of silica sand is placed in a small glass vial. Accordingly, 5.65 ml of water is added into the sand in this case. Next, the vial is placed in the crystallizer and pressurized with methane up to 8.0MPa. The temperature of the system is kept constant at 4.0°C. The pressure of the system is continuously monitored. Gas consumed and water-to-hydrate conversion is calculated as explained in Section 3.3.1. The experiment lasted for 153 hours and the final water-to hydrate conversion achieved was 76.2%. During this experiment, pictures were taken at several time intervals. An increase in the bed size would mean hydrate formation on top of the silica sand bed, however if no increase in height has occurred, that would mean hydrate is formed within the sediment in the interstitial space between the sand particles. A dash mark is put on the vial as a reference point to note any difference in the height of the bed more easily. Figure 4.23 shows a series of these pictures taken during hydrate formation. The time elapsed until the picture is taken and the water-to-hydrate conversion is reported along with the pictures.



Figure 4.23: Morphology experiment (8.0MPa) - Series of pictures showing the height of the bed at different times during hydrate formation

This figure clearly shows that the hydrate formation occurs within the sediment since the gassolid interface remains constant during hydrate formation. This experiment visualized the uniformity of the hydrate presence within the sediment.

4.5.1 Hydrate phase characterization

Hydrate phase characterization experiments were also conducted and the procedure for those experiments is explained next. A straight glass vial having an OD of 20 mm and a wall thickness of 2 mm was filled with sand & water mixture (20g & 4.34ml), and was placed along the vertical axes of an empty reactor. The crystallizer was pressurized with methane and depressurized at a pressure below the equilibrium hydrate formation pressure three times in order to eliminate the presence of any air bubbles in the system. Hydrate was allowed to grow for 4 days at 4.0°C and 8.0MPa and was recovered at liquid nitrogen temperature for further analysis by Raman spectroscopy. Three different portions (top, middle and bottom section along the vertical axis) of sand-hydrate matrix were chosen for Raman spectroscopic analysis. Each portion was crushed with mortar and pestle in liquid nitrogen and the hydrate was separated from silica sand for spectroscopic analysis. Hydrate was analyzed at atmospheric pressure and liquid nitrogen temperature with Raman spectroscopy, thus marking the signals of methane in the hydrate cages. An Acton Raman spectrograph with fibre optics and equipped with a 1200 grooves/mm grating and a CCD detector was used in this study. An Ar-ion laser was used as the excitation source, emitting at 514.53 nm. The laser was focused on the sample by a 10x microscope objective. The spectrograph was controlled with a computer and the spectra were recorded with a 1s integration time over 50 scans.

Figure 4.24 shows a typical Raman spectrum of the C-H (2800-3000 cm⁻¹) and O-H regions (3000 to 3400 cm⁻¹) of the methane hydrate sample. The peak doublet at approximately 2906 cm⁻¹ and 2917 cm⁻¹ indicate CH₄ molecules encaged in large cages and small cages, respectively. Two large, broad peaks at approximately 3090 cm⁻¹ and 3220 cm⁻¹ are due to the internal vibrational modes of water molecules making up the host lattice of the hydrate structure (Tulk et al., 2000). Additionally, a minor band for methane was present at about 3050 cm⁻¹ indicative of methane in the hydrate phase (Kumar et al., 2008). Raman spectroscopy performed on different samples confirmed the presence of hydrate in the sand-hydrate matrix. The hydrate was also found to be evenly distributed in the sand-hydrate matrix along the vertical axis.



