HYDRATE DEPOSITION IN WATER SATURATED LIQUID
CONDENSATE PIPELINES

by
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A key uncertainty in oil and gas pipelines is whether or not hydrates deposit on the pipe wall. This work investigated the feasibility of hydrate deposition within liquid condensates, in the absence of free water, via two mechanisms (1) hydrate deposition from particles formed in the bulk phase, and (2) hydrate deposition via hydrates formed on the steel or the existing deposit itself.

Hydrate deposition from particles formed in the bulk phase was investigated by measuring adhesive forces between preformed cyclopentane (CyC5) hydrates and carbon steel (CS). These forces were found to be significantly lower than CyC5-CyC5 measurements and slightly lower than ice-CS forces. The measured force of 2 mN/m* was used in a particle removal force balance assuming the hydrate particles were within the viscous boundary layer. The force balance calculations predicted hydrates, 3 microns or larger, would be removed during typical pipeline operating conditions.

These predictions suggest that entrained particles will not deposit on the pipe wall in the absence of free water. However, experimental observations demonstrated that hydrates formed on the steel surface had a significantly higher force than the preformed particles and would likely remain on the pipe wall under normal operating conditions. Because the pipe wall is the coldest point in the system and provides the most nucleation sites, it is probable that deposition via hydrate formation at the steel/hydrate interface occurs in pipelines.

Hydrate deposition via formation at the steel/hydrate interface was investigated using a single pass flowloop with a dissolved water condensate. Equilibrium water concentrations in the presence of hydrate/ice were measured using the test section
outlet water concentrations. Four deposition experiments were conducted, in which two different hydrate/ice plugging mechanisms were observed:

1. A rapid pressure drop increase (>1 psi/hour) was observed when the condensate was cooled past the liquid water (L_w) saturation curve. Crossing the L_w saturation curve resulted in free water coalescing and forming a localized hydrate/ice restriction in the flowloop.

2. Uniform/dispersed deposition from a dissolved water phase resulted in a slow pressure drop increase (<1 psi/hour) throughout the first 40–120 ft of the flowloop. During uniform/dispersed deposition it was found that the hydrate/ice deposit acted as insulation on the pipe wall, resulting in the solid deposit propagating downstream.

The uniform hydrate/ice deposits were removed using two approaches: (1) dehydrating the inlet condensate stream and (2) injecting methanol. Dehydrating the condensate stream reduced the inlet water concentration below the 2-phase equilibrium concentration, while the outlet concentration remained at the equilibrium concentration. This behavior was accompanied by a decrease in pressure drop as hydrate/ice was removed from the test section wall. MeOH was similarly effective at removing solid deposits.

A mass and energy balance was used to model the uniform/dispersed deposit from dissolved water. One set of modeling parameters was used to model three experiments (2 deposition experiments and 1 dissociation experiment) with reasonable accuracy, assuming an ice deposit with a 67% void fraction.
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Chapter 1

INTRODUCTION

In the mid-1930s, Hammerschmidt determined hydrates were plugging natural gas transmission lines, marking the beginning of clathrate hydrate research in the oil and gas industry (Hammerschmidt, 1934). Clathrate hydrates are crystalline inclusion compounds wherein hydrogen bonded water molecules form “host” cages containing “guest” molecules (Sloan and Koh, 2008). Hydrates form at high pressures and low temperatures, similar to flow line conditions on the seafloor. Because hydrocarbons act as “guest” molecules, offshore pipelines are prime candidates for hydrate formation and plugging. In addition to lost production and revenue, hydrates pose a significant safety hazard. Hydrate plugging often results in severe pressure increase upstream of the plug. This increased pressure may result in rupturing of the pipeline or a hydrate projectile if the plug is dislodged (Sloan, 2000). The potential plugging capability of a hydrate plug can be seen in Figure 1.1.

1.1 Introduction to Hydrates

The three most common gas hydrate crystal structures are: Structure I (sI), Structure II (sII), and Structure H (sH). As shown in Figure 1.2, the sI unit cell consists of 46 water molecules, which form two small cages ($5^{12}$) and six large cages ($5^{12}6^2$). Common nomenclature for describing a cage, $X^Y$, was suggested by Jeffrey (1984), where $X$ represents the number of sides per face and $Y$ is the number of faces per cage. For example, the $5^{12}$ cage is comprised of twelve pentagonal faces. The sII
Figure 1.1. Hydrates recovered at the pig receiver of a Petrobras® rig, Campos basin 2001.
unit cell contains 136 water molecules arranged in sixteen small cages ($5^{12}$) and eight large cages ($5^{12}6^4$). The third hydrate structure, sH, is formed by 34 water molecules arranged in three different sized cages: three small cages ($5^{12}$), two medium cages ($4^{3}5^{6}6^{3}$), and one large cage ($5^{12}6^8$).

Figure 1.2. Building blocks for each of the three major hydrate structures sI, sII, and sH. Cage illustrations made by K.T.Miller using CrystalMaker®.

Hydrate structure, equilibrium temperature, and equilibrium pressure depend on the guest molecules present. This work focuses primarily on sII hydrates, which is the most common structure in the petroleum industry. Detailed discussions on the guest molecule’s effect on hydrate structure can be found in *Clathrate Hydrates of Natural Gases* (Sloan and Koh, 2008).
1.2 Hydrates In Flow Assurance

Flow assurance is the practice of ensuring production fluids are successfully transported from the wellhead to the production platform, refinery, or gas market. As shown in Figure 1.3, flow assurance typically deals with the portion of pipe between the wellhead and the top of the riser.

![Figure 1.3. Schematic illustrating the flowline connecting the wellhead to the production platform (reprinted from Sloan (2000)).](image)

Major issues in flow assurance include plugging and deposition from hydrates, waxes, and asphaltenes. A recent study involving interviews with 45 senior flow assurance engineers concluded that waxes are ten times the problem as asphaltenes and hydrates are ten times the problem of waxes (Sloan, 2004). Severe economic and safety ramifications of hydrate plugging have led the petroleum industry to operate...
in a hydrate preventative mode. Throughout the past 70 years, hydrate phase equilibria has developed to the extent that flow assurance engineers now have a variety of commercial and proprietary hydrate prediction models at their disposal (Mehta and Klomp, 2005). These tools allow operators to accurately predict the amount of thermodynamic inhibitors (e.g. methanol or monoethylene glycol) required to completely prevent hydrate formation.

Although the petroleum industry has been remarkably successful preventing hydrate formation through thermodynamic inhibition or pipe insulation, industry is shifting towards hydrate management. Hydrate plugging potential is escalating as offshore production moves to deeper water with longer tiebacks and higher pipeline pressures (Mehta and Klomp, 2005). These increasingly adverse operating conditions, combined with aging production fields and higher watercuts, are beginning to limit the economic feasibility of preventing hydrates via thermodynamic inhibitors. As industry shifts towards hydrate management, a central question is whether production fluids can be successfully produced while operating within the hydrate stability zone.

1.3 Thesis Objectives and Outline

Throughout the past five years, several researchers such as, Turner et al. (2005), Carmargo and Palermo (2002), and Hernandez et al. (2006) have investigated hydrate formation and plugging in oil pipelines. However, with the exception of a conceptual predictive model by Shagapov and Urazov (2004), little work has been completed for predicting hydrate formation and plugging in export gas pipelines. As the energy demand continues to increase, projects such as the Alaska gas pipeline are beginning to take form and will require predictive hydrate formation and plugging models.

A key uncertainty in gas pipelines is whether or not hydrates deposit on the pipe
wall (Matthews et al., 2006). The principle objective of this thesis is to investigate conditions which result in hydrate deposition within a liquid condensate system in the absence of a free water phase. Below, is a list of the individual chapters in this thesis and a brief overview of their purpose:

Chapter 2 presents the need for a hydrate formation and plugging model. This chapter details the difference between oil and gas systems and reviews the current state of the art in gas pipeline hydrate plugging mechanisms.

Chapter 3 defines the scope of this thesis and discusses why the scope of this thesis is limited to water saturated systems (no free water). Two possible hydrate deposition mechanisms are also discussed.

Chapter 4 probes hydrate deposition from hydrates formed in the bulk phase. Adhesive forces between hydrates and steel are measured then applied to a force balance.

Chapter 5 investigates hydrate/ice deposition at the pipe wall using a single pass flowloop.

Chapter 6 discusses a hydrate/ice wall growth model, which is used to match flowloop data.

Chapter 7 applies the model to field conditions and investigates the model’s limitations.

Chapter 8 discusses major conclusions of this thesis and Chapter 9 follows up with future work and recommendations.
Chapter 2

NEED FOR A HYDRATE FORMATION AND PLUGGING MODEL

A model capable of predicting hydrate formation and plugging characteristics in oil and gas pipelines is necessary in helping industry move from hydrate prevention to hydrate management. Such a model would have two immediate impacts:

1. Pipeline design. Knowledge of hydrate formation and plugging will allow optimization of: insulation, electrical heating, chemical injection, geometry, and maximum tieback length. Models will also provide valuable parameters for completing decision and risk analysis throughout the design phase.

2. Pipeline operation. As energy companies develop projects in deeper water and colder environments, they will have a better understanding of operational limits and the associated plugging risk. By predicting where and when plugging is likely to occur, it may be possible to monitor problematic sections of a pipeline and remedy hydrate plugging prior to catastrophic failure.

2.1 Colorado School of Mine’s Hydrate Plugging Model (CSMHyK-OLGA) In Oil Pipelines

The Center for Hydrate Research at Colorado School of Mines (CSM) is currently developing the second generation of CSMHyK. CSMHyK is a hydrate formation simulator that is run concurrently with OLGA®2000 to model hydrates in oil pipelines.
OLGA®2000, developed by ScandPower Petroleum Technology, is the industry standard transient multiphase flowline simulator. Figure 2.1 shows CSM’s conceptual hydrate model for oil systems. The model assumes water is entrained in oil phase before being encrusted by a hydrate film and forming individual hydrated droplets (Turner et al., 2005). The hydrated particles then agglomerate, thereby increasing the effective viscosity of the hydrate slurry. The quantitative model is run in CSMHyK-OLGA using a first order reaction rate to predict hydrate formation and dissociation. The Camargo-Palermo model is then used to predict effective viscosity (Carmargo and Palermo, 2002). CSMHyK considers the oil flowline to be plugged after the effective viscosity becomes sufficiently high to prevent flow.

Figure 2.1. Conceptual picture of CSM’s hydrate plugging model in oil pipelines.

This laboratory has successfully modeled hydrate formation for four different oils in two separate flow loops using one pair of fitted parameters. Additionally, the model’s flow loop pressure drop predictions show the same qualitative behavior as experimental pressure drop (pressure drop is the only quantitative means of measuring plugging in a flowloop). Ongoing work in this lab is currently focusing on refining both the hydrate formation model and the agglomeration model for the CSMHyK-OLGA
model. Although the early success of the CSMHyK-OLGA model is encouraging, the model is only designed for oil pipelines (fully emulsified water) and does accurately predict gas pipeline data (Davies et al., 2008). Thus the focus of this proposal is to form the building blocks for a hydrate prediction model in a gas pipeline.

2.2 Differences Between Oil and Gas Pipelines

Two major differences exist between oil and gas pipelines:

1. Liquid loading. Oil pipelines have a much higher liquid content than gas pipelines. The oil model assumes water is fully dispersed in the oil phase and the hydrocarbons required for hydrate formation are supplied by the oil phase. Conversely, in gas pipelines the water-gas condensate interactions are unknown and hydrates are likely to form at either the water-gas interface, water-gas condensate interface or from a super-saturated gas phase.

2. Flow regimes. Oil pipelines typically flow in either slug or stratified flow, while gas pipelines are generally operated in stratified, stratified-wavy, or annular-mist flow. Predicting hydrocarbon-water interfaces in stratified-wavy and annular-mist flows is difficult. See Appendix A for descriptions of the various flow regimes.

The combined low solubility of hydrocarbons in water and low water vapor pressure typically limits hydrate formation to the water-hydrocarbon interface. As discussed above, predicting the hydrocarbon-water interface may be more difficult for a gas pipeline, thus creating difficulties in predicting hydrate formation rate. Furthermore, the low liquid fraction and annular-mist flow regimes complicate the plugging mechanism because hydrate deposition on the pipe wall may occur. CSMHyK-OLGA
currently predicts hydrate plugging through an increase in relative viscosity, whereas gas pipelines are more likely to plug from a large hydrate agglomerate, hydrate slurry buildup or hydrate deposition as suggested by Lingelem et al. (1994). Speculation of a deposition mechanism is fueled by the fact that gas pipelines often operate in the annular-mist flow regime, where hydrates may form on entrained droplets and stick to the water wet pipe walls. Additionally, several field and flowloop studies indicate that a hydrate deposition mechanism may have occurred in the respective tests.

2.3 Previous Field and Laboratory Studies

The following sections discuss the prior relevant hydrate plugging and deposition studies completed to date. Notably, two hydrate plugging tests in field gas pipelines and one flowloop test.

2.3.1 Hydrate Plugging in Field Gas Pipelines

Two prominent hydrate tests previously conducted in field gas pipelines are: (1) Werner Bolley, and (2) Gamma Tomelitten.

*Werner Bolley Field Test*

The Werner Bolley field study was conducted in an aging Wyoming gas field in 1997. Gas, condensate, and water rates in the flowline were typically 4 million standard cubic feet per day (MMSCFD), 100 barrels of condensate per day (BCPD), and 10 barrels of water per day (BWPD), respectively. Four hydrate forming tests were conducted, in which methanol injection (thermodynamic inhibition) was stopped and the line was then pigged (a method of sweeping fluids and solids from the pipeline). Normal production was then resumed until hydrates formed (Hatton and Kruka, 2002).
Pressure and gamma-ray densitometer measurements were made throughout the course of the four Werner Bolley field trials. Pressure measurements were taken from five different bellhole locations (access locations to the buried pipeline). An elevation profile, showing the various bellhole locations, is shown in Figure 2.2. Figure 2.2 also shows the location of the gamma-ray densitometer, used to measure flowline density changes, in the fourth bellhole.

Figure 2.2. Elevation profile for Werner Bolley pipeline (modified from Hatton and Kruka (2002)).

Hydrate formation from the four tests was broken into four subcategories (Hatton and Kruka, 2002):

1. Early-stage behavior (ESB). During the ESB time period, gradual pressure-drop increases were measured throughout the system. Hatton and Kruka (2002)
hypothesized the gradual pressure drop increase was due to hydrates displacing liquid condensate holdup in the pipeline.

2. Middle-stage behavior (MSB). The MSB period was represented by cycles of pressure buildup and collapse across upstream sections of the pipeline. These pressure differences were translated downstream as the cycle continued.

3. Final-stage behavior (FSB). FSB was defined as the period when hydrate restrictions were freed, thereby colliding with downstream restrictions until a blockage preventing flow was formed.

4. Post-flow behavior (PSB). PSB occurred after the line had been fully plugged. Upstream pressure was maintained at the same pressure that stopped flow. The clearing process then took place, in which the line was depressurized.

Deciphering the plugging mechanism in gas pipelines is a critical step in developing a hydrate formation and plugging model. The MSB behavior is of particular interest, because this period shows the magnitude of the pressure fluctuations rapidly increased until a plug was formed. One pressure buildup and falloff cycle is shown in Figure 2.3.

P1 represents the pressure reading at bellhole 1 (Figure 2.2), similarly, P2 - P5 represent the pressure readings from bellholes 2 - 5. Figure 2.3 shows a gradual pressure increase at sites 1 and 2 at approximately 23:20. However, a pressure increase was not observed at sites 3 - 4, indicating a blockage between sites 2 - 3. Approximately 20 minutes later, the pressure increase fell off and pressure fluctuations were observed at sites 3 - 4. This pressure fall off and consequent pressure fluctuations indicate the blockage broke free and was transported downstream. Evidence of the blockage being transported downstream was also observed in the gamma-ray densitometer.
Figure 2.3. Pressure buildup and falloff cycle in the Werner Bolley field study (modified from Hatton and Kruka (2002)).
reading (left ordinate), which had a sharp spike in concurrence with the pressure fluctuations. Flow rate also spiked, as indicated by the yellow curve, which represents pressure drop across an orifice plate in bellhole 1. Pressure drop across the orifice plate was measured in inches of water (IOW). These pressure fluctuations, gamma ray measurements, flow rates are a typical example of middle-stage behavior (MSB), showing a hydrate blockage and release. These buildup and release cycles eventually led to plugging of the pipeline.

_Tommeliten Gamma Field Test_

Hydrate experiments were also conducted in the Tommeliten Gamma field, located in the North Sea. Field experiments were carried out in a 6 inch test/service line in 1994. Hydrates were formed by both reducing chemical inhibition and reducing gas flow rate, thereby decreasing the flowline temperature. Several observations in Austvik’s study were (Austvik et al., 1995):

1. Pressure fluctuations were observed prior to plugging.

2. Hydrate plugs formed in most experiments.

3. Hydrates were observed to be transported through the system without sticking to the pipe wall (particularly during plug dissociation).

The Werner Bolley and Tommeliten Gamma field tests provide valuable insight into the hydrate plugging mechanism in gas pipelines. Both studies show pressure fluctuations prior to complete plugging of the flowline, indicating hydrates form partial plugs that become dislodged. These partial plugs eventually form one large plug, completely restricting flow. A key question to be addressed is whether the partial plugging is a result of hydrate agglomeration or hydrate deposition on the pipe wall.
2.3.2 Flowloop Studies

Because flowline data are not readily available and are extremely expensive and difficult to produce, flow loops are commonly used to investigate flowing systems. Flow loops range in size from $\frac{1}{2}$ - 4 inch inner diameter and from several feet to several hundred feet in length. Fluids are typically propelled through the loop with some type of pumping device.