Figure 4.24: Typical Raman spectra for methane hydrate synthesized in silica sand matrix showing the C-H stretch of methane encaged in hydrate cages as doublet at 2906 and 2917 cm⁻¹ (inset). Also note the broad water band for O-H stretching between 3000 and 3500 cm⁻¹. Hydrate was synthesized at 4°C and 8MPa and spectra were obtained at atmospheric pressure and liquid nitrogen temperature.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study of CH₄ formation and dissociation in a silica sand matrix was carried out. Two different types of decomposition techniques were utilized; thermal stimulation and depressurization. Using each technique, the effect of silica sand bed size on the hydrate formation and decomposition was studied by installing one and two copper cylinders in the crystallizer thereby narrowing the size of the bed with the height of the bed kept constant at 7.0cm. Furthermore, the effect of the degree of the driving force on the rate of methane recovery has been investigated. Moreover, experimental data for different conditions were provided to simulators which will enable them to model the hydrate formation and decomposition scenarios more accurately. Conclusions that were drawn from the experimental results obtained are explained in this section.

First of all, it was found out that water-to-hydrate conversion achieved is higher with a lower experimental temperature. When the experiments are conducted at 7.0°C, the conversion was limited at ~11% whereas it reached to ~80% with 4.0°C and 1.0°C experimental temperatures. The difference between 4.0°C and 1.0°C was not very distinct and since conducting our experiments at 1.0°C would require more energy, 4.0°C was found satisfactory and applied for the subsequent experiments.

Multiple nucleation points were observed during the formation experiments carried out at 4.0°C. Thermocouples located in various positions within the silica sand bed have shown

sudden local temperature increases indicating that formation (nucleation) of hydrate occur almost at the same time at all locations in the cell. Addition of the copper cylinders to narrow the bed size improved the heat removal from the system; therefore the local temperature changes in the crystallizer became less distinct.

In the decomposition by thermal stimulation method, it was observed that a higher driving force (i.e. temperature) causes a significant increase in the rate of recovery. At a higher driving force (10.0°C) the methane recovery from hydrates was faster compared to the lower driving force (4.0°C). In these experiments, methane recovery in the range of 95 to 99% was achieved. Methane recovery occurred in two stages for all the decomposition by thermal stimulation experiments and the rates of recovery for these stages are presented in Table 4.2. It is found out that the rate of recovery displays an increasing trend at the first stage by the changing bed size while the rates were approximately the same for the second stage. Another observation for the thermal stimulation experiments was that the temperature profile of T_1 (thermocouple located at the bottom of the crystallizer and also near the cylindrical wall, Figure 3.2) follows a different path from the other thermocouples since the gas from hydrate decomposition is released in the upward direction, thus leading to a decrease in the temperature along this direction. That is why the other thermocouples showed lower temperature profiles but eventually caught up with T_1 .

Decomposition experiments utilizing depressurization techniques gave us some different results compared to thermal stimulation technique. To begin with, higher methane recovery percentages were achieved with a lower driving force (20%) compared to the higher driving

83

force (40%). The reason for that is the amount of gas lost during the depressurization process is greater with a higher driving force. That is because a longer time elapses until a pressure 40% below the equilibrium pressure is reached.

The behaviour of the temperature profiles at different locations within the silica sand bed is random in the depressurization experiments and unlike the decomposition via thermal stimulation method the temperature of the system is not controlled. However, the temperature profiles inside the crystallizer eventually reached to the external temperature, which was maintained as 4.0°C. The thermocouples closer to the gas-solid interface showed a slower increasing trend due to the transfer of the excess gas from the crystallizer towards the reservoir. Once the decomposition is over, they catch up those of T_1 and T_2 .

Unlike the results obtained from the thermal stimulation technique, methane recovery occurred in three stages for all of the experiments and the rates of recovery for these stages are presented in Table 4.4. Again, the rate of recovery at stage 1 was found to be strongly dependent on the silica sand bed size for the scale on which the experiments were conducted. As the bed size is narrowed down, the rate of recovery was found to increase. However, the rate of recovery did not follow the same trend at stages 2 and 3 and was not affected by changing the bed size.

5.2 **Recommendations**

Major conclusions have been drawn regarding the effects of the bed size on the rate of methane recovery from hydrate decomposition through this study. However, some recommendations can still be made in order to improve and broaden future investigations that will be conducted.