Numerous hydrate studies have been performed in flowloops, however, the majority of these flowloop studies have only investigated high liquid systems. The lack of gas dominated studies is due, in large part, to flow loop limitations. Most flow loops are equipped with multiphase pumps, which require high liquid loading in order to prevent overheating. Among the few low liquid studies performed, only two have been published.

Matthews et al. (2000) performed experiments using gas compositions comparable to the Werner Bolley field study. This study primarily investigated conditions in which hydrate formation occurred. In conjunction with the Werner Bolley study, hydrates were found to form whenever there is a combination of liquid holdup and a subcooling (degrees below equilibrium temperature) of 6.5°F. Matthew's flow loop study provided valuable insight into hydrate formation, but relatively little information regarding the plugging mechanism.

The second flow loop study investigating gas systems was published by Dorstewitz and Mewes (1993). R-134a (1,1,1,2-tetrafluoroethane) was used as a model hydrate former, permitting hydrate formation at low pressures (~17 psia at 4°C). Hydrates were observed to first form on the pipe wall at the water-gas interface. The hydrate layer then grew along the pipe wall, until the entire perimeter of the pipe was covered with hydrates. This stenosis (inward growth of deposits) buildup on the
pipe wall has been suggested as a possible plugging mechanism in gas pipelines and is a direct analogy from ice formation in water pipes (Lingelem et al., 1994).

A third flowloop study, illustrating the possibility of hydrate deposition, was never published. The experiments were conducted by the Southwest Research Institute (SWRI) in San Antonio, TX. The SWRI study showed evidence of a stenosis buildup as shown in Figure 2.4 (Hatton and Kruka, 2002).

Figure 2.4. Stenosis buildup in the SWRI flowloop (reprinted from Hatton and Kruka (2002)).

Following the SWRI study, a hypothesis was developed that a stenosis buildup
may be occurring in gas pipelines. For example, in the Werner Bolley field study, the pressure increase at sites 1 and 2 (Figure 2.2 and 2.3) may have been due to a stenosis buildup as shown in Figure 2.4. If stenosis occurred in the Werner Bolley study, the sudden decrease in pressure at sites 1 and 2 would represent sloughing of the hydrate buildup (Hatton et al., 2005). However, there was concern about translating stenosis buildup in the flow loop to an actual pipeline (Matthews et al., 2006). The stenosis buildup in Figure 2.4 may have been a result of a short test section or the manner in which water was added to the system, preventing a fully developed flow regime. Although SWRI and Werner Bolley tests helped develop the hypothesis of hydrate deposition in gas pipelines, fundamental investigations were required to verify this hypothesis.

2.3.3 Bench Top Deposition Experiments

Burgass and Tohidi (2003) investigated solid deposition using a quartz crystal microbalance (QCM). The QCM was sensitive to mass changes as minute as 1 nanogram. Various surface coatings were applied to the QCM, which was then placed in a stirred tank containing either wax, sea water (scaling) or hydrates. Mass changes on the QCM were measured to investigate the effect of different coatings. Surface coatings were found to have a significant impact in the scale and wax deposition experiments. Conversely, hydrate deposition was never detected on the QCM, regardless of the surface coating. The QCM provides a unique way of comparing relative deposition rates between various surface coatings. However, measuring any parameters that are directly transferable to pipeline geometries is difficult with the QCM apparatus. The combined difficulties of relating stirred tank phenomena to pipeline geometry and the inability to measure hydrate deposition, despite the surface coating, suggest the
QCM is an inappropriate tool for the present study.

2.4 Current State of the Art

As hydrate formation and plugging models for oil pipelines continue to mature, there is a growing focus on a gas pipeline formation and plugging model. The need for a gas pipeline hydrate plugging model is further accelerated by the growing demand for natural gas and the resulting projects, such as the Alaska North Slope gas pipeline (Sutton, 2008).

Previous field experiments exhibited pressure buildup behavior, which was followed by pressure fluctuations and rapid pressure fall offs (prior to hydrate plugging). This pressure behavior can be explained by either hydrate slurry and agglomerate buildup or hydrate deposition on the pipe wall. Both scenarios indicate a restriction as pressure builds up and a release in the restriction as the pressure falls off.

The two flowloop experiments conducted by Dorstewitz and Mewes (1993) and SWRI (Figure 2.4) indicate that hydrate deposition on the pipe wall is possible. However, questions still surround the flowloop geometries, methods of injecting water, and use of refrigerant hydrate formers.

The combination of field and flowloop data has helped develop a hypothesis of hydrate deposition in gas pipelines; however, further fundamental experiments are required to confirm this hypothesis. The current work studies the feasibility of hydrate deposition on the pipe wall, which is suspected as a fundamental plugging mechanism in gas pipelines. As discussed in the subsequent chapter, the scope of this thesis is further refined by focusing on water saturated pipelines (such as export and residential gas lines), rather than pipelines containing a free water phase.
Chapter 3

WATER SATURATED PIPELINES IN THE ABSENCE OF FREE WATER

Chapter 2 discussed the need for a hydrate plugging model in gas pipelines. Determining the role of deposition in gas systems will help advance a hydrate plugging model. However, as discussed in Appendix A, gas pipelines operate in many different flow regimes and each is likely to have a unique deposition mechanism. In addition, gas condensates do not typically emulsify water, so the mechanism in Figure 2.1 is neglected. Due to the complexity of varying flow regimes and deposition mechanisms, the scope of the problem must be narrowed to focus on a fundamental aspect of hydrate deposition. The author has chosen to narrow the scope of the current project by focusing on water saturated condensate systems in the absence of free water.

Eliminating free water from the scope of investigation significantly reduces a number of unknowns. Eliminating free water also allows for a fundamental study in the most basic gas pipeline scenario, which will serve as a key building block in advancing future deposition models.

3.1 Application to the Field

Predicting hydrate formation and deposition in water saturated systems has a direct application to gas export and sales pipelines. Prior to entering sales lines, gas is usually dehydrated to 4–7 lb water/million standard cubic feet (MMscfd). Occasionally, these specifications are still within hydrate formation conditions (Kane
Potential of operating within the hydrate formation becomes exacerbated when flowline conditions fluctuate with ambient temperatures, which is the case in many onshore pipelines. Gas export and sales lines affected by seasonal temperatures include: arctic pipelines (e.g. Alaska pipeline), residential pipelines, and other lines exposed to harsh winters. This work will allow gas companies to predict the consequences of operating slightly inside the hydrate formation conditions during seasonal cool downs. Such a model will also be beneficial in planning maintenance procedures such as pigging.

In a recent publication by Kane et al. (2008), the authors explain that export pipelines often operate within the hydrate stability region, even while meeting contractual obligations. The Kane et al. (2008) publication discusses a hydrate blockage which developed in the gas export pipeline of the Matterhorn platform operated by TOTAL. Approximately four days before the restriction was detected, the re-boiler in the glycol dehydration unit malfunctioned and resulted in ‘off-specification’ gas. After detecting the plug, production was shut-in for 3 days while the hydrate plug was dissociated (a plug prior to this incident resulted in 16 days of lost production). Situations similar to the Matterhorn platform would benefit from a predictive model that could be used in the event of a dehydrator malfunction.

3.2 Hydrate Deposition Mechanisms

The present work pertains specifically to hydrate formation from a water saturated phase. This phenomenon is illustrated in Figure 3.1. The vertical blue line in Figure 3.1 designates the area of focus in this thesis. To the right of the blue line, hydrates will form directly from the vapor or condensate phase, without moving through a liquid water phase.
Two possible mechanisms are possible for hydrate deposition, as illustrated in Figure 3.2:

1. Hydrate formation in the bulk fluid and subsequent deposition on the pipe wall (Figure 3.2 (1)).

2. Hydrate formation on the pipe wall itself (Figure 3.2 (2)).
Figure 3.1. Methane hydrate T-x phase diagram, illustrating the area of focus in this thesis (modified from Huo et al. (2003)). Note that this diagram is not drawn to scale. Certain portions of the diagram have been enlarged to illustrate all phase regions, thus the ordinate cannot be labeled with the absolute temperature.
Figure 3.2. Possible deposition mechanisms investigated in this thesis (1) formation in the bulk phase and subsequent deposition, and (2) hydrate growth directly on the pipe wall.
3.3 Experimental Techniques to Investigate Hydrate Deposition

Each of the aforementioned deposition mechanisms was investigated using a separate experimental apparatus and technique.

3.3.1 Hydrates Formed In the Bulk Phase

Hydrate deposition from hydrates formed in the bulk fluid phase was investigated through a combination of adhesive force measurements and force balances. The present work expands upon the work of Taylor (2006) in which adhesive forces between hydrate particles and stainless steel were measured. Taylor’s experimental procedure was modified to measure adhesive forces between cyclopentane hydrate and steel. These forces were used in a force balance model to predict whether hydrate particles would deposit on the pipe wall.

3.3.2 Hydrates Formed On the Pipe Wall

Hydrate formation/deposition at the pipe wall was investigated using a single-pass flowloop which was designed, built, and operated, at the Intertek Westport Technology Center. The experimental program was supported by Imperial Oil, ExxonMobil, Shell, and ConocoPhillips.

Experiments were conducted to investigate hydrate plugging mechanisms in a water saturated condensate system. The test fluid was cooled in a test section, before being reheated and reconditioned with dissolved water. Reconditioning the condensate allowed the test fluid to enter the test section at a constant composition and temperature over the course of several days. Solid deposition on the pipe wall was detected by measuring pressure drop in the test section.
3.3.3 Using Condensate as an Analogy for Gas

Adhesive force measurements were conducted using cyclopentane as a bulk fluid, which allowed sII hydrates to be measured at atmospheric conditions. Cyclopentane was also deemed more suitable than alternative low pressure hydrate formers (e.g. tetrahydrofuran) because cyclopentane is immiscible with water, similar to pipeline hydrate formers like methane and ethane. The differences in gas and liquid properties were accounted for in the force balance model.

Gas condensate was used as an analog for gas in flowloop experiments. Using a liquid phase significantly reduced operational difficulties, by eliminating the need for a gas compressor. Additionally, reconditioning the gas phase with water would have been extremely difficult. The hydrate growth mechanism on the pipe wall is expected to be similar for both gas and liquid condensate systems (as long as the correct fluid properties are taken into account). Details of extrapolating the condensate wall growth model to gas systems are discussed in Chapter 7.

The present work used liquid condensate in both the adhesive force measurements and the flowloop experiments. The use of liquid condensate was necessary to reduce the technical difficulties associated with the experiments. The following chapters in this thesis discuss how the liquid condensate results were extrapolated to gas systems.

3.4 Advancing the Current State of the Art

The role of hydrate deposition in gas pipelines is currently unknown. This thesis investigates the feasibility of hydrate deposition from a water saturated phase as illustrated in Figure 3.1. Two possible deposition mechanisms were investigated using: (1) adhesive force measurements and a force balance, and (2) a single pass flowloop apparatus. The results of these experiments will allow gas operators to predict hydrate
deposition in sales export lines and serve as an initial starting point for developing a hydrate deposition model in gas pipelines containing a free water phase.
Chapter 4

HYDRATE DEPOSITION FOLLOWING FORMATION IN THE BULK PHASE

Chapter 3 discussed two possible hydrate deposition mechanisms from a dissolved water phase. This chapter investigates deposition following hydrate formation in the bulk phase. The present analysis was completed using a combination of adhesive force measurements and force balance predictions.

4.1 Particle Removal in Colloidal Literature

Numerous studies have been conducted on particle removal (Cleaver and Yates, 1973; Burdick et al., 2001, 2005; Yiantsios and Karabelas, 1995). Typically these studies have focused on industrial processes, such as contaminant removal from wafer surfaces. The studies of interest used laminar flow channels to investigate hydrodynamic removal of polystyrene particle spheres adhering to a quartz surface. In past studies, several authors have experimentally validated hydrodynamic force balance models for particle removal (Burdick et al., 2001, 2005; Yiantsios and Karabelas, 1995). This work used a similar approach to investigate the feasibility of hydrate deposition from the bulk fluid phase.

Figure 4.1 illustrates a hydrodynamic force balance on a particle in laminar flow. Using this force balance, particle removal is possible via three different mechanisms: (1) rolling, (2) sliding, and (3) lifting. The removal mechanism can be predicted using the force balance illustrated in Figure 4.1, which requires knowledge of the following
parameters: adhesive force between the particle and surface, shape of the particle, fluid properties, and the fluid velocity profile.

Figure 4.1. Hydrodynamic force balance on a particle in laminar flow (modified from Burdick et al. (2005)).

Adhesion force (F_A), drag force (F_D), lift force (F_L), gravity (F_g), and buoyancy (F_B) all act on the particle of diameter, d. Additionally, there is one external moment of surface stresses (M_D), acting through the center of the particle. Predicting F_A is typically the crux of the problem in colloidal literature. The difficulty of predicting F_A was circumvented in this study by directly measuring the adhesive forces between cyclopentane (CyC5) hydrates and carbon steel.

O’Neill (1968) derived an exact solution of linearized Stokes flow equations for viscous flow around a fixed sphere in contact with a fixed plane wall as shown in Equations 4.1 and 4.2.
\[ F_D = 1.7009 \times 3\pi \mu d V_p \] (4.1)

\[ M_D = 0.943993 \times 2\pi \mu d^2 V_p \] (4.2)

where \( V_p \) is the fluid velocity at the center of the particle, \( \mu \) is the dynamic fluid viscosity, and \( d \) is the particle diameter. The constants, 1.7009 and 0.943993, account for surface effects on the drag force and external moment, respectively. The Saffman lift force \( (F_L) \) is calculated using (Saffman, 1965)

\[ F_L = 1.615\mu d^2 \left( \frac{\rho}{\mu} \frac{du}{dz} \bigg|_{z=d/2} \right)^{1/2} V_p \] (4.3)

where \( \rho \) is the fluid density, \( u \) is the fluid velocity parallel to the surface and \( z \) is the direction normal to the surface (Busnaina et al., 1993). Using the force balance in Figure 4.1, it can be determined that the lifting mechanism occurs when

\[ F_L + F_B \geq F_A + F_g \] (4.4)

whereby the particle is removed in the vertical direction. The sliding criterion

\[ F_D \geq f(|F_A + F_g| - F_L - F_B) \] (4.5)

is derived from the force balance in the horizontal direction, where \( f \) is the static coefficient of friction between the particle and surface. Finally, the criterion for rolling is

\[ M_D + F_D \cdot l_1 + (F_L + F_B) \cdot l_2 \geq (F_A + F_g) \cdot l_2 \] (4.6)
where $l_1$ and $l_2$ are the vertical and horizontal moment arms (surface roughness) around which the particle rolls (Burdick et al., 2005; Sharma et al., 1991).

4.2 Adhesive Force Measurements

As discussed in the previous section, the adhesive force between hydrates and steel is the key unknown in predicting hydrate removal. Past studies have measured attractive forces between both ice particles and hydrate particles.

4.2.1 Previous Force Measurements

Holser et al. (1957) measured adhesive forces between ice spheres while investigating aggregation in clouds. As shown in Figure 4.2, Hosler measured an increase in adhesive forces as the temperature was increased (subcooling represents the melting temperature minus the experimental temperature). The exponential increase in adhesion force was suspected to be a result of an increased quasi-liquid layer on the ice spheres as temperature was increased towards the melting point ($0^\circ$C).

Evidence of a quasi-liquid layer was measured by Petrenko (1997) and Doppen-schmidt and Butt (2000) using scanning force microscopy and atomic force microscopy, respectively. Both studies measured a liquid-like layer on the surface of ice at sub-freezing temperatures. Similar to the measurements in Figure 4.2, Doppen-schmidt measured an exponential increase in the liquid-like layer thickness as temperature was increased (Figure 4.3).

Fan et al. (2003) measured the adhesive forces between ice particles in both air and sucrose. The authors found that adhesion force between ice particles increased with particle size and contact time. They were also able to model their data using Johnson-Kendall-Roberts (JKR) solid adhesion theory. The authors did note that the
Figure 4.2. Force to separate ice spheres as a function of subcooling (data adapted from Holser et al. (1957)).
Figure 4.3. Thickness of liquid-like layer on ice as a function of subcooling from melting (adapted from Doppenschmidt and Butt (2000)).
theory was unlikely to be completely correct due to two reasons: (1) the ice particles are not elastic, and (2) a well known liquid layer exists on ice surfaces at sub-freezing temperatures.

Later, this lab measured adhesive forces between both ice particles and tetrahydrofuran (THF) hydrate particles (Yang et al., 2004; Taylor, 2006; Taylor et al., 2007). These measurements were completed using n-decane as the bulk fluid surrounding the hydrates. Similar to Hosler’s work, the THF hydrate measurements found that adhesive forces increased with increasing temperature (decreased subcooling). The temperature dependence of the adhesive forces was attributed to capillary forces, assuming the particles were joined by a liquid bridge as illustrated in Figure 4.4.

![Figure 4.4. Illustration of ice or hydrate particles surrounded by a quasi-liquid layer and being joined by a capillary bridge](image)

As a part of larger scoping study, Taylor (2006) also conducted preliminary adhesive force measurements between cyclopentane (CyC5) hydrates. Taylor’s technique was further refined by Dieker et al. (2008). Dieker found THF hydrates to be a poor
model system for pipeline hydrates due to two reasons:

1. Unlike pipeline hydrate formers, which are immiscible in water, THF is miscible in water.

2. THF adhesive force measurements almost always suffer from ice/liquid contamination, as illustrated in Figure 4.5. The stoichiometric ratio of THF in water is 5.56 mol% THF, as illustrated by the vertical line in Figure 4.5. Above 5.56 mol% THF ratio, a THF liquid is present; below the ratio, water or ice is present. Because THF is volatile, the THF concentration in hydrate particles decreases with time, resulting in water/ice contamination of the sample.

Figure 4.5. THF/water T-x diagram, modified from Dyadin et al. (1973)
Figure 4.6 shows Dieker’s adhesive force measurements between CyC5 hydrate particles. Similar to Hosier’s measurements, the forces increased with decreasing subcooling (increased temperature). The melting temperature of CyC5 hydrate at atmospheric conditions is 7.7°C (Sloan and Koh, 2008).

![Figure 4.6. Adhesive force measurements between cyclopentane hydrate particles. The error bars represent the standard deviation of the measurements and the points correspond to the average value of each experiment (Dieker et al., 2008).](image)

Each point in Figure 4.6 represents approximately 40 measurements with the same particles. The points represent the average value and the error bars represent
the standard deviation of the forces measured. The adhesive forces were normalized using the harmonic mean radius:

$$\frac{1}{R^*} = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$  \hspace{1cm} (4.7)

where $R^*$ is the harmonic mean radius and $R_1$ and $R_2$ are the radii of the two particles.

The work discussed in this section laid the foundation for analyzing adhesive forces between hydrate particles and steel.

### 4.2.2 Comparison of Adhesive Forces Models

Adhesive forces between the cyclopentane hydrates are likely explained via van der Waals forces, capillary forces (Israelachvili, 2000), Johnson-Kendall-Roberts (JKR) theory (Johnson et al., 1971), or Derjaguin-Muller-Toporov (DMT) theory (Derjaguin et al., 1975). Van der Waals forces between spheres are calculated using

$$\frac{F_A}{R^*} = \frac{A}{12D^2}$$  \hspace{1cm} (4.8)

where $A$ is the Hamaker constant and $D$ is the distance between spheres (Israelachvili, 2000). Carmargo and Palermo (2002) estimated the Hamaker constant for hydrate particles was 5.2E-21 J. Assuming the distance between the particles was 1nm, the predicted van der Waals force was $F/R^* = 0.5 \text{ mN/m}^*$. This value is approximately $\frac{1}{4}$ the value of the smallest force measured by Dieker (Dieker et al., 2008). Additionally, Equation 4.8 shows that $F/R^*$ is inversely proportional to the square of the distance between the particles ($D$). Figure 4.7 shows a picture of a CyC5 hydrate particle that is 730 microns in diameter. This figure shows that the surface asperities are on the order of microns (1000 nm). Given the illustrated surface roughness, it is unlikely that
the distance between the particles was less than 1 nm, which would further reduce the predicted van der Waals force of 0.5 mN/m* and suggests that an alternative force dominated the measurements in Figure 4.6.

Figure 4.7. Cyclopentane hydrate on a test cantilever, illustrating the surface roughness of the particle.

Two theories commonly used to explain solid contact between spheres are JKR and DMT models. These models incorporate the surface energy between the particles and the surrounding medium. Heim and Blum (1999) note that “The JKR is appropriate for large soft bodies with high surface energies. For small, hard solid particles with low surface energy, the DMT model should be applied” (Muller et al., 1983).
The JKR model is defined as (Johnson et al., 1971)

\[ \frac{F_{JKR}}{R^*} = \frac{3}{2} \pi \gamma_{SL} \]  

(4.9)

where \( \gamma_{SL} \) is the solid-liquid interfacial tension between the particle and the surrounding fluid.

The DMT model is defined as (Derjaguin et al., 1975)

\[ \frac{F_{DMT}}{R^*} = 2\pi \gamma_{SL} \]  

(4.10)

and assumes both spheres have identical radii. Recent interfacial tension measurements were completed in this lab, by Jennifer Gallardo, (Gallardo, 2008). Cyclopentane-water interfacial measurements were conducted using a KSV Instruments CAM 200 contact angle meter. The cyclopentane-water interfacial tension was measured to be 45 mN/m. Assuming the cyclopentane-water interfacial tension value is similar to cyclopentane hydrate in cyclopentane fluid, the predicted adhesive forces are 212 mN/m* and 283 mN/m* using the JKR and DMT models, respectively. The predicted JKR and DMT forces are approximately 2 orders of magnitude greater than the measured forces in Figure 4.6. A key assumption in Equations 4.9 and 4.10 is that the particles are smooth. Israelachvili (2000) notes that surface asperities as small as 12 nm may significantly decrease the adhesion. Thus, the discrepancy between the solid adhesion models and experimental data may be explained by the surface roughness illustrated in Figure 4.7. However, neither the JKR nor DMT model accounts for the temperature dependence of the force measurements. Although the interfacial tension is temperature dependent, the values are not likely to change by a factor of 2 over a 5°C range (Zeppieri et al., 2001) as observed in Figure 4.6.
The final adhesive force discussed in this section is the capillary bridge theory. Capillary bridging occurs when a liquid bridge is formed between two particles as demonstrated in Figure 4.4. Capillary bridges form a Laplace pressure, which acts as a force in the form of

\[ \frac{F_{CBT}}{R^*} = 2\pi\gamma_{LL} \cos \theta \]  

(4.11)

where \( \gamma_{LL} \) is the liquid-liquid interfacial energy and \( \theta \) is the liquid contact angle on the solid particle. Assuming \( \theta = 0^\circ \), and \( \gamma_{LL} = 45 \) mN/m, the predicted adhesive force is 283 mN/m. This value is identical to the predicted force using DMT theory.

Similar to the JKR and DMT theory, surface roughness likely results in under predicting the force; however, the capillary bridge theory can be used to explain the temperature dependence of the adhesive forces. Assuming the CyC5 hydrate behaves similar to ice, a quasi-liquid layer existed, which increased with temperature. An increase in the quasi-liquid layer would also increase the contact area and reduce the effects of surface roughness. Taylor (2006) illustrated the effect of surface roughness on capillary forces as shown in Figure 4.8.

Figure 4.8. Example of capillary bridging at (A) low temperatures and (B) high temperatures (reprinted from Taylor (2006)).
Adhesive forces between ice-ice and THF hydrate-THF hydrate forces have been measured by several researchers. Recently Dieker et al. (2008) determined that cyclopentane hydrates are a better model system than THF hydrates. Although the capillary bridge theory significantly over predicts experimental data, this can be explained by the surface roughness of the particles. Additionally, capillary bridging may also explain the temperature dependence of adhesive forces; whereby a quasi-liquid layer increases with temperature and fills in the surface asperities.

4.2.3 Experimental Apparatus

The micromechanical force (MMF) apparatus was developed in our laboratory to measure attractive forces between two particles submerged in a cool liquid. The same apparatus (Figure 4.9) used by Yang et al. (2004), Taylor (2006), and Dieker et al. (2008), was used in this work. Figure 4.9 shows the micromechanical apparatus, which used an inverted light microscope (Carl Zeiss Axiovert S100) to observe the cooling cell attached to the microscope stage. Two micromanipulators were attached to the microscope. One manipulator was a low precision hand-operated manipulator (Narishige MN-151) used to hold a hydrate particle in the microscope’s field view. The second cantilever, a high precision remote operated micromanipulator (Eppendorf Patchman 5173), was used to move the steel sample (see later discussion with Figure 4.11). Digital video images were recorded by a grayscale $1/2$" CCD camera (Cohu, Model 4915–2030) attached to the microscope. The video was digitized using a framegrabber card (Scion, LG3) in a personal computer and subsequently examined using ImageJ (v.1.32j) software.
Figure 4.9. Picture of micromechanical force apparatus (reproduced from Taylor (2006)).
4.2.4 Experimental Technique

As part of a larger scoping study, Taylor (2006) measured adhesive forces between THF hydrates and stainless steel. Taylor’s technique was modified in this work and adhesive forces between CyC5 hydrate and carbon steel were measured.

Oil and gas pipelines are typically constructed out of carbon steel. Therefore carbon steel 318, was selected as the sample surface representative of the pipe wall. The carbon steel samples were prepared in the CSM metallurgy laboratory by polishing 1 cm² pieces of steel and cutting small test samples using a high precision saw. Sample surfaces were polished using either 1 micron diamond polish or 240 grit sandpaper (corresponding to a surface roughness of approximately 59 microns) as shown in Figure 4.10.

![Carbon steel samples polished with 240 grit sandpaper and 1 micron diamond polish, prior to cutting test samples with a high precision saw.](image)

The test samples were cleaned in an ultrasonic bath using an Alcanox detergent solution for 15 minutes. The samples were rinsed with deionized water and again
cleaned in the ultrasonic bath for 15 minutes using acetone. Finally, samples were rinsed with ethanol and dried using a heat gun. After cleaning the samples, they were attached to a cantilever arm, which was controlled by the high precision manipulator (Figure 4.11).

The wettability of the samples was briefly investigated by placing a drop of water on the sample surface (in air). The water was observed to rapidly wet the carbon steel surface to the extent that a wetting angle could not be measured with this laboratory’s equipment. Thus the carbon steel samples were assumed to be water wetting and representative of most pipelines, which are generally made of carbon steel.

Ice and Carbon Steel Measurements

Ice particles used in the ice-carbon steel (CS) measurements were formed by placing a water droplet on the end of the glass fiber (Figure 4.11) and quenching the droplet in liquid nitrogen. The ice particle was then placed in the MMF cooling chamber, containing n-decane. The particles and the CS sample were maintained at constant temperature for 30 minutes, prior to testing.

CyC5 Hydrates and Carbon Steel Measurements

Cyclopentane particles were formed in a procedure similar to the ice particles, except cyclopentane (CyC5) was used as a bulk fluid. The quenched ice particles were placed in the cell with the CyC5 below 0°C. The CyC5 temperature was then slowly raised above freezing, allowing the ice particles to convert to cyclopentane hydrate. Analogous to the ice experiments, the hydrate and steel were allowed to reach thermal equilibrium over the course of 30 minutes.

An example of one measurement is shown in Figure 4.12. A preload force of 1–3 μN was applied to the ice/hydrate particle by moving the steel sample. The preload
Figure 4.11. Schematic of handheld manipulator (left) and high precision manipulator (right). (a) Manipulators in initial configuration, (b) high precision manipulator is moved down to apply preload to particle, (c) high precision manipulator is moved up until the particle is removed from steel sample, and (d) distance (δ) required to remove the particle from steel is measured.
force was held for approximately 5 seconds. Then the steel sample was moved in the opposite direction until the particle was removed from the steel. The precision operated manipulator was moved at a speed of 5 \( \mu \text{m/s} \).

Figure 4.12. Example of one measurement. (a) CS sample and hydrate in initial configuration, (b) preload is applied to particle by moving high precision manipulator, (c) high precision manipulator is moved in the opposite direction until the particle is detached from steel sample, and (d) distance required to remove particle from steel is measured.

The maximum displacement \( \delta \) required for the ice/hydrate to detach from the CS sample was related to the adhesive force using Hooke’s Law

\[
F = k\delta
\]  

(4.12)

where \( k \) is the spring constant of the glass fiber. The technique for calibrating the glass fiber spring constant is detailed in Taylor’s thesis (Taylor, 2006). Measurements were normalized using Equation 4.7 in order to be consistent with previous measurements. In the case of carbon steel measurements, the radius of the CS sample (\( R_2 \)) was assumed infinite.
4.2.5 Experimental Results and Discussion

Initial experiments measured adhesive forces between ice and carbon steel. Measurements were conducted using both the 1 micron and 240 grit polished samples. Each steel sample was measured at three different temperatures, using a new particle for each measurement. Contact force (CF) between the ice particle and steel sample (Figure 4.11) ranged from 1.37–2.77μN. Figure 4.13 shows that adhesive force increased with increasing temperature, which is consistent with the idea of a quasi-liquid layer. It can also be observed that the steel surface roughness did not affect adhesive forces within the range of surface roughness’ tested.

Figure 4.14 compares cyclopentane (CyC5) hydrate-CS forces with ice-CS and CyC5-CyC5 measurements. Measurements were completed at various subcoolings for each system, where subcooling is defined as the melting temperature minus the experimental temperature. Figure 4.14 shows that CyC5-CyC5 forces were substantially higher than either ice or hydrate forces with carbon steel. Furthermore, CyC5-CS measurements were substantially lower than ice-CS forces. CyC5-CS forces were only measurable at low subcoolings, near the dissociation temperature. CyC5-CS forces also appeared to decrease with increasing CS surface roughness.

Discussion

Section 4.2.2 concluded that capillary forces best represented the adhesive forces between CyC5 hydrate particles. Although the measured ice-CS and CyC5-CS measurements were significantly lower than the CyC5-CyC5 forces, it is still hypothesized that the carbon steel forces were dominated by capillary forces. Evidence of capillary forces is shown in Figure 4.15. This measurement was conducted near the ice melting point (0°C) and the steel sample was thought to be slightly warmer than the bulk fluid (n-decane), due to thermal conduction through the cantilever. Figure 4.15c
Figure 4.13. Cumulative probability distributions of measured adhesive forces between carbon steel and ice (forces are normalized by the mean harmonic radius).
Figure 4.14. Adhesive force comparisons for various subcoolings. CyC5 represents cyclopentane hydrates and CS corresponds to carbon steel with varying surface roughnesses. Error bars show the standard deviation of the data (Figure 4.13) and forces are normalized by the mean harmonic radius.
shows evidence of a liquid bridge joining the ice particle and carbon steel sample. Figure 4.15c should be considered an extreme case, as the particle was near the two-phase (ice-water) temperature; however, the image does exemplify the likelihood of capillary bridging in these measurements.

Figure 4.15. Adhesive force measurement between ice and carbon steel near melting point (a) ice particle and carbon steel before contact (b) the particle was partially melted after contact with steel sample (c) the particle and steel are joined by a water bridge.

Rabinovich et al. (2005) developed an expression to predict capillary forces between a sphere and a flat plate. Rabinovich’s expression, which is based on the pressures inside and outside of the liquid bridge, incorporates the variables shown in Figure 4.16. Unfortunately, these variables were not measured in these experiments and would be difficult to measure. However, Rabinovich et al. (2005) did find that capillary forces increased with the volume of water, which is consistent with this work.

The data in Figure 4.14 shows adhesive forces between the carbon steel and hydrate/ice particles were a factor of 2–5 times lower than the forces between pairs of hydrates. The decrease in force is likely due to a decrease in the volume of water in the liquid bridge and the wetting angle ($\theta_f$) of water on the carbon steel. As previously noted, capillary forces increase with an increasing liquid bridge volume. It is reasonable to expect the liquid volume to be lower than the volume present between
two ice/hydrate particles, considering the carbon steel is dry. Additionally, the carbon steel sample is expected to be more hydrophobic than hydrate/ice particles, further reducing $\theta_f$, and thereby reducing the capillary forces.

Rabinovich et al. (2002) notes that capillary adhesion can be significantly reduced by surface roughness on the order of microns. Previous measurements in this lab have shown ice-ice forces are approximately one order of magnitude greater than CyC5-CyC5 measurements (Yang et al., 2004; Dieker et al., 2008). These results indicate that ice particles may be smoother than CyC5 hydrates and/or have a thicker quasi-liquid layer encompassing the particle. Similarly, the ice-CS forces were greater than the CyC5-CS measurements. A larger liquid layer on the ice particles would explain the lack of force dependence on the steel surface roughness, whereby the liquid layer was able to fill in the asperities. Conversely, the rougher CyC5 particles enclosed by

Figure 4.16. Variables required to predict capillary force between a sphere and a plate (reproduced from Rabinovich et al. (2005)).
a smaller liquid exhibited a dependency on the CS surface roughness. The author hypothesizes that the liquid layer on the rougher CyC5 particles was not thick enough to fill in the asperities of the rougher carbon steel samples.

4.3 Applying Adhesive Force Measurements to Force Balance Predictions

Section 4.1 discussed three mechanisms for particle removal in laminar flow. The key unknown in predicting those removal mechanisms is the adhesive force between hydrates and carbon steel. These values were measured experimentally and presented in Section 4.2.5.

4.3.1 Hydrate Removal Assumptions

Equations 4.4 - 4.6 are only applicable if the particle is in laminar flow. Because methane and condensate have such low viscosities, these pipelines typically operate in turbulent flow. Fortunately, even within turbulent systems, there is a laminar region near the wall (Lin et al., 1953; Bird et al., 2002). This region is illustrated in Figure 4.17.

Figure 4.17 depicts the velocity profile of a fluid in turbulent flow over a flat plate. The boundary layers are defined by the dimensionless height

\[
y^+ = \frac{y \nu_* \rho}{\mu}
\]  

(4.13)

where \(y\) is the height, \(\rho\) is the fluid density, and \(\mu\) is the fluid viscosity. The friction velocity, \(\nu_*\), is defined as

\[
\nu_* = \sqrt{\frac{\tau_0}{\rho}}
\]  

(4.14)
where $\tau_0$ is the wall shear stress. Wall shear stress was calculated using (Wilkes, 1999)

$$\tau_0 = \frac{1}{2} f_f \rho \bar{v}^2$$

where $f_f$ is the Fanning friction factor (assumed to be 0.02) and $\bar{v}$ is the average fluid velocity.

Figure 4.17 shows that the fluid flow is in laminar (viscous) flow when $y^+ < 5$. At slightly higher dimensionless heights ($5 < y^+ < 30$), the flow is still considered to be within the buffer layer. Hydrate removal predictions were completed assuming entrained hydrate particles would be within the buffer layer.