- Only one silica sand particle size has been experimented throughout this study. A broader study can be conducted with different particle-sized silica sand.
- 2. The thermal stimulation technique can be simulated by passing a coil through the bed that will circulate steam or hot water inside the reactor. That way, the effects of the heat transfer through the reactor walls can be minimized and this would be a better approximation to the real-case thermal stimulation scenario.
- 3. The reactor can be modified to allow the experimentalist to observe the experiment visually as well. A window can be added on the reactor and morphology studies could be conducted along with the kinetic data obtained.
- 4. Only pure methane is used in our experiments. Multi-component gas mixtures can be tested and the effect on the rate of gas recovery from hydrates can be observed.
- Infrared imaging system can be implemented in order to monitor the heat flow during hydrate formation experiments.
- 6. In addition to the kinetic data acquired, developing a model about hydrate formation and decomposition could be of help in understanding the concept better.

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Figure A.1: Temperature profiles as a function of time for formation at 7.0°C (Exp. 1, Table 4.1)



Figure A.2: Temperature profiles as a function of time for formation at 7.0°C (Exp. 2, Table 4.1)



Figure A.3: Temperature profiles as a function of time for formation at 4.0°C (Exp. 3, Table 4.1)



Figure A.4: Temperature profiles as a function of time for formation at 4.0°C (Exp. 4, Table 4.1)



Figure A.5: Temperature profiles as a function of time for formation at 4.0°C (Exp. 5, Table 4.1)



Figure A.6: Temperature profiles as a function of time for formation at 4.0°C (Exp. 6, Table 4.1)



Figure A.7: Temperature profiles as a function of time for formation at 1.0°C (Exp. 7, Table 4.1)



Figure A.8: Temperature profiles as a function of time for formation at 1.0°C (Exp. 8, Table 4.1)


Figure A.9: Temperature profiles as a function of time for formation at 4.0°C (Exp. 9, Table 4.1)



Figure A.10: Temperature profiles as a function of time for formation at 4.0°C (Exp. 10, Table 4.1)



Figure A.11: Temperature profiles as a function of time for formation at 4.0°C (Exp. 11, Table 4.1)



Figure A.12: Temperature profiles as a function of time for formation at 4.0°C (Exp. 12, Table 4.1)



Figure A.13: Temperature profiles as a function of time for formation at 4.0°C (Exp. 13, Table 4.1)



Figure A.14: Temperature profiles as a function of time for formation at 4.0°C (Exp. 14, Table 4.1)



Figure A.15: Temperature profiles as a function of time for formation at 4.0°C (Exp. 15, Table 4.1)



Figure A.16: Temperature profiles as a function of time for formation at 4.0°C (Exp. 16, Table 4.1)



Figure A.17: Methane uptake curve and the rate of methane consumption per mole of



Figure A.18: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 2, Table 4.1)



Figure A.19: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 3, Table 4.1)



Figure A.20: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 4, Table 4.1)



Figure A.21: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 5, Table 4.1)



Figure A.22: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 6, Table 4.1)



Figure A.23: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 7, Table 4.1)



Figure A.24: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 8, Table 4.1)



Figure A.25: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 9, Table 4.1)



Figure A.26: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 10, Table 4.1)



Figure A.27: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 11, Table 4.1)



Figure A.28: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 12, Table 4.1)



Figure A.29: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 13, Table 4.1)



Figure A.30: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 14, Table 4.1)



Figure A.31: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 15, Table 4.1)



Figure A.32: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 16, Table 4.1)



Figure A.33: Comparison of rate of methane uptake per mole of water at 7.0°C



Figure A.34: Comparison of rate of methane uptake per mole of water at 4.0°C



Figure A.35: Comparison of rate of methane uptake per mole of water at 1.0°C



Figure A.36: Comparison of rate of methane uptake per mole of water at 4.0°C with CC_1



Figure A.37: Comparison of rate of methane uptake per mole of water at 4.0°C with CC₁ and CC₂



Figure A.38: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 1, Table 4.2)



Figure A.39: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 2, Table 4.2)



Figure A.40: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 3, Table 4.2)



Figure A.41: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 4, Table 4.2)



Figure A.42: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 5, Table 4.2)