Equations 4.1 - 4.3 require knowledge of the fluid velocity profile. The dimensionless velocity profiles within the viscous and buffer boundary layers are defined by (Bird et al., 2002)

$$v^+ = y^+ \left[ 1 - \frac{1}{4} \left( \frac{y^+}{14.5} \right)^3 \right] \quad (0 < y^+ < 5)$$
\[ v^+ = 5 \ln (y^+ + 0.205) - 3.27 \quad (5 < y^+ < 30) \quad (4.17) \]

where \( v^+ \) is the dimensionless velocity. The average velocity can then be calculated by multiplying the dimensionless velocity by the friction velocity.

\[ \bar{v} = v^+ \times \nu_* \quad (4.18) \]

Hydrate removal predictions were completed assuming fluid properties for both a pure methane and pure condensate system. These predictions were completed using an adhesive force of 0.002 N/m*, which was larger than any force measured between cyclopentane hydrates and carbon steel. The parameters used for both the methane and condensate pipeline predictions are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Methane</th>
<th>Condensate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>115</td>
<td>700</td>
</tr>
<tr>
<td>Viscosity (Pa-s)</td>
<td>1.59E-5</td>
<td>5.0E-4</td>
</tr>
<tr>
<td>Adhesive Force (N/m*)</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Static coefficient of friction</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Hydrate Density (kg/m³)</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>( l_1 ) (m) (Figure 4.1)</td>
<td>0.3*d</td>
<td>0.3*d</td>
</tr>
<tr>
<td>( l_2 ) (m) (Figure 4.1)</td>
<td>0.1*d</td>
<td>0.1*d</td>
</tr>
<tr>
<td>Pipe Diameter (m)</td>
<td>0.303</td>
<td>0.303</td>
</tr>
</tbody>
</table>

Table 4.1. Parameters used to predict hydrate removal in both methane and condensate pipelines.

Hydrate removal predictions were completed using fluid properties at 60°F and 2000 psia; pipe diameter was assumed to be 0.303 m (12 in) in diameter. Both the methane and condensate phase were assumed to be incompressible. The moments, which the particle rolls around, were assumed to be fractions of the particle diameter.
4.3.2 Hydrate Removal Predictions

Hydrate removal predictions were completed using the adhesive forces measured in Figure 4.14 and the force balance illustrated in Figure 4.1. The predictions assumed the particles were entrained in a bulk condensate or methane phase in the absence of free water. The results for the condensate and methane systems are shown in Figures 4.18 and 4.19, respectively.

![Figure 4.18. Hydrate removal velocities and corresponding dimensionless heights of particles with various diameters in a condensate system.](image)

As in the colloidal literature, the particle removal mechanism was predicted to be
Figure 4.19. Hydrate removal velocities and corresponding dimensionless heights of particles with various diameters in a methane system.
rolling. Figure 4.18 shows the average pipeline velocity required to remove particles of various diameters on the left ordinate. The right ordinate is the dimensionless height of the particle, corresponding to the particle size (abscissa) and average removal velocity (ordinate). The dimensionless height in the condensate system is always less than 5, indicating the particles are within the (laminar) viscous boundary layer. Figure 4.18 shows that particles as small as 2 microns in diameter will be removed around 2.3 m/s. The removal velocity rapidly decreases to 1.5 m/s as particle size is increased to 5 microns. These velocity ranges are within pipeline operating conditions and suggest that particles entrained in a condensate phase are not expected to deposit on the pipe wall.

Figure 4.19 is analogous to Figure 4.18, except Figure 4.19 examines particles in a methane system. Because methane has a much lower viscosity, the dimensionless heights are greater than the condensate system. However, particles as large 25 microns are still within the buffer boundary layer. Particles as small as 3 microns are expected to be removed at methane velocities just above of 4 m/s. Analogous to the condensate system, removal velocities rapidly decrease with increasing particle diameter. Gas velocities of 4 m/s should be considered within normal operating conditions, indicating particle deposition would not be expected in a methane pipeline. Additionally, as particles grow beyond 25 microns, they will be exposed to turbulent bursts and are expected to be removed at even lower gas velocities (Cleaver and Yates, 1973).

Hydrate removal mechanisms were investigated using adhesive force measurements and force balance calculations. Hydrate particles with a diameter of 3 microns or greater are expected to be removed, via rolling mechanism, during normal operations in both condensate and methane pipelines.
4.4 Experimental Observations upon Forming Hydrates on Steel

Thus far, this chapter has concluded that hydrate particles entrained in the bulk phase are unlikely to deposit on the pipe wall in the absence of free water. However, several experimental observations indicate hydrates, which are formed on the steel surface, may behave differently. This difference in behavior is especially important considering hydrate nucleation likely occurs at the pipe wall, which is the coldest point in the system and offers many nucleation sites.

Figure 4.20 shows a picture of a THF hydrate particle that was formed on the steel sample. The bulk fluid in this experiment was n-decane (further details about THF and n-decane systems can be found in Taylor (2006)). The stoichiometric solution of THF-water solution was placed on the glass fiber and brought into contact with the steel. The temperature of the cell was then decreased and the particle nucleated on the steel. Particles formed on the steel surface could not be removed from the steel sample. The strong adhesion force was hypothesized to occur due to water molecules permeating the steel’s imperfections and forming a strong adhesive bond. These observations indicate that hydrates formed on the pipe wall will not be removed in flow.

The second observation exemplifying the need for a wall growth model is shown in Figure 4.21. THF hydrate was formed on the steel sample by dipping the sample in stoichiometric THF-water solution and quenching the sample in liquid nitrogen. The carbon steel was then placed in the n-decane fluid. Separately, a THF-water droplet was placed on the glass fiber and brought into contact with the hydrate coated steel sample. Figure 4.21 shows the droplet absorbing into the hydrate interface in a fraction of a second.

The observations discussed in this section provide evidence that hydrate particles
Figure 4.20. Picture of THF hydrate particle that was formed on the steel surface.

Figure 4.21. THF-water droplet being brought into contact with hydrate coated steel (a) THF-water droplet and hydrate coated steel before contact, (b) THF-water droplet after contacting hydrate coated steel, (c) droplet absorbing onto hydrate on steel, and (d) droplet has been fully absorbed onto hydrate on the steel.
formed directly on the pipe wall are likely to adhere to the pipe wall. After depositing an initial hydrate layer, there is evidence that water will be immediately absorbed onto the existing hydrophilic hydrate layer. Because hydrates are likely to nucleate at the pipe wall, there appears to be a need for a hydrate wall growth (stenosis) model, whereby hydrates grow from the pipe wall inward.

4.5 Chapter Conclusions

Adhesive forces between cyclopentane (CyC5) hydrates and carbon steel (CS) were measured. These forces were found to be substantially lower than CyC5 hydrate-CyC5 hydrate measurements and were also lower than ice-CS measurements. The measured adhesive forces were used in a force balance to predict particle removal, assuming no free water was present. The predictions show that entrained particles, 3 microns and larger, would be removed at typical operating flow rates.

Hydrate removal predictions suggest entrained hydrate particles will not deposit on the pipe wall. However, experimental observations show that hydrates formed on the steel surface have a significantly increased force and would likely remain on the pipe wall under normal flowing conditions. Considering the pipe wall is the most likely point of hydrate nucleation, the author hypothesizes that a hydrate deposit will form via hydrate growth on the pipe wall. This work exemplifies the need to examine hydrate deposition/wall growth behavior in a flowing system.
Chapter 5

SINGLE PASS FLOWLOOP WALL GROWTH EXPERIMENTS

Chapter 4 discussed the feasibility of entrained hydrate particles depositing on the pipe wall from the bulk fluid phase. Using a combination of measured adhesive forces and predictive force balances it was concluded that entrained hydrate particles, larger than 3 microns, would not deposit on the pipe wall. However, experimental observations suggested that hydrates forming on the pipe wall would adhere to the wall under normal operating conditions. This chapter investigates hydrate wall growth in a dissolved water condensate system.

5.1 Flowloop Experimental Apparatus

The flowloop used in the following experiments was originally designed, in communication with CSM, by the Intertek Petroleum Chemical Laboratory. The flowloop was then constructed at the Intertek laboratory in Houston, TX with funding from Imperial Oil Limited, ExxonMobil, ConocoPhillips, and Shell. Figure 5.1 shows a schematic of the single pass flowloop. The flowloop consisted of a cooling section, test section, and reheat section. The cooling and reheat sections were each 60 ft (18.3 m) in length, while the test section was 280 ft (85.3 m) in length. The flowloop was constructed using a series of 20 ft (6.1 m) long, coiled, pipe-in-pipe heat exchangers with an inner diameter of 0.37 inches (0.94 cm) as illustrated in Figure 5.2a.

Fluid flow in the apparatus was maintained using a micro gear pump labeled on the left of Figure 5.1, upstream of the two-phase separator. The separator was
a 5 L vessel with a high pressure sight glass to monitor fluid levels. Fluid level and composition were maintained using separate ISCO pumps for methane, condensate, and water. The flowloop was originally designed to measure the water concentration and volumetric flow rates of both the gas and liquid condensate (L_{Cond}) streams leaving the separator. However, due to cavitation issues, the loop was limited to operating at 100% liquid fraction in all experiments. Operating at 100% liquid was acceptable to the experimental program because the water concentrations were too low to use all the L_{Cond} of hydrate formers during a single pass through the test section. Additionally, the gas content in the L_{Cond} was replenished in the separator after each pass through the loop.

The test fluid’s moisture content was measured before entering the cooling section where the fluid was chilled from 15°C to the desired operating temperature. Next, the chilled fluid’s moisture content was measured using GE Panametrics moisture probes at both the test section inlet and outlet. After leaving the test section, the fluid was reheated to 15°C and the water concentration and flow were measured before reentering the two phase separator. Figure 5.3 shows a picture of the test section during operation.

The loop was instrumented with thermocouples and pressure transducers spaced every 40 ft (12.2 m). Additionally, the operator had the option of placing a camera and/or a Mettler Toledo Focused Beam Reflectance Measurement (FBRM) tool at the test section inlet, or alternatively placing the tools at the exit of the test section.

The condensate used in all flowloop experiments was a proprietary condensate provided by one of the partner companies. Details of the condensate composition are located in Appendix B.
Figure 5.1. Schematic of flowloop and data acquisition.

Figure 5.2. (a) Three heat exchanger sections used in the flowloop, and (b) GE moisture probe.
Figure 5.3. Picture of flowloop test section during operation.
5.1.1 Flowloop Commissioning and Thermodynamic Testing

Prior to conducting hydrate/ice deposition and plugging experiments, the flowloop required commissioning the thermodynamic boundaries of the condensate system needed to be established.

5.1.2 Test 1a and 1b - Commissioning Testing

The purpose of the commissioning testing was to establish confidence in the flowloop equipment and instrumentation.

Procedure

The flowloop was loaded with 11.9 kg (90% of total loop volume) condensate. Propane was then added at a mass fraction of 3.5% to ensure structure II (sII) hydrate formation. The loop was charged to 300 psi using methane gas and liquid condensate was circulated through a molecular sieve unit until the system was bone dry.

Water was injected in 100 microliter increments, allowing the water moisture probe readings to stabilize between injections. After reaching a concentration of 30-35 ppmw, the loop pressure was increased to 1000 psi and temperature was decreased to -21°C.

Results

Figure 5.4 shows the increase in moisture detection upon injecting water into the loop. Water was injected upstream of a 5 micron filter, allowing free water to continually contact condensate as the condensate passed through the filter.

The first water injection event shown in Figure 5.4 resulted in a lower moisture increase than the expected 9.8 ppmw increase. The latter two injection events were followed by a 6.8-10 ppmw increase in moisture readings which was within the 30% probe accuracy of the predicted 9.8 ppmw (based solely on water/condensate ratio).
Figure 5.4. Water addition in the commissioning stage, illustrating change in moisture probe reading with time.
increase. Appendix C.1 describes the GE moisture probes and limitations resulting in 30% accuracy while measuring a liquid phase.

Approximately 300 µl of water was added to the loop before any moisture content was detected. The lag in moisture response was consistent with the first injection shown in Figure 5.4 and can be explained by adsorption to the loop walls, seals, filters and/or free water accumulating in a low mixing zones within the loop.

After reaching equilibrium conditions the flowloop pressure was increased to 1000 psia (6.89 MPa) and the cool down and test sections were lowered to -21.5°C. Figure 5.5 shows the water content in the $L_{\text{Cond}}$ decreased with temperature.

![Figure 5.5. Moisture probe response to cooling the test and cool down sections.](image)
Figure 5.5 shows that Probes 3 and 6, which were exposed to a constant fluid temperature, decreased with temperature and exhibited consistent trends. Probes 1 and 2 were both exposed to a rapid decrease in fluid temperature resulting in two negative effects: (1) as discussed in Appendix C.1, ppmw is a calculation and a change in the probe temperature also changes the calculation constants (2) rapidly decreasing the fluid temperature can result in saturation of the moisture probe, yielding artificially high readings.

Figure 5.5 suggests ice/hydrate was depositing on the pipe wall of the test and cool down sections, lowering the water concentration in the $L_{\text{Cond}}$ to the solid-$L_{\text{Cond}}$ equilibrium concentration. Probes 3 and 6 reached a plateau at 11:20 AM implying that the water concentration in equilibrium with $L_{\text{Cond}}$ and ice/hydrate solids was $\sim 7$ ppmw at -21.5°C.

Discussion

Results from the commissioning experiments show the flowloop instrumentation was working properly and that ice/hydrate deposited in the cool down and test sections. Moisture probes exhibited the expected response when water was injected into the loop and when the loop test section temperature was decreased. The measured equilibrium value was within 2 ppmw of the predicted value (Multi-Flash w/CPA model (INFOCHEM, 2007)), further increasing confidence in the warm moisture probes.

The commissioning results indicate the warm probes (Probes 3 and 6) were most suitable for monitoring water concentration in the $L_{\text{Cond}}$. Because the moisture probe water constants change with temperature (Appendix C.1), investigating qualitative trends with Probes 1 and 2 was best accomplished using the dew point reading.
5.1.3 Test 1 and 2 - Thermodynamic Testing

The primary purpose of Tests 1 and 2 was to measure the solid-$L_{\text{Cond}}$ phase equilibria and establish phase boundaries for conducting deposition experiments. The secondary objective of these experiments was to determine whether ice and hydrates were distinguishable at low water concentrations.

Procedure

The objective in the equilibrium experiments was to perform a cooling and re-heating loop as shown in Figure 5.6. The initial run, Test 1a, was conducted using the same liquid loading as the commissioning experiments and the loop was pressurized with methane to 1000 psia (6.89 MPa). Water concentration was increased to 15 ppmw at a loop temperature of 15°C. All experiments were run at constant pressure, using the methane-filled ISCO pump to maintain pressure. The cool down section was adjusted to 3°C above the test section temperature to avoid saturating moisture Probe 1, which was located between the two sections. The cool down and test sections were rapidly cooled until the test section reached -7°C. The two sections were then cooled at a rate of 2°C/hour until the test section reached -15°C. After moisture readings stabilized, temperature was increased to 0°C at 1°C/hour, whereupon the rate was increased to 2°C/hour up to 20°C. The reheat section was maintained at 15°C throughout all experiments.

Figure 5.6 shows an ideal cooling loop, with the experiment starting at point 1. The temperature is then decreased, crossing the hydrate curve at point 2. At point 2a ice or hydrate nucleates and moisture content drops to point 3 with continued cooling. By slowly raising the temperature, the water concentration follows the hydrate equilibrium line from point 4 to point 2. The water concentration at point 2 represents the equilibrium water concentration in the presence of hydrate at -2°C.
Figure 5.6. Predicted condensate water concentrations in the presence of water/ice and hydrate. Points 1–4 show the ideal cooling loop for thermodynamic experiments.
Test 1b was conducted with the same liquid loading as Test 1a. Test 1b used slightly slower cooling rates. The test and cooling sections were initially lowered to 0°C at 5°C/hour. The loop was then chilled to -15°C at 2°C/hour. After stabilizing at -15°C, the temperature was increased to 20°C at 1°C/hr.

Test 2 used an initial water concentration of 40 ppmw (increased from 15 ppmw in Test 1). The cooling section and test sections were chilled to -15°C at rate of 2°C/hour. After moisture readings stabilized, the temperature was increased at a rate of 1°C/hour. Eight to ten hour stops were held at -10°C and -5°C before proceeding to 15°C.

Results

During test Test 1a, moisture content in the $L_{\text{Cond}}$ decreased immediately after the loop temperature was decreased, even before the hydrate or ice formation temperatures were reached (Figure 5.7). The moisture content was expected to remain constant until the temperature dropped below the equilibrium temperature at a given water concentration (Figure 5.6). In addition, Figure 5.7 shows the water concentration continued to climb above the initial concentration of ~14 ppmw as fluid temperature was raised above the initial 15°C. This increase in water concentration (above the initial concentration) suggests water was adsorbing to the pipe wall in the cool down and test sections as the fluid was cooled, then desorbing from the pipe wall to the fluid stream as the system was heated.

Further evidence of water adsorption is shown in Figure 5.8. Figure 5.8 shows water concentration in the $L_{\text{Cond}}$ increased as temperature was increased. However, the measured concentrations were well below the predicted ice/hydrate saturation curves for any given temperature. Assuming the predicted water concentrations had less than a 100% error for a given temperature, adsorption dominated Test 1a and
Figure 5.7. Test 1a, $L_{Cond}$ moisture probe response to cooling and heating the cool down and test sections.
The previous results indicate water was adsorbed from the gas condensate to the pipe wall, decreasing the \( L_{\text{Cond}} \) water concentration and preventing the system from reaching hydrate/ice equilibrium water concentrations.

The Test la and lb reheating curves in Figure 5.8 show excellent agreement between the two runs. The curves diverge slightly after 0°C, probably because the heating rate was increased from 1°C/hr to 2°C/hr in Test la, whereas the cooling rate in Test lb was held constant at 1°C/hr. The similarities between the two curves, particularly below 0°C, where the cooling rates were equal, imply that the experimental
results were reproducible.

The results from Test 2 are shown in Figure 5.9. Figure 5.9 shows the equilibrium concentration at -15°C was much closer to the predicted value (10 ppmw) than the 7 ppmw observed in Test 1. The increased water concentration at -15°C was evidence that water adsorption was responsible for the decreasing water concentration in the Test 1 results and prevented the flowloop from reaching ice/hydrate equilibrium conditions.

Figure 5.9. Test 2 temperature and water concentration profiles. An initial increase in water concentration initially occurred due to water injection, which was followed by the response of water concentration in $L_{\text{Cond}}$ as the temperature in the cool down and test section was changed.
Figure 5.9 shows the moisture content decreased with the fluid temperature in the cool down and test section and the moisture content stabilized within 1–2 ppm at each temperature isotherm plateau (-15°C, -10°C, -5°C). Figure 5.10 better illustrates that ice and/or hydrate were controlling the equilibrium conditions in Test 2. The water content decreased with temperature from 15°C to 0°C which was due to wall adsorption as explained earlier in this section. However, shortly after 0°C an inflection point was observed, which was believed to be the formation of ice. Upon reheating, the water concentrations remained below the cooling curve until reaching an inflection point at 2.5°C. The combination of: (1) the hysteresis of this profile compared to the ideal cooling and heating curve shown in Figure 5.6, and (2) the evidence of inflection points at 0°C and 2.6°C, suggest ice initially formed and converted to hydrate as the system was heated.

Figure 5.11 compares Multi-Flash (CPA model) predictions with experimental data (tabulated data are in Appendix C.2). The data point at -21.5°C was taken from the commissioning test, while the point at 2.6°C was taken from the inflection point shown in Figure 5.10.

As illustrated in Figure 5.11, the measured thermodynamic equilibrium points agree well with Multi-Flash predictions at -21°C (INFOCHEM, 2007). As the temperature was increased from -21°C to 3°C, the measured flowloop points trend differed from the Multi-Flash predictions. However, within the targeted temperature range of subsequent deposition experiments, the predictions were within the experimental accuracy.

Discussion

Test 2 results show the decreasing water concentration observed in Test 1a and 1b can be explained by water adsorption in the cool down and test sections. Test 2 results
Figure 5.10. Experimental cooling and heating curves compared with the predicted phase equilibrium curves.
Figure 5.11. Test 2 comparison of experimental data with Multi-Flash predictions (INFOCHEM, 2007).
suggest water adsorption was responsible for the initial decrease in the \( L_{\text{Cond}} \) water concentration. In order for solids to nucleate, the \( L_{\text{Cond}} \) water concentration had to be above the ice/hydrate equilibrium concentration corresponding to the specific test temperature. Once solids nucleated on the pipe wall, equilibrium water concentrations were controlled by the ice/hydrate phase, instead of wall adsorption. Initial solid nucleation appeared to be in the form of ice, which then converted to hydrate upon reheating. Measured hydrate-\( L_{\text{Cond}} \) equilibrium points, below \(-9^\circ\text{C}\), were within the experimental accuracy of the Multi-Flash CPA model predictions.

5.1.4 Summary of Commissioning and Thermodynamic Testing Tests

The Intertek single pass flowloop was successfully commissioned and the first thermodynamic solid-\( L_{\text{Cond}} \) measurements were completed. The constant temperature moisture probes located after the test separator and reheat section yielded reliable measurements of water concentration in liquid condensate. Unfortunately, the probes located after the cool down and test sections did not yield reliable concentrations due to the change in probe temperature and probe saturation. These probes may still be used to investigate qualitative trends using dew point readings and latter experiments were conducted without insulation on the cold probes. The data acquisition from the probes was determined to be acceptable for the experimental program.

The most probable explanation for the behavior seen during the cool-down period was that water adsorbed on the stainless steel in the cool down and test sections. Water mass balance calculations were non-feasible except from a steady-state condition.

The dissolved water concentration in the \( L_{\text{Cond}} \) was believed to have reached equi-
librium with the ice/hydrate deposited on the pipe walls. Equilibrium measurements, at 1000 psia (6.89 MPa), were conducted at temperatures ranging from -21°C to 2.5°C. Measurements completed below -9°C were within the probe accuracy (30%) of predicted values using Multi-Flash with the CPA model (INFOCHEM, 2007). Given the minute difference between hydrate and ice equilibrium concentrations at temperatures below 0°C, it is unlikely that the two phases can be distinguished. This was not expected to be detrimental to the experimental program, as both ice and hydrate will have similar effects on flowloop pressure drop.

Tests 1 and 2 successfully established baseline conditions for the ensuing deposition experiments.

5.2 Preliminary Deposition Testing Above and Below the Ice Point

Tests 1 and 2 established the thermodynamic boundaries for deposition experiments. They also confirmed that moisture Probes 3 (outlet) and 6 (inlet)(Figure 5.1), which were maintained at constant temperature, yielded accurate readings within ±30%.

Prior to conducting hydrate deposition testing, a method of maintaining a constant inlet water concentration was developed. This chapter discusses the experimental modifications required to achieve steady state injection and the subsequent deposition experiments (Test 3 and 4). Tests 3 and 4 were completed at temperatures slightly above and slightly below the ice point (∼1°C and -2°C). The condensate equilibrium water concentrations at these temperatures were higher than at -21°C and offered a wider range of flexibility in water injection rates and the opportunity to investigate the effects of crossing the free water/ice point. Results from Test 3 and 4 were then used to design and operate deposition experiments at -21°C. The primary
objectives of Tests 3 and 4 were to:

1. Prove the concept of steady state injection,

2. Investigate flowloop response to deposition and data acquisition sensitivity,

3. Provide operating guidelines for future experiments and,

4. Determine whether deposition behavior differs above and below the ice point.

5.2.1 Water Injection System

A major hurdle during Tests 1 and 2 was the inability to mix water and condensate. Several injection points were tested, including injecting water prior to a Kenics static mixer, each with little success. These water injection locations required hours to days before water fully dissolved in the condensate. The water injection points used in Tests 1 and 2 were not sufficient for conducting deposition experiments, which required the condensate water concentration to be continuously increased as water deposited in the test section.

The difficulty of mixing two immiscible fluids at steady state conditions was overcome using an experimental design developed by Lee Nuebling, an employee at Intertek, where the loop was located. The design, shown in Figure 5.12, incorporated an ultrasonic mixer which was surrounded by two static mixers.

Figure 5.12 shows the 1/16 inch water injection line, which injected water directly onto an ultrasonic horn. The ultrasonic horn was recessed ~1/4 inch from the main channel, allowing water to be emulsified into the condensate. The static mixer upstream of the ultrasonic unit created turbulence, forcing the highly concentrated fluid in the 1/4 inch recess to mix with the bulk fluid. Finally, the fluid passed through a 2 foot long Kenics static mixer, ensuring that the highly concentrated condensate was
mixed with the bulk condensate. This injection mixing process allowed a step change in homogeneous condensate water concentration as the condensate flowed through the mixing system.

The water injection system illustrated in Figure 5.12 was located upstream of the micro gear pump. Figure 5.1 shows the injection point connecting the ISCO Pump C to the flowloop.

### 5.2.2 Preliminary Deposition Experiments

Test 3 and 4 were both conducted using condensate (Appendix B) with 3.5% wt. propane to form sII hydrates. Pressure in the flowloop was maintained at 1000 psia ± 50 psia via the pressure regulator on the methane cylinder. The condensate flow rate was maintained at ~0.5 gallons per minute (gpm) in these experiments, unless otherwise stated.
5.2.3 Test 3 – Deposition Testing above the Ice Point

Test 3 results

Test 3 was conducted after several days of testing the water injection system and solids had already nucleated in the flowloop. The cool down and test sections were operated at 3.7°C ± 0.3°C and 1.2°C ± 0.5°C, respectively. Figure 5.13 shows the water concentration profiles indicating solid deposition was occurring in either the cool down or test section of the flowloop.

Figure 5.13. Test 3 water concentrations at flowloop inlet and outlet suggesting the water injection system was working correctly and hydrates were depositing on the flowloop wall.
Figure 5.13 shows the flowloop operating at equilibrium conditions (30 ppmw) when the injection rate was 0 μL/min on 10/1/07 12:00. Upon starting water injection, Probe 6 increased 12 ppmw to 42 ppmw, which was the expected increase as shown in Appendix C.4. Probe 3, which measures the loop outlet concentration, did not increase, indicating water was depositing as hydrate in either the cool down or test section. The cause of the sudden decrease and increase in Probe 3’s reading at 10/1/07 12:00 and 10/2/07 14:00 is unknown, but two possible explanations are:

1. Flow rate through Probe 3 decreased, causing the probe reading to decrease at 10/1/07 12:00. The operator may have readjusted the flow through Probe 3 at 10/2/07 14:00, which would have increased the ppmw reading. Evidence for the flow rate dependence can be seen in Appendix C.3, Figure C.2, where Probe 3’s reading briefly increased when the loop flow rate was manually increased, or

2. Hydrates formed in small localized area of the test section at 1.2°C, which would have an expected equilibrium concentration of ~25 ppmw. The hydrate deposit may have been dislodged at 10/2/07 14:00 and the concentration rose to 30 ppmw - the hydrate equilibrium concentration at the cool down temperature and the water adsorption equilibrium concentration at the test section temperature.

The experiment was originally designed to deposit hydrate in the test section, but Figure 5.14 shows hydrate deposited in the cool down section. The cool down section pressure drop increased while the test section pressure drop remained constant. The flow rate began to decrease as pressure drop increased. The step change at 10/2/07 9:30 was a result of manually increasing the pump speed to maintain a flow rate of 0.5 gallons/minute, which also caused the step change in pressure drop in Figure 5.14.

A gradual pressure drop increase was observed at the beginning of the experiment, which was then followed by a rapid pressure drop increase at 10/3/07 12:00.
Figure 5.14. Test 3 pressure drop in the test section and cool down section shown with the corresponding flow rate.
The gradual pressure drop occurred when the inlet concentration (Probe 6) was lower than the liquid water saturation concentration. An inlet concentration lower than the liquid water saturation resulted in hydrates depositing on the pipe wall from the dissolved water phase, yielding a uniform/dispersed solid deposit. The rapid change in pressure drop observed at 10/3/07 12:00 resulted from the inlet water concentration exceeding the $L_w$-condensate single phase limit, 46 ppmw, at 3.7°C (see Figure 5.6 and Figure 5.10). Figure 5.15 shows the rapid pressure drop to be coincident with increasing the inlet water concentration to 65 ppmw. A magnified portion of Figure 5.14 illustrating the rapid pressure drop increase in the cool down section can be found in Figure C.3.

In contrast to the uniform deposition over an extended length of flowloop, the rapid pressure increase in Figures 5.14 and 5.15 likely resulted from free water dropping out of condensate and rapidly forming a localized restriction in the initial section of the flow loop.

Test 3 discussion

The results from Test 3 indicated a major finding of this thesis. The data suggest that hydrate formation from dissolved water in the condensate resulted in lengthwise uniform/dispersed deposition and a slow increase in pressure drop, as shown in Figure 5.15 (10/1/07 13:00 – 10/3/07 11:30). However, cooling the water-condensate mixture below the liquid water saturation temperature resulted in a rapid pressure drop increase as shown at the end of the experiment in Figure 5.15 and Figure C.3. Crossing the $L_w$ saturation line at a given water concentration resulted in water coalescing from the condensate mixture (see Figure 5.10); this liquid water phase then rapidly formed a localized hydrate restriction in the initial portion of the flowloop.
Figure 5.15. Test 3 combined cool down and test section pressure drop compared with corresponding moisture readings from Probes 3 and 6.
5.2.4 Test 4 - Deposition below the Ice Point

Nucleation

Test 4 was conducted by first drying the loop and then injecting water at 2μL/min until hydrate/ice nucleated. The cool down and test sections were operated at ~10.5°C and -2.0°C, respectively. These temperatures were selected to prevent solid deposition in the cool down section and to induce hydrate/ice formation below the ice point in the test section. Initial water injection is shown in Figure 5.16.

Figure 5.16. Test 4 initial water injection and nucleation.

Figure 5.16 shows that moisture Probes 3 and 6 increased as water was injected
Figure 5.17. (a) Test 4 initial water injection and probe response, illustrating the failure of the water injection system (b) zoomed in version of the box in Figure 5.17a, illustrating the probe inaccuracies.

at 2 µL/min. The divergence of Probes 3 and 6 at 10/12/07 22:00 is attributed to probe error as opposed to solid deposition or water adsorption. Evidence of these probe inaccuracies and failure of the water injection system at 10/14/07 22:00 is shown in Figure 5.17b.

Figure 5.17b shows that both probes remained constant when water injection was ceased. If both probes were reading accurately and deposition or adsorption was taking place, Probe 6 would have collapsed onto Probe 3. Because neither adsorption nor deposition was occurring, the water concentrations should have continued to increase if the water injection system was working properly. The fact that the probe concentrations remained constant indicates the water injection system failed at the time that Probes 3 and 6 reached the plateau (Figure 5.16).

The initial decrease in the moisture probes, shown in Figure 5.16 and 5.17a, is attributed to hydrate/ice nucleation; indicating that a driving force of ~5 ppmw was
required to nucleate solids. Figure C.4 shows that hydrates nucleated between 40 and 80 feet into the test section. Although Probes 3 and 6 were not consistent with each other, they both showed the same type of relative change. In Test 4, the baseline solid equilibrium moisture concentration was 18 ppmw and 24 ppmw for Probes 3 and 6, respectively (Figure 5.17b).

Rapid pressure drop

Upon resuming water injection, the liquid water saturation curve was likely crossed, similar to that in Test 3. Figure 5.18 shows the rapid increase in pressure drop upon successfully restarting water injection at 10/16/07 12:20.

Figure 5.18. Test 4 pressure drop increase and moisture readings.
Figure 5.18 shows that as water injection was resumed and Probe 6 climbed to ~30 ppmw, the pressure drop rapidly increased (> 1 psi/hour). Figure 5.10 shows that the saturation concentration ($L_w$ line) at 0°C is approximately 30 ppmw. Due to the inaccuracies in both the moisture probes and predicted saturation concentrations, the experimental and predicted values are difficult to compare in great detail. However, the rapid pressure rise is consistent with observations in Test 3, indicating free water dropped out of the condensate solution and formed a localized restriction in the initial part of the flowloop. Figure C.4 shows the restriction occurred between 40–80 ft in the test section.

*Hydrate removal attempt*

Following the formation of a localized hydrate/ice restriction, an effort was made to dislodge the hydrate by increasing flow rate. Figure 5.19 shows the hydrate/ice restriction could not be removed by increasing pump speed by 60%.

While pump speed was increased to 0.8 gpm, video feed and FBRM data were monitored downstream of the test section. Neither the FBRM nor the video feed detected any solid particles traveling through the test section. Additionally, there were no fluctuations in pressure drop at 0.8 gpm and the pressure drop returned to the original 15 psi pressure drop (cool down + test section) previously associated with a 0.5 gpm flow rate.

*Redistributing localized hydrate deposit*

After resuming a 0.5 gpm flow rate, the hydrate restriction, illustrated in Figure 5.18, was dissociated and transported downstream as a uniform/dispersed hydrate deposit (Figures 5.20 and 5.21). This step removed the localized restriction and allowed for further testing without draining the flowloop. The hydrate restriction was dissociated and transported downstream by shutting off the cooling fluid to the first
Figure 5.19. Test 4 response to increasing the pump speed in an attempt to dislodge the hydrate/ice restriction.
40 ft in the test section (sections 4 and 5 in Figure 5.1). Although there was still approximately 6 feet of cooled tubing prior to the test section, the fluid temperature at the hydrate restriction was significantly increased. Figures 5.20 and 5.21 show the flowloop response to closing the cooling fluid valves and increasing fluid temperature.

Figure 5.20. Test 4 temperature response, 40 ft into the test section after closing the cooling fluid valves on heat exchangers 4 and 5. The increase led to an initial increase in pressure drop, before the restriction moved downstream.

Figure 5.20 shows the inlet temperature increased after the cooling fluid to test sections 4 and 5 was shut off. As the fluid temperature initially increased, the pressure drop between 40 and 80 ft continued to increase. The author hypothesizes that water was deadsorbing and/or hydrate was dissociating in the first 40 ft of the test section,
Figure 5.21. Test 4 pressure drop and moisture response, after closing the cooling fluid valves on heat exchangers 4 and 5.
saturating the condensate, as fluid temperature was increased. This dissolved water then deposited on the existing localized restriction between 40 ft and 80 ft as the condensate cooled below the saturation temperature. However, once the adsorbed water was completely removed, the warmer condensate was capable of carrying more dissolved water. The hydrate/ice deposit was then dissolved into the under-saturated condensate solution. As the condensate continued to move downstream and was cooled, uniform/dispersed deposition occurred in the flowloop, preventing a noticeable pressure drop increase. Figure 5.21 confirmed that the water was redistributed within the test section rather than being transported out of the section. If water had been removed from the test section, the moisture content in Probes 3 and 6 would have increased. It should be noted that the sudden pressure drop increase at 10/17/07 15:30 was a result of the data acquisition losing power. Although approximately 30 minutes of data were lost during the acquisition outage, all experimental equipment continued to run. Additionally, the rapid pressure drop decrease at 10/17/07 17:30 was a result of decreasing flow rate as illustrated in Figure C.5.