Figure A.43: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 6, Table 4.2)



Figure A.44: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 7, Table 4.2)



Figure A.45: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 8, Table 4.2)



Figure A.46: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 9, Table 4.2)



Figure A.47: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 10, Table 4.2)



Figure A.48: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 11, Table 4.2)



Figure A.49: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 12, Table 4.2)



Figure A.50: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 13, Table 4.2)



Figure A.51: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 14, Table 4.2)



Figure A.52: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 15, Table 4.2)



Figure A.53: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 16, Table 4.2)



Figure A.54: Methane release curve and the rate of methane release per mole of water (Exp. 1, Table 4.2)



Figure A.55: Methane release curve and the rate of methane release per mole of water (Exp. 2, Table 4.2)



Figure A.56: Methane release curve and the rate of methane release per mole of water (Exp. 3, Table 4.2)



Figure A.57: Methane release curve and the rate of methane release per mole of water (Exp. 4, Table 4.2)



Figure A.58: Methane release curve and the rate of methane release per mole of water (Exp. 5, Table 4.2)



Figure A.59: Methane release curve and the rate of methane release per mole of water (Exp. 6, Table 4.2)



Figure A.60: Methane release curve and the rate of methane release per mole of water (Exp. 7, Table 4.2)



Figure A.61: Methane release curve and the rate of methane release per mole of water (Exp. 8, Table 4.2)



Figure A.62: Methane release curve and the rate of methane release per mole of water (Exp. 9, Table 4.2)



Figure A.63: Methane release curve and the rate of methane release per mole of water (Exp. 10, Table 4.2)



Figure A.64: Methane release curve and the rate of methane release per mole of water (Exp. 11, Table 4.2)



Figure A.65: Methane release curve and the rate of methane release per mole of water (Exp. 12, Table 4.2)



Figure A.66: Methane release curve and the rate of methane release per mole of water (Exp. 13, Table 4.2)



Figure A.67: Methane release curve and the rate of methane release per mole of water (Exp. 14, Table 4.2)



Figure A.68: Methane release curve and the rate of methane release per mole of water (Exp. 15, Table 4.2)



Figure A.69: Methane release curve and the rate of methane release per mole of water (Exp. 16, Table 4.2)



Figure A.70: The calculated rates along with the standard errors plotted against different bed volumes for all the decompositions experiments carried out at a driving force of 10.0°C. (CR: experiment 6, CR+CC₁: experiment 11 & 12, CR+CC₁+CC₂: experiment 15 & 16).


Figure A.71: The calculated rates along with the standard errors plotted against different surface areas for all the decompositions experiments carried out at a driving force of 4.0°C. (CR: experiment 6, CR+CC1: experiment 11 & 12, CR+CC1+CC2: experiment 15 & 16).



Figure A.72: The calculated rates along with the standard errors plotted against different surface areas for all the decompositions experiments carried out at a driving force of 10.0°C. (CR: experiment 6, CR+CC1: experiment 11 & 12, CR+CC1+CC2: experiment 15 & 16).



Figure A.73: The calculated rates along with the standard errors plotted against different radiuses of the bed for all the decompositions experiments carried out at a driving force of 4.0°C. (CR: experiment 6, CR+CC1: experiment 11 & 12, CR+CC1+CC2: experiment 15 & 16).



Figure A.74: The calculated rates along with the standard errors plotted against different radiuses of the bed for all the decompositions experiments carried out at a driving force of 10.0°C. (CR: experiment 6, CR+CC1: experiment 11 & 12, CR+CC1+CC2: experiment 15 & 16).