Repeat rapid pressure drop attempt

Following the redistribution of localized hydrate, an attempt was made to reproduce the rapid pressure drop increase shown in Figure 5.18. Figure 5.22 shows that the rapid pressure drop increase was not reproducible. The inlet concentration was increased to as high as 40 ppmw, yet a rapid pressure drop increase (> 1 psi/hr) was never observed. Figure C.6 demonstrates that the hydrate pressure drop occurred between 40 and 80 ft, where the initial hydrate plug was located.

Figure 5.23 illustrates a hypothesis explaining why a rapid pressure drop was not always observed when the inlet water concentration was above the liquid water saturation concentration at 0°C. Figure 5.23 shows that the presence or absence of
Figure 5.22. Test 4 moisture and pressure drop readings while attempting to repeat rapid pressure drop experiments.
existing hydrate on the pipe wall played a critical role in determining what type of plugging mechanism was observed. In the case where hydrates were not on the pipe wall, the inlet water concentration remained constant until the condensate passed the liquid water saturation curve. Once the condensate passed the $L_w$ saturation curve, free water dropped out of solution, creating a localized restriction.

However, if hydrates were present on the pipe wall, they slowly removed water from the condensate-water mixture. Upon reaching the hydrate deposit, water was incrementally removed from the condensate as the condensate flowed through the flowloop. The water content of the condensate was likely in equilibrium with hydrate as the condensate moved downstream, preventing the condensate water content from crossing the free water ($L_w$) line, and resulting in uniform/dispersed deposition. The uniform deposition may have been an artifact of the small diameter (0.37 inch) flow loop, which yielded a high surface area to volume ratio. Further calculations will be required to predict whether the flowloop behavior would be expected in larger diameter pipelines with smaller area to volume ratios.

**Visual image of hydrate deposit**

The final objective of Test 4 was to obtain a visual image of the hydrate/ice deposit. Because the camera and observation test section were located at the end of the test section, the hydrate deposit had to be moved downstream. Cooling fluid to test sections 6–15 was shut off over a course of 48 hours (Figure 5.1). Figure 5.24 shows the solid deposit being transported downstream as the cooling fluid was obstructed.

Figure 5.24 shows the top two pressure drop curves (0–240 ft and 0–280 ft) diverged from the lower curves, indicating the solid restriction was being moved downstream. As the system was equilibrating, the test section temperature (in the remaining test sections) was decreased to -21°C at a rate of -2°C/hour. Once the
Figure 5.23. Hypothesized conceptual picture describing rapid pressure drop increase and uniform/dispersed deposition. Fluid temperature decreases as the fluid flows downstream, resulting in lower equilibrium concentrations for both the hydrate and L_w-ice saturation curves. Figure C.7 shows a similar schematic on the phase diagram.

temperature reached -21°C, the loop was shut down and the observation section was isolated from the loop. The top cap on the isolation section was removed and a boro­scope was inserted down the pipe. The boroscope used a 90° head, allowing visual observation of the pipe wall. Note that the image shown in Figure 5.25 could only be taken after the system was depressurized and the hydrate likely dissociated and reformed as ice.

Test 4 discussion

Hydrates in Test 4 nucleated with a driving force of \(~5\) ppmw between 40–80 ft into the test section. Upon increasing the test section inlet concentration \(~32\) ppmw, a rapid pressure drop increase was observed. The condensate was cooled below the liquid water saturation curve and free water dropped out of solution. This free water
Figure 5.24. Test 4 pressure drop response after closing the cooling fluid valves to sections 6–15.
then nucleated into a solid and created a localized restriction.

It was found that the solid restriction could not be dislodged by increasing flow rate from 0.5 gpm to 0.8 gpm. The localized restriction was then dissociated and redistributed as a uniform deposit by closing the cooling fluid valves on the first 2 sections of the heat exchanger. The rapid pressure drop increase (localized restriction) was not reproducible. The presence of hydrate on the pipe wall was hypothesized to reduce the condensate water concentration as the condensate flowed downstream, preventing the liquid water saturation curve from being crossed.

5.2.5 Summary of Deposition Above and Below the Ice Point

The single pass flowloop was modified with an ultrasonic water injection system, which was capable of producing a step change in the dissolved water concentration in a gas condensate. This injection technique allowed deposition experiments to be conducted by maintaining a constant inlet water concentration in the flowloop test
Two deposition experiments were conducted in the present study, one above the ice point (Test 3) and one below the ice point (Test 4). As expected, no significant difference was observed between operating above and below the ice temperature. Hydrate deposition in Test 3 occurred in the flowloop cool down section, while Test 4 was designed to promote hydrate/ice deposition in the test section. In both experiments, two different hydrate/ice deposition mechanisms were observed:

1. A rapid pressure drop (>1 psi/hour) increase was observed when the condensate was cooled past the liquid water (L_w) saturation curve. Crossing the L_w saturation curve resulted in free water dropping out of solution and forming a localized restriction in the initial portion of the flowloop.

2. Deposition from dissolved water resulted in lengthwise uniform/dispersed deposit resulting in a slow pressure drop increase (<1 psi/hour). Solid deposition from dissolved water resulted in a uniform hydrate deposit throughout a longer length of the flowloop.

It was also found that hydrate/ice deposits were transported downstream by raising the upstream fluid temperature. After moving the hydrate deposit downstream in Test 4, the rapid pressure drop increase was not repeatable. It is hypothesized that an existing hydrate deposit on the flowloop wall prevented a rapid pressure drop increase in the flowloop. As condensate flowed past the hydrate deposit, water was incrementally removed from the condensate and deposited as hydrate, preventing the L_w-condensate phase boundary from being crossed. Thus, preventing free water accumulation and the subsequent formation of a localized hydrate/ice restriction.

Test 3 and 4 confirmed that the data acquisition system was sensitive enough to measure pressure drop as solids deposited on the pipe wall. Latter experiments,
conducted at -21°C, maintained the cool down section at 15°C and ensured that the inlet water concentration was maintained below the \( L_w \) saturation condition at 0°C (~30 ppmw).

5.3 Deposition Testing at -21°C

Previous experiments (Tests 1 - 4) established baseline operating conditions for deposition experiments. Key findings from these experiments were:

1. Water adsorption to the stainless steel flowloop walls decreased condensate water content as temperature decreased. However, once solids deposited on the flowloop walls, measured condensate water concentrations were in equilibrium with ice/hydrate after passing through the flowloop test section (Figure 5.1).

2. Probes 3 and 6 (Figure 5.1), which were maintained at constant temperature, yielded accurate readings within 30%. Probes 3 and 6 represent the outlet and inlet water concentrations, respectively. Probes 1 and 3 were not used due to changing fluid temperatures and probe saturation (Appendix C.1).

3. Thermodynamic equilibrium water concentrations were measured; these measurements were within the 30% probe accuracy of predicted values using MultiFlash (CPA model) at temperatures ranging from -21°C to -9°C.

4. No significant difference was found between depositing solids above and below the ice point (0°C).

5. Hydrate/ice deposits formed from dissolved water resulted in uniform/dispersed deposition and a slow increase in pressure drop.
6. Hydrate/ice formation from free water resulted in a localized restriction and a rapid pressure drop increase. The rapid pressure drop occurred when a water saturated condensate was cooled below the liquid water equilibrium line.

7. Hydrate restrictions could not be removed by increasing the condensate flow rate.

8. Hydrate restrictions were moved downstream by increasing the inlet test section temperature of the condensate stream.

Tests 5 and 6 were the final experiments completed in the experimental matrix. These tests utilized the cumulative knowledge developed throughout the commissioning process and the first four experiments. The experiments were designed to improve confidence in each of the following topics:

1. Metastability prior to hydrate nucleation.
   
   (a) What water concentration driving force is required for solid nucleation and what is the induction time period?

2. Water concentrations required for rapid pressure drop.
   
   (a) Does the \( L_w \)-ice saturation curve need to be crossed above 0°C?

3. Long term uniform deposition testing.
   
   (a) How long will it take to plug the flowloop under uniform deposition conditions?

(a) Can the hydrate restriction be removed by drying the gas below equilibrium concentrations or via methanol injection?

Test 5 and 6 were both conducted at 1000 psia (6.89 MPa) and -21°C. A condensate and 3.5% wt propane mixture was used as the test fluid and the flowloop was pressurized with commercial grade methane. Test 5 was completed using a flow rate of 0.5 gallons per minute (gpm) (1.9 l/min) and hydrate/ice restrictions were dissociated by drying the inlet condensate stream. Test 6 investigated hydrate deposition at a flow rate of 0.75 gpm (2.8 l/min) and hydrate/ice restrictions were remedied via methanol injection.

5.3.1 Test 5 – Deposition Test at 0.5 gpm and -21°C

The initial objective of Test 5 was to investigate water supersaturation concentrations (metastability) and corresponding induction times prior to nucleation. Following nucleation, rapid pressure drop conditions were investigated. The restrictions formed during the rapid pressure drop phase of the experiment were displaced and removed by increasing flowloop temperature and running the molecular sieve unit. After reducing the test section pressure drop, a long term uniform deposition test was conducted over the course of 11 days. Finally, the uniform hydrate/ice deposit was removed by drying the inlet condensate and lowering water content below hydrate equilibrium conditions.

**Nucleation**

Test 5 was originally designed to investigate hydrate/ice metastability at 3 water concentrations: 7 ppmw, 10 ppmw, and 13 ppmw. Each concentration was to be run for 24 hours or until nucleation was observed. The flowloop was dried using a molecular sieve and the test section was lowered to -21°C, while the cool down and
reheat section were held constant at 13.5°C and 18°C, respectively. Water was then injected at a rate of 2 microliters/minute until Probes 3 and 6 read 3.5 ppmw and 5.4 ppmw as shown in Figure 5.26. Because the time was late in the day, water injection was stopped at 10/30/07 15:16 and injection was to resume the next morning.

Figure 5.26. Test 5 initial water injection rate and corresponding response from Probes 3 and 6.

Figure 5.26 shows the moisture content increasing as water was injected into the flowloop at 2 microliters/min. The divergence in the probes at 10/30/07 12:00 was a result of probe inaccuracies as shown in Appendix C.6, Figure C.8. The subsequent decrease in moisture content at 10/30/07 19:00 was attributed to nucleation in the
Figure 5.27. Test 5 probe readings during initial injection and corresponding test section pressure drop.

Figure 5.27 shows pressure drop across the test section increased when probe readings began to decrease, indicating solid nucleation was occurring in the flowloop at 10/30/07 19:00. Figure 5.29, shows the restriction occurred between 80 ft and 160 ft.

After Probe 6 was replaced, water injection was resumed to ensure nucleation had taken place. Flowloop response to second water injection event is shown in Figure 5.28. Figure 5.28 shows that Probes 3 and 6 were within 0.5 ppmw of each
other after Probe 6 was replaced (11/1/07 8:00–11/1/07 11:30). Upon resuming water injection at 11/1/07 11:30, the inlet concentration (Probe 6) increased and the outlet concentration (Probe 3) remained constant. The difference in concentrations indicated hydrates/ice had already nucleated and were depositing in the test section; which was also confirmed by the pressure drop increase. Figure 5.29 confirms that the restriction was growing in the test section between 40 ft and 120 ft, slightly upstream of the nucleation location.

Figure 5.28. Test 5 water concentration and pressure drop measurements throughout the second injection event.

Figure 5.28 raised a major concern relating to the equilibrium water concentra-
tions at -21°C. Probe 3 and 6 measurements between 11/1/07 8:00 – 11/1/07 11:30 in Figure 5.28 suggest the equilibrium water concentration in Test 5 was 3 to 3.5 ppmw. One initial explanation for the low concentrations was that condensate was in equilibrium with hydrate/ice in the upstream sections of the flowloop and in equilibrium with wall adsorption in latter portions of the test section. This would result in measuring a water concentration lower than that for hydrate/ice equilibria. However, the combined hydrate and adsorption equilibrium possibility was dismissed for two reasons:

1. The entire flowloop wall should already have been in equilibrium with water adsorption. This is illustrated in Figure 5.26, where Probe 3 concentrations decreased upon nucleation. Had the flowloop walls been undersaturated, with respect to adsorption, Probe 3 should never have risen above the 4 ppmw post-nucleation concentration.

2. As will be discussed later in this report, flowloop temperature was increased; thereby increasing the equilibrium water concentration. The loop temperature was then slowly decreased, ensuring the flowloop was in equilibrium with hydrate/ice. The resulting equilibrium concentrations were the same as those shown in Figure 5.28 (3–4 ppmw).

Figure 5.29 shows pressure drop increased between 80 ft and 160 ft during the initial hydrate/ice nucleation at 10/30/07 19:00. During nucleation, there was a slight increase in the 0 ft – 80 ft profile and an additional increase in the 0 ft – 160 ft pressure drop; signifying the hydrate restriction was located between 80 ft – 160 ft. However, during the second water injection at 11/1/07 14:15, pressure build up was primarily between 40 ft and 120 ft. This observation demonstrates the ability of hydrate/ice
Figure 5.29. Test 5 pressure drop profiles and the corresponding condensate flow rate. The pressure drop profiles illustrate the pressure drop in the test section in 40 ft increments.
crystals to rapidly grow upstream on the pipe wall. Figure 5.29 also shows the 0 gpm flow rate and corresponding pressure drop curves while the loop was shutdown (10/31/017 12:20 – 10/31/07 16:50) to replace Probe 6.

Figures 5.26 and 5.27 show that hydrates/ice nucleated with a driving force of 1–2 ppmw after approximately 5 hours. The initial divergence in Probes 3 and 6 resulted from probe inaccuracies, which were remedied by replacing Probe 6. However, the measured equilibrium concentration, 3–4 ppmw, was significantly lower than the expected 7 ppmw, which was either a result of probe inaccuracies or a change in the loop composition. Although equilibrium water concentration issue was never resolved in Test 5, the probes were still suitable for monitoring relative change while conducting deposition studies.

*Rapid pressure drop increase*

Following the nucleation portion of Test 5, the water injection system failed. A number of modifications were made to the system between 11/2/07 9:00 and 11/4/07 12:40. As a result, the initial water deposited as hydrate or ice was unknown. Once the water injection system was fixed, water injection was resumed. The purpose of this portion of the experiment was to investigate water concentrations resulting in a rapid pressure drop increase. Water inlet concentration was gradually increased to study rapid pressure drop behavior as elucidated in Figure 5.30.

As discussed in previous experiments, the liquid water phase boundary was expected to occur near 30–40 ppmw (Figure 5.10). Figure 5.30 shows inlet water concentration was increased to as high as 53 ppmw, yet a rapid pressure drop was never observed (>1 psi/hour). Figure 5.31 shows that the hydrate and/or ice was depositing in the first 40 ft of the test section. The rapid pressure drop portion of the experiment required water injection rates as high as 45 microliters/min as shown in Figure C.9.
Figure 5.30. Test 5 pressure drop response while increasing inlet water concentration.
Figure 5.31. Test 5 pressure drop and flow rate changes during rapid pressure drop investigations.
Figure 5.31, shows the hydrate/ice restriction formed in the first 40 ft of the test section. The step change in pressure drop and flow rate at 11/4/07 12:50 and 11/4/07 20:25 was a result of the operator changing pump speed.

The same phenomena discussed in Section 5.2.4 and Figure 5.23 also explains why a rapid pressure drop increase was not observed in Figure 5.30. In the case where hydrates are present on the pipe wall, hydrates will slowly remove water from the condensate-water mixture. Upon reaching the hydrate front, water will be incrementally removed from the condensate as the condensate flows through the flow loop test section. The water content of the condensate may be in equilibrium with hydrate as the condensate moves downstream, preventing the condensate water content from crossing the free water ($L_w$) line, resulting in uniform deposition. Such uniform deposition may be an artifact of the small diameter (0.37 inch/0.94 cm) flow loop, which yields a high surface area to volume ratio. Calculations are required to predict whether flowloop behavior would be expected in larger diameter pipelines with smaller area to volume ratios.

The hydrate buffering hypothesis simply requires hydrates be present before the $L_w$ saturation curve is reached. Figure 5.29 illustrates that hydrates initially formed between 80 ft and 160 ft, while the second injection formed a restriction between 40 ft and 120 ft. Thus it is highly probably that hydrates moved upstream into the first 40 ft of the test section, where the deposits were formed in the rapid pressure drop investigation (Figure 5.31).

Initial dehydrator testing

Although a rapid pressure drop was never observed in the previous portion of the experiment, a large quantity of water was injected into the flowloop (Figure 5.30) which primarily deposited in the first 40 ft of the test section. Prior to conducting
a long term deposition test, a portion of hydrate/ice was removed by increasing flowloop temperature and running the molecular sieve unit. Figure 5.32 shows that the condensate water concentration increased as flowloop temperature was increased.

Figure 5.32. Test 5 temperature and moisture profiles during initial dehydrator test.

Figure 5.32 shows the cool down and test sections of the flowloop were ramped to 20°C and -3°C, respectively. As the flowloop temperature was increased the hydrate/ice equilibrium water concentrations also increased, as shown by Probes 3 and 6 in Figure 5.32. At 11/5/07 19:10 the dehydrator, between the reheat section and the pump, was placed in line with the flow. Figure 5.32 shows an immediate drop in Probe 6 concentrations, while Probe 3 remains constant, indicating the molecular
sieve unit was drying the inlet condensate. The dry condensate then dissolved the hydrate/ice until the condensate reached its saturation concentration, before the end of the test section, as suggested by the constant reading from Probe 3. The advantage of operating at a warmer temperature is that a higher concentration driving force, Probe 3 minus Probe 6, was used to dissociate hydrate.

Figure 5.33 shows the flowloop response to increasing fluid temperature and placing the dehydrator in line with condensate flow. This figure shows the hydrate/ice deposit being transported downstream as the temperature was increased at 11/5/07 9:00. The transporting of hydrate was evident by the decrease in pressure drop from 0–40 ft and the increasing distance between the 0–40 ft and 0–80 ft pressure drop curves. The remaining pressure drop profiles stay evenly spaced, indicating the warm condensate fluid dissolved the hydrate/ice from the first 40 ft of the test section and re-deposited the water between 40–80 ft from 11/5/07 9:00 and 11/5/07 19:00.

After the temperature was ramped to -3°C in the test section (Figure C.10), the dehydrator was installed at 11/15/07 19:00; simultaneously the loop flow rate was increased from 0.5 gpm to 0.6 gpm. Similar to increasing temperature, the flow rate was increased to accelerate the dissociation of hydrate/ice deposits. Once the dehydrator was installed, the test section pressure drop continued to decrease, resulting in an increase in flow rate. The deposit also continued to move from 0–40 ft to 40–80 ft, which is analogous to the behavior observed upon increasing the test section temperature. Nonetheless, installing the dehydrator proved the concept of dissociating hydrate with an undersaturated condensate. A molecular sieve was used to dehydrate the inlet condensate and the outlet condensate water concentration remained constant at the equilibrium concentration, suggesting water was being removed from the test section.
Figure 5.33. Test 5 pressure drop response while increasing temperature and running the dehydrator. The loop flow rate is also shown to explain the step changes in pressure drop. The pressure drop profiles illustrate the pressure drop in the test section in 40 ft increments.
Long term uniform deposition test

After applying the dehydrator, pressure drop across the test section was reduced from approximately 10 psi to 6 psi (at 0.5 gpm). More importantly, the pressure drop across the first 40 ft of the test section was reduced to the initial pressure of 1.1 psi (Figure 5.29 and Figure 5.33). Following the dehydration portion of the experiment, the test section temperature was decreased from -3°C to -21°C at a rate of -1°C/hour (Figure C.11).

The long term, uniform deposition, experiment was carried out by injecting water at rates of 24 and 25 microliters/min. Figures 5.34 and 5.35 show the water injection rates, moisture readings and resulting pressure drop increase.

Figure 5.34 shows the test section inlet concentration (Probe 6) increased as water injection rate was increased from 0 to 25 microliters/min at 11/7/07 10:00. Meanwhile, the outlet water concentration (Probe 3) remained constant, indicating water was depositing as hydrate/ice in the test section. Figure 5.35 confirms that uniform deposits were being formed in the test section, as is indicated by the gradual pressure drop increase. Note that there was a leak in the water injection system, which temporarily interrupted the experiment from 11/11/07 10:00 to 11/13/07 9:23. Details of this interruption and the decision to continue the experiment are discussed in Appendix C.7. Also, Figure 5.35 shows that the pressure drop profile essentially resumed from the loop’s pre-leak value of 17 psi once water injection was restarted at 11/13/07 9:23.

Figure 5.36 shows distance between the pressure drop curves stayed relatively constant, while the first curve (0–40 ft) continued to increase, indicating that hydrates were depositing uniformly in the first 40 ft of the test section.

The temperature profiles shown in Figure 5.37 confirm that hydrates/ice were
Figure 5.34. Test 5 water injection and corresponding water concentration profiles throughout the uniform deposition experiment.
Figure 5.35. Test 5 moisture profiles and pressure drop across the test section during the uniform deposition test.
Figure 5.36. Test 5 test section pressure drop profiles and corresponding flow rates during the uniform deposition testing. Each pressure drop curve represents the pressure drop across an additional 40 ft in the test section (see Figure 5.1).
Figure 5.37. Test 5 temperature profiles and the loop flow rate during uniform deposition testing. The temperature curves represent temperatures measured at 40 ft (T203), 80 ft (T204), and 120 ft (T205) in the test section.

depositing on the pipe wall, particularly within the first 40 ft, whereby hydrate/ice acted as insulation on the flow loop wall. Evidence of the deposit acting as insulation is illustrated by the temperature increase in the 203 thermocouple (40 ft into the test section as shown in Figure 5.1). By comparing temperatures at similar flow rates, the insulation effect of hydrate/ice deposition can be observed 40 ft into the test section, where temperature increased from -17°C to -14°C. Similarly, a slight temperature increase in the 204 thermocouple was observed, indicating a small amount of hydrate/ice was depositing between 40 ft and 80 ft. However, the temperature profiles are
consistent with the pressure drop profiles in Figure 5.36, indicating the majority of the hydrate/ice was depositing in the first 40 ft test section (Figure C.12).

**Dehydrator results at -21\(^\circ\)C**

The final area of investigation in Test 5 was to dissociate the hydrate/ice deposit at -21\(^\circ\)C, using a molecular sieve dehydrator. Once the test section pressure drop reached approximately 70 psi, water injection was stopped and condensate was routed through the dehydrator (located between the reheat section and the separator).

![Figure 5.38. Test 5 water concentrations and test section pressure drop while running the dehydrator.](image)

Figure 5.38. Test 5 water concentrations and test section pressure drop while running the dehydrator.

Figure 5.38 shows the inlet concentration dropped below the outlet concentra-
tion after the dehydrator was installed at 11/16/07 16:15. Consequently, water was removed from the test section and pressure drop decreased. The gap at the end of the Probe 6 data at 11/24/07 6:00 was a result of losing condensate flow to the moisture probe.

Figures 5.39 and 5.40 show the hydrate/ice was displaced from the first 40 ft of the test section. The decrease in the 0–40 ft line (Figure 5.39) shows the deposit was removed from the first 40 ft. At approximately 11/18/07 6:00 the separation between the 0–40 ft and 0–80 ft lines began to increase, indicating a portion of hydrates/ice re-deposited between 40 and 80 ft in the test section. Because the pump operated at a constant frequency, the flow rate began to increase as the deposit was removed and pressure drop increased. The pump frequency was manually adjusted to maintain a flow rate of 0.5 gpm as shown in Figure 5.39.

Figure 5.40 shows that the temperature at thermocouple 203 (40 ft into the test section) decreased as the hydrate was removed. There was a sharp increase and decrease in temperature at 11/19/07 9:00 and 11/20/07 15:35, respectively. These temperature fluctuations resulted from decreasing the cooling rate from 65% to 50% of the max value and then increasing the rate back to 65% of max. The cooling rate was reduced during this time period to reduce the loss of cooling fluid while waiting for a new shipment of cooling fluid to arrive.

Test 5 discussion

Deposition tests were conducted at a flow rate of 0.5 gpm. Hydrates/ice nucleated with a driving of approximately 1–2 ppmw. The equilibrium concentrations measured were approximately 3.5 ppmw, which was half of the expected 7 ppmw. The low equilibrium concentrations were either a result of probe errors or a change in test fluid composition and was resolved in Test 6.
Figure 5.39. Test 5 pressure drop profiles and flow rate while running the dehydrator.
Figure 5.40. Test 5 flow rate and temperature profiles while running the dehydrator.
An attempt was made to induce a rapid pressure drop behavior. However, similar to Test 4, the presence of hydrates/ice buffered the condensate water concentration and prevented the \( L_{ew} \) line from being crossed. Uniform deposition was carried out over the course of 10 days. The majority of hydrate/ice deposited in the first 40 ft of the test section, resulting in an increase in fluid temperature throughout that section, indicating hydrate/ice was acting as insulation in this section.

Following the uniform deposition, the hydrate/ice deposit was removed by drying the inlet condensate concentration. The inlet water concentration was dried below the equilibrium concentration and the outlet concentration remained steady at the equilibrium concentration. These readings were accompanied by a decrease in pressure drop and fluid temperature 40 ft into the test section, both indicating that the hydrate/ice deposit was dissociating.

5.3.2 Test 6 – Deposition Test at 0.75 gpm and -21°C

The sixth and final test in the experimental matrix was designed to investigate nucleation, equilibrium concentrations, uniform/dispersed deposition behavior, and hydrate dissociation via methanol (MeOH) injection. Test 6 was conducted at a flow rate of 0.75 gpm (2.8 L/m) and a pressure of 1000 psia (6.9 MPa), using modified Test 5 procedures to reduce equipment and experimental uncertainties. Key modifications to the Test 6 procedure were:

1. Water was slowly added to the flowloop prior to cooling the loop. This allowed Probes 3 and 6 to be tested against each other in the absence of deposition or severe adsorption.

2. The flowloop leaks were reduced and the ISCO pump was used to maintain pressure at 1000 psia. The ISCO pump provided much better pressure control.
than the methane tank regulator.

3. Rapid pressure drop testing was not conducted, eliminating uncertainties sur-
rounding the initial conditions of the uniform hydrate/ice deposition testing.

Probe initialization and nucleation

The first step in Test 6 was to ensure that Probes 3 and 6 were consistent with
each other. The flowloop cool down, test, and reheat sections were all maintained at
a temperature of 15°C. Water was injected at a rate of 1 microliter/min until water
concentrations were just over 6 ppmw. Figure 5.41 shows that approximately 180
microliters of water were required before either moisture probe detected an increase in
water concentration. This was the volume of water required to fill the void space in the
injection line and bring the adsorbed water on the flowloop walls into equilibrium with
the condensate. Figure 5.41 shows that the probes exhibited nearly identical behavior,
thereby increasing confidence in the probe calibrations. The probe response was also
able to account for 70% - 80% of the water injected, which should be considered
successful considering water adsorption, probe accuracy, and water partitioning in
the two-phase separator.

After initializing the moisture probes, the test section temperature was decreased
to -21°C at a rate of -2.5°C/hr. As expected, water concentrations decreased with
decreasing flowloop temperature as illustrated in Figure 5.42. The water content in
the condensate dropped from approximately 6 ppmw to 3 ppmw as the test section
was cooled from 15°C to -21°C. As the test section was cooled, water adsorbed to the
test section walls, reducing adsorption uncertainties while investigating nucleation
metastability.

Nucleation metastability was probed by injecting water at rate of 1 micro-
liter/min until hydrate/ice nucleated. Figure 5.43 shows the water concentration in
Figure 5.41. Test 6 water injection rate and corresponding water concentrations during the probe initialization.
Figure 5.42. Test 6 water concentrations during the flowloop temperature ramp, prior to nucleation.
the condensate was increasing as water was slowly injected into the flowloop. After reaching \( \sim 9\text{-}10 \text{ ppmw} \), hydrate/ice nucleated on the flowloop wall at 12/4/07 23:00 and the water concentration decreased to the equilibrium concentration of \( \sim 7 \text{ ppmw} \). Figure 5.43 demonstrates that a water concentration driving force of \( \sim 3 \text{ppmw} \) was required to nucleate the solid phase. Additionally, the 7 ppmw water concentration measured at -21°C is consistent with previous experimental results and confirms there were probe inaccuracies in Test 5.

Figure 5.43. Test 6 water injection and concentration profiles before and after nucleation at -21°C.
Nucleation was also detected by an increase in test section pressure drop as shown in Figure 5.44. Pressure drop increased at 12/4/07 23:00, when the hydrate/ice nucleated. The pressure drop profiles indicate that the hydrate/ice nucleated between 80 ft and 120 ft in the test section. The increase in pressure drop also corresponded to a decrease in flow rate.

Figure 5.44. Test 6 pressure drop and flow rate profiles before and after nucleation.
Uniform deposition testing

After nucleating hydrate/ice, the water injection rate was increased to 28 microliters/min. This injection rate resulted in an inlet concentration (Probe 6) of 24–25 ppmw, as illustrated in Figure C.16 and Figure 5.45. Figure 5.45 shows the inlet concentration (Probe 6) was held at approximately 23–25 ppmw, while the outlet concentration (Probe 3) remained at the equilibrium concentration of 7 ppmw. Similar to previous experiments, the water concentrations indicated that water was depositing in the flowloop test section as hydrate or ice, resulting in a test section pressure drop increase. The sudden decrease in Probe 3 concentration at 12/9/07 6:30 was a result of a probe error and is discussed in Appendix C.8, Figure C.17.

Figure 5.46 shows that the hydrate deposit initially formed in the first 40 ft of the test section then slowly started to deposit downstream. Initially the 0–40 ft curve in Figure 5.46 began to increase and the rest of the curves followed, with constant separation, indicating hydrate/ice was building up in the first 40 ft of test section. Similar to previous experiments, pressure drops must be compared at similar flow rates. Because the pump speed was manually controlled, the pump frequency had to be increased as the flow rate decreased due to increasing pressure drop.

At approximately 12/6/07 8:00 the two bottom curves started to diverge (0–140 ft and 0–80 ft) indicating hydrate was also starting to deposit between 40 and 80 ft in the test section. The divergence of the pressure curves occurred because the hydrate/ice deposit was acting as insulation and increasing the fluid temperature in the first 40 ft.

Figure 5.47 shows the temperature 40 ft into the test section gradually increased as hydrate/ice deposited in the flowloop and acted as insulation. Similar to the pressure drop profiles, the temperature profiles must be compared at comparable
Figure 5.45. Test 6 water concentrations and resulting pressure drop during uniform deposition testing.
Figure 5.46. Test 6 flowloop flow rates and test section pressure drop profiles during the uniform/dispersed deposition testing. Each of the pressure drop profiles represents pressure drop across an additional 40 ft in the test section (see Figure 5.1).
Figure 5.47. Test 6 condensate temperature profiles and flow rate during deposition testing. Temperature readings are at 40 ft (203), 80 ft (204), and 120 ft (205) into the test section as illustrated in Figure 5.1.
flow rates. Figure 5.47 also confirms that hydrate/ice was depositing between 40 ft and 80 ft, as well as a slight deposition between 80 and 120 ft.

A uniform/dispersed deposition experiment was conducted immediately after solid nucleation at -21°C, 1000 psia and a loop flow rate of 0.75 gpm. Water injection was maintained at a rate of 28 microliters/min, resulting in an inlet water concentration of 23–25 ppmw, while the outlet concentration remained at 7 ppmw. The solid accumulation on the pipe walls resulted in a pressure drop increase, across the test section, from approximately 10 psi to 60 psi over the course of 5 days. The majority of the hydrate deposited in the first 80 ft of the test section, which also resulted in an increase in condensate temperature throughout those sections.

*Hydrate/ice dissociation via methanol injection*

The purpose of this portion of the experiment was to determine whether hydrate/ice could be dissociated using methanol (MeOH) dissolved in the condensate phase. Multi-Flash (INFOCHEM, 2007) was used to predict the MeOH saturation concentration in pure condensate, as well as, the 3-phase water-hydrate-condensate MeOH concentrations at -21°C. The predicted MeOH saturation concentration in pure condensate was 3.9% by weight. The 3-phase MeOH concentrations at -21°C are shown in Table 5.1. (It is important to note that Ng (2008) suggested most thermodynamic prediction packages over predict the MeOH saturation concentration in gas and condensate systems).

The goal of this portion of the experiment was to dissociate the hydrate by maintaining a MeOH concentration of 0.1% wt in the condensate, thus preventing a free MeOH phase from forming (< 3.9% wt). The condensate volume circulating through the loop was estimated to be 10.2 kg and 323 g of water were injected during the nucleation and deposition experiments. Based on the MeOH concentration in water
Table 5.1. Predicted MeOH concentration in the condensate and water phase at the water-hydrate-condensate 3-phase line (1000 psia and -21°C).

<table>
<thead>
<tr>
<th></th>
<th>Condensate Phase</th>
<th>Water Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Percent MeOH</td>
<td>0.1%</td>
<td>61.2%</td>
</tr>
</tbody>
</table>

at the 3-phase line (61.2% wt) approximately 250 ml of MeOH was required to dissociate 100% of the hydrate. MeOH was injected at a rate of 25 microliters/min, which was predicted to dissociate the hydrate over 5 days. MeOH was injected through the ISCO pump previously used for water injection.

Based on the 25 microliter/min injection rate it was expected that the MeOH concentration would reach the 3-phase concentration (0.1%) in the condensate after 6 hours. As shown in Figure 5.48 hydrates began to dissociate after approximately 4 hours.

MeOH injection began at 12/12/07 21:00 (Figure C.18) and water concentration rates immediately increased to 11-14 ppmw. The reason for this immediate step change is uncertain, the 3-phase water concentration in condensate was expected to be 10 ppmw; but 10 ppmw should not have been reached until MeOH concentration in the condensate reached 0.1% wt. It is possible that the MeOH changed the adsorption coefficients between water and the aluminum oxide sensors on the moisture probes.

The pressure drop slowly decreased prior to MeOH injection, which resulted from flowing an undersaturated condensate solution past the warmer (upstream) portions of the test section. The step change upon starting MeOH injection is due to opening the valve at the injection port. Hydrate dissociation via MeOH can be observed by the change in slope at approximately 12/13/07 1:00 (Figure 5.48), which was 2 hours
Figure 5.48. Test 6 water concentration profiles and test section pressure drop while injecting MeOH.
less than the expected dissociation onset time. Throughout the MeOH injection, water concentrations remained constant, indicating the water was trapped in a low spot in the test section and 3-phase equilibria existed as hydrate was increasingly dissociated.