Figure A.75: Comparison of rate of methane release per mole of water for the experiments carried out at the driving force of 10.0°C



Figure A.76: Comparison of rate of methane release per mole of water for the experiments carried out at the driving force of 4.0°C



Figure B.1: Temperature profiles as a function of time for formation at 4.0°C (Exp. 1, Table 4.3)



Figure B.2: Temperature profiles as a function of time for formation at 4.0°C (Exp. 2, Table 4.3)



Figure B.3: Temperature profiles as a function of time for formation at 4.0°C (Exp. 3, Table 4.3)



Figure B.4: Temperature profiles as a function of time for formation at 4.0°C (Exp. 4, Table 4.3)



Figure B.5: Temperature profiles as a function of time for formation at 4.0°C (Exp. 5, Table 4.3)



Figure B.6: Temperature profiles as a function of time for formation at 4.0°C (Exp. 6, Table 4.3)



Figure B.7: Temperature profiles as a function of time for formation at 4.0°C (Exp. 7, Table 4.3)



Figure B.8: Temperature profiles as a function of time for formation at 4.0°C (Exp. 8, Table 4.3)



Figure B. 9: Temperature profiles as a function of time for formation at 4.0°C (Exp. 9, Table 4.3)



Figure B.10: Temperature profiles as a function of time for formation at 4.0°C (Exp. 10, Table 4.3)



Figure B.11: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 1, Table 4.3)



Figure B.12: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 2, Table 4.3)



Figure B.13: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 3, Table 4.3)



Figure B.14: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 4, Table 4.3)



Figure B.15: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 5, Table 4.3)



Figure B.16: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 6, Table 4.3)



Figure B.17: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 7, Table 4.3)



Figure B.18: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 8, Table 4.3)



Figure B.19: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 9, Table 4.3)



Figure B.20: Methane uptake curve and the rate of methane consumption per mole of water (Exp. 10, Table 4.3)



Figure B.21: Comparison of rate of methane uptake per mole of water at 4.0°C



Figure B.22: Comparison of rate of methane uptake per mole of water at 4.0°C with $\rm CC_1$



Figure B.23: Comparison of rate of methane uptake per mole of water at 4.0°C with CC₁ and CC₂



Figure B.24: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 1, Table 4.4)



Figure B.25: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 2, Table 4.4)



Figure B.26: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 3, Table 4.4)



Figure B.27: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 4, Table 4.4)



Figure B.28: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 5, Table 4.4)



Figure B.29: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 6, Table 4.4)



Figure B.30: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 7, Table 4.4)



Figure B.31: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 8, Table 4.4)



Figure B.32: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 9, Table 4.4)



Figure B.33: Temperature profiles and number of moles of gas released per mole of water as a function of time for decomposition (Exp. 10, Table 4.4)



Figure B.34: Methane release curve and the rate of methane release per mole of water (Exp. 1, Table 4.4)



Figure B.35: Methane release curve and the rate of methane release per mole of water (Exp. 2, Table 4.4)



Figure B.36: Methane release curve and the rate of methane release per mole of water (Exp. 3, Table 4.4)



Figure B.37: Methane release curve and the rate of methane release per mole of water (Exp. 4, Table 4.4)



Figure B.38: Methane release curve and the rate of methane release per mole of water (Exp. 5, Table 4.4)



Figure B.39: Methane release curve and the rate of methane release per mole of water (Exp. 6, Table 4.4)



Figure B.40: Methane release curve and the rate of methane release per mole of water (Exp. 7, Table 4.4)



Figure B.41: Methane release curve and the rate of methane release per mole of water (Exp. 8, Table 4.4)



Figure B.42: Methane release curve and the rate of methane release per mole of water (Exp. 9, Table 4.4)



Figure B.43: Methane release curve and the rate of methane release per mole of water (Exp. 10, Table 4.4)



Figure B.44: The average calculated rates along with the standard errors plotted against different surface areas for all the decompositions experiments carried out by depressurization method.



Figure B.45: The average calculated rates along with the standard errors plotted against different radiuses of the bed for all the decompositions experiments carried out by depressurization method.



Figure B.46: Comparison of rate of methane release per mole of water for the experiments with CR



Figure B.47: Comparison of rate of methane release per mole of water for the experiments with CR and CC₁



Figure B.48: Comparison of rate of methane release per mole of water for the experiments with CR, CC₁ and CC₂



Figure B.49: Comparison of rate of methane release per mole of water for all depressurization experiments