The majority of the solid deposit dissociated from the first 40 ft of the test section, as shown in Figure 5.49. The constant spacing between the pressure drop profiles in Figure 5.49 shows that the hydrate was primarily dissociated in the first 40 ft. It is hypothesized that the free water was trapped in the in the coils of the first 40 ft of test section and this free water continued to remove MeOH from the condensate solution, preventing dissociation of hydrates further downstream.

Figure 5.50 confirms the majority of hydrate was dissociated in the first 40 ft, suggesting free water was held up in that section. The primary decrease in temperature, as the hydrate/ice melted and reduced wall insulation, was in the first 40 ft. Figure 5.50 shows the temperature drop 40 ft into the loop was from -10.5°C to -13.8°C. Whereas the temperature 80 ft into the test section only dropped from -17°C to -17.8°C. It appears that the temperatures reached a plateau, and the temperature at 80 ft would have taken an extremely long time to reach the original -19°C temperature (Figure 5.47).

The idea of water partitioning from the condensate phase to the free water phase in the test section was further reinforced by MeOH concentrations measured in the condensate phase directly downstream of the injection point. Test standards and experimental measurements conducted at the Westport Intertek facility are shown in Table 5.2 and Table 5.3.

Two standard samples were made gravimetrically and sent to the Intertek lab to assess quality control of the measurements. Table 5.2 shows that the measurements
Figure 5.49. Test 6 flowloop flow rates and test section pressure drop profiles during MeOH injection. Each of the pressure drop profiles represents pressure drop across and additional 40 ft in the test section (see Figure 5.1).
Figure 5.50. Test 6 condensate temperature profiles and loop flow rate during deposition testing. Temperature readings are at 40 ft (203), 80 ft (204), and 120 ft (205) into the test section as illustrated in Figure 5.1.
Table 5.2. Standard MeOH in condensate solutions compared with Intertek's measured concentrations.

<table>
<thead>
<tr>
<th>Standard Solution MeOH wt percent in condensate</th>
<th>Measured wt percent by Intertek</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0% ± 0.06%</td>
<td>0.816%</td>
<td>15%</td>
</tr>
<tr>
<td>0.08% ± 0.06%</td>
<td>0.185%</td>
<td>24%</td>
</tr>
</tbody>
</table>

Table 5.3. MeOH concentrations in condensate during MeOH injection. Measurements were conducted by Intertek.

<table>
<thead>
<tr>
<th>Date/Time</th>
<th>MeOH wt percent in condensate</th>
</tr>
</thead>
<tbody>
<tr>
<td>12/13/07 8:00</td>
<td>0.011%</td>
</tr>
<tr>
<td>12/13/07 17:37</td>
<td>0.017%</td>
</tr>
<tr>
<td>12/14/07 10:57</td>
<td>0.011%</td>
</tr>
<tr>
<td>12/15/07 14:59</td>
<td>0.037%</td>
</tr>
</tbody>
</table>

were within 25% of the expected values, which was deemed acceptable for monitoring MeOH concentrations during the dissociation experiment. Table 5.3 shows that the measured MeOH concentrations in the condensate were approximately an order of magnitude lower than the expected 0.1% at the 3-phase equilibrium.

MeOH was injected at a rate of 25 microliters/min to dissociate hydrate deposits in the test section. It was found that hydrates dissociated within 2 hours of the predicted time, calculated by Multi-Flash, which was well below the predicted free MeOH saturation concentrations. Hydrates were dissociated in the first 40 ft of the flowloop and free water became trapped in the heat exchanger coils. The MeOH then partitioned from the condensate to the water phase and prevented hydrate dis-
sociation further downstream in the flowloop. This experiment proved the concept of dissociating hydrate with a dissolved MeOH phase in the condensate, but it also shows that water holdup can be detrimental to the dissociation process.

*Test 6 discussion*

Test 6 was conducted at a pressure and temperature of 1000 psia (6.9 MPa) and -21°C, respectively. The target flow rate throughout the experiment was 0.75 gpm (2.8 L/m). Prior to decreasing the loop temperature, a small amount of water was injected to ensure Probes 3 and 6 were measuring identical water concentrations.

Nucleation and metastability were probed by injecting water at rate of 1 micro-liter/min. Nucleation occurred after a water concentration driving force of approximately 3 ppmw was reached. The equilibrium concentration was determined to be 7 ppmw, which is consistent with earlier measurements and verified there was a probe error in Test 5.

The uniform deposition experiment was carried out by maintaining an inlet water concentration of ~25 ppmw. The majority of the water deposited in the first 40 ft of the test section with subsequent deposition occurring between 40-120 ft. Similar to Test 5, it was found that the hydrate/ice deposit acted as insulation, increasing the condensate temperature in flowloop sections containing large amounts of solid deposits on the pipe wall.

Following the uniform deposition experiment, the hydrate/ice deposit was dissociated via MeOH injection. The deposit began to dissociate within 30% of the predicted dissociation concentration, which was calculated using Multi-Flash. The MeOH injection primarily dissociated hydrates in the first 40 ft of the test section. It is suspected that the free water became trapped in the early section of the flowloop, and MeOH subsequently partitioned from the condensate phase to the free water
phase. The partitioning of MeOH effectively lowered the condensate MeOH concentration, preventing solid dissociation in the latter parts of the test section.

5.3.3 Summary of Deposition Testing at -21°C

Tests 5 and 6 were conducted at pressures and temperatures of 1000 psia (6.9 MPa) and -21°C, respectively. Test 5 employed a loop flow rate of 0.5 gpm (1.9 L/m), while Test 6 was carried out at 0.75 gpm (2.8 L/m).

Test 5 nucleated hydrate/ice at a driving force of approximately 1 ppmw after an induction time of ~5 hours. The equilibrium concentration measured in Test 5 was 3.5 ppmw, but the low water concentrations were later determined to be the result of probe errors. Test 6 was initiated after verifying the probes were measuring precisely. Nucleation was induced by injecting water at a rate of 1 microliter/min and occurred after a driving force of ~3 ppmw was reached. The equilibrium concentration, 7 ppmw, measured in Test 6 is consistent with the baseline measurements made earlier in the testing program and the Multi-Flash predictions.

Uniform deposition was carried out over the course of 7 days (actual injection time) and 5 days for Tests 5 and 6, respectively. Due to probe errors and flowloop leaks in Test 5, it is difficult to directly compare the results of the two tests. However, in both tests, pressure drop in the test section increased to greater than 60 psi. Additionally, it was found that the hydrate/ice deposit acted as insulation on the pipe wall, resulting in the solid deposit propagating downstream.

The deposits were removed using two approaches: (1) dehydrating the inlet condensate stream, and (2) injecting MeOH. Test 5 investigated dehydrating the condensate stream. The inlet concentration was decreased below the equilibrium concentration, while the outlet concentration remained at the equilibrium concentra-
tion. The concentration difference was accompanied by a decrease in pressure drop as water was removed from the test section.

During MeOH injection, hydrate/ice was successfully dissociated using dissolved MeOH in the condensate phase (~0.1% wt). The MeOH injection primarily dissociated hydrates in the first 40 ft of the test section. It is suspected that the free water became trapped in an early section of the flowloop, and MeOH subsequently partitioned from the condensate phase to the free water phase. Partitioning of MeOH effectively lowered the condensate MeOH concentration, preventing solid dissociation in the latter parts of the test section.

5.4 Conclusions of Flowloop Tests

A single pass flowloop was successfully designed, constructed, and commissioned to measure solid-liquid condensate (LCond) equilibria and investigate plugging tendencies in a dissolved water, single-phase gas condensate system. GE Moisture Probes were used to measure water concentrations in the flowloop. It was imperative that probe temperatures were held constant and at a minimum of 10°C above the dew point. Although the probes did not always yield accurate absolute results, they were sufficient to track the relative change in moisture while injecting water or dehydrating the condensate.

Water concentrations in equilibrium with hydrate or ice were indistinguishable below 0°C. However, solid-LCond equilibrium concentrations were measured using the flowloop outlet concentration (Probe 3). Hydrate/ice typically nucleated with a water concentration driving force of 1–3 ppmw above the measured solid-LCond equilibrium concentration of 7 ppmw at 1000 psia (6.9MPa) and -21°C.

Four deposition experiments were conducted, in which two different hydrate/ice
plugging mechanisms were observed:

1. A rapid pressure drop increase (>1 psi/hour) was observed when the condensate was cooled below the liquid water \((L_w)\) saturation curve. Crossing the \(L_w\) saturation curve resulted in free water coalescing and forming a localized hydrate/ice restriction in the flowloop.

2. Uniform/dispersed deposition from a dissolved water phase resulted in a slow pressure drop increase (<1 psi/hour) throughout the first 40–120 ft of the flowloop. During uniform/dispersed deposition it was found that the hydrate/ice deposit acted as insulation on the pipe wall, resulting in the solid deposit propagating downstream.

The uniform hydrate/ice deposits were removed using two approaches: (1) dehydrating the inlet condensate stream and (2) injecting MeOH. Dehydrating the condensate stream reduced the inlet water concentration below the 2-phase equilibrium concentration, while the outlet concentration remained at the equilibrium concentration. The concentration difference was accompanied by a decrease in pressure drop as water was removed from the test section.

During MeOH injection, hydrate/ice was successfully dissociated using dissolved MeOH in the condensate phase (~0.1% wt). The MeOH injection primarily dissociated hydrates in the first 40 ft of the test section. It is believed that free water then formed, becoming trapped in the first 40 ft of the flowloop, and MeOH subsequently partitioned from the condensate phase to the free water phase. The MeOH partitioning effectively lowered the condensate MeOH concentration, preventing solid dissociation in the later parts of the test section.
Chapter 5 investigated hydrate/ice plugging mechanisms in a single pass flowloop. Experiments were conducted using a gas condensate containing dissolved water whereby hydrate/ice were found to deposit on the pipe wall via two mechanisms. Solid formation from the dissolved water phase resulted in a dispersed (lengthwise) deposit and was detected by a gradual increase in pressure drop and condensate temperature along the pipe length. Conversely, in the event that the condensate was cooled below the liquid water ($L_w$) saturation temperature, water coalesced and formed a free water phase. The free water phase rapidly converted to a solid phase, forming a localized restriction and resulted in a rapid pressure drop increase.

Chapter 5 suggests that the presence of free water will result in catastrophic failure and must be treated by chemical injection or depressurization. However, flowloop results indicate that there is a water concentration range between the hydrate and $L_w$ saturation curve where operators may continue to operate in the absence of chemical injection for a limited time frame.

The objective of this chapter is to develop a model which is capable of modeling the flowloop data from Chapter 5. The present model will then be extrapolated to field geometries in Chapter 7 and used to provide rules of thumb or heuristics in the event of a dehydrator upset.
6.1 Existing Deposition Literature

Deposition mechanisms from a dissolved phase have previously been studied in both the frost and wax literature. The following sections give a brief overview of the work that has been completed in both areas; there has also been one hydrate deposition publication, which is discussed.

6.1.1 Frost Literature

Hayashi et al. (1977) studied hydrate formation by flowing saturated air over a cold steel plate. Hayashi was able to classify frost growth into 3 distinct stages:

1. Crystal growth period. During the crystal growth stage, thin crystals sparsely coated the surface and grew in the vertical direction. The frost growth in this stage was primarily characterized by linear growth in the vertical direction.

2. Frost layer growth period. The rough frost growth from the previous stage began to fill in. Branches grew between the tops of the rod type crystals and eventually formed a mesh between the crystals. The frost layer became more uniform and the surface becomes almost flat.

3. Frost layer full growth period. The shape of the frost layer did not drastically change in the full growth stage until the surface of frost reached 0°C, due to thermal resistances. After reaching 0°C, the surface began to melt, draining into the frost and forming an ice layer. The cycle of melting, freezing, and growth then repeated itself until the layer reached a steady state height due to heat transfer resistances.

Recently, this lab has conducted experiments similar to those completed by Hayashi et al. (1977). Richard Tsau, an undergraduate researcher at the Center...
for Hydrate Research conducted frost growth studies by flowing saturated air across a cooled 1/8 inch Swagelock pipe (Tsau, 2008). Hayashi’s experiments successfully reproduced Hayashi’s three stages and are illustrated in Figure 6.1.

Following Hayashi’s work, numerous studies were completed as documented in O’Neal’s review (O’Neal and Tree, 1985). However, most of these modeling approaches used the assumption of a constant density throughout the entire deposit. Tao et al. (1993) were among the first authors to model both the spatial and temporal variation in frost density and temperature. The authors developed a rigorous model using spatial averaging, which resulted in a coupled pair of mass and heat transfer equations. The difficulty in this approach was further exacerbated by the fact that the equations were non-linear with a moving boundary.

Lee et al. (1997) also measured ice formation across a flat plate and modeled the data using a coupled heat and mass transfer model. Lee significantly reduced the difficulty of solving the equations by assuming: (1) an average density throughout the deposit and (2) the amount of water absorbed into the frost layer was proportional to the water-vapor density in the frost layer. The proportionality constant was used to couple the mass and energy equations and surface temperature of the frost was solved iteratively. Although Lee’s approach is simpler than Tao’s, the use of the proportionality constant is questionable.

Le Gall and Grillot (1997) modeled frost growth using an approach similar to Tao’s. Figure 6.2 illustrates the mass and energy balances used in Le Gall’s work. Figure 6.2 shows the frost properties were discretized into volume-averaged sections with volume fractions of ice and gas represented by $\epsilon_i$ and $\epsilon_g$, respectively. The increase in frost height ($\eta$) was calculated using the difference in total convective mass transfer ($n_t$) and diffusive mass transfer ($n_d$) at the surface. The water vapor density
Figure 6.1. Pictures of frost formation on cooled tube (a) crystal growth period, (b) frost layer growth period, and (c) frost layer full growth period.
Figure 6.2. Schematic used to explain heat and mass transfer phenomena in frost modeling (modified from Le Gall and Grillot (1997))

\( \rho \) was the mass transfer driving force and was assumed to be in local equilibrium \( \rho_{usi} \) with the frost temperature \( T_i \). Total heat transfer removed from the plate was defined as the sum of convective heat transfer \( q_{conv} \) and latent heat \( q_{lat} \) associated with ice formation.

The phenomena illustrated in Figure 6.2 results in the following mass and heat balances

\[
\begin{align*}
\Delta Flux + Generation &= Accumulation \\
D_{eff} \frac{d^2 \rho_i}{dy^2} + \dot{m} &= \left( \frac{\partial \rho_i \varepsilon_i}{\partial t} \right) \\
\dot{m} &= -\rho_i \left( \frac{\partial \varepsilon_i}{\partial t} \right)
\end{align*}
\]

\[
\Delta Flux + Generation = Accumulation
\]

\[k \frac{d^2 T}{dy^2} - L_{sv} \dot{m} = \rho C_p \left( \frac{\partial T}{\partial t} \right)
\]

where \( D_{eff} \) is the effective diffusivity, \( k \) is the thermal conductivity, and \( L_{sv} \) is the latent heat of formation of ice from water vapor. Equations 6.1 and 6.2 were then solved numerically to yield the frost’s temperature, height and density profiles versus time.
6.1.2 Wax Literature

In addition to hydrates, wax deposition is another nuisance encountered by the oil and gas industry in offshore production. Oils containing high molecular weight paraffins (wax) frequently develop a paraffin buildup in cold sections of the pipeline as their solubility decreases. A plethora of research has been conducted on wax deposition; however, recent researchers have modeled the problem using an approach similar to frost literature (Singh et al., 2000, 2001; Hernandez et al., 2004; Venkatesan and Fogler, 2004). Wax deposition models usually incorporate the following behavior, as discussed by Singh et al. (2000):

1. Gelation of the waxy oil at the cold surface.

2. Diffusion of soluble waxes from the bulk to the gel layer (the wax concentration in the gel layer decreases as waxes precipitate out).

3. Internal diffusion of the wax molecules through the oil phase in the gel deposit.

4. Counter diffusion of the de-waxed oil out of the gel layer.

In summary, the wax models incorporate both a growth and aging aspect, which is analogous to the frost literature.

6.1.3 Hydrate Literature

Shagapov and Urazov (2004) developed a deposition model for gas pipelines. The authors suggest that the in order for hydrates to form on the pipe wall, the wall temperature must be below the dewpoint (free water must be present). This assumption is contrary to the experiments discussed in Chapter 5, which found hydrates could form by simply reaching hydrate equilibrium conditions. However, in a gas system,
there is a limited range of water concentrations that will form hydrate before reaching the dewpoint (discussed in further detail in Chapter 7).

The model developed by Shagapov and Urazov (2004) assumes that the system is heat transfer limited in the early portions of the pipe line. During the early time period, hydrate formation is limited by heat transfer through the pipe wall. At some distance, $z$, the model switches to a mass transfer limited case. While mass transfer limited, the authors assume gas is dry at the hydrate interface and the driving force is provided by the water vapor concentration in the gas phase.

6.2 Flowloop Modeling Approach

All of the deposition mechanisms previously mentioned have similar characteristics. The depositing medium must diffuse from the bulk phase to the surface and the latent heat of crystallization must be removed through the plate/pipe wall. In the present work, an approach analogous to Singh’s (Singh et al., 2000) was used and the solid deposit was modeled using basic heat and mass balances.

6.2.1 Matching Initial Flowloop Pressure Drop and Temperature

Prior to modeling solid deposition/wall growth, the test section pressure drop and temperature profiles were matched in the absence of solid deposits. Two long term deposition tests, Test 5 and 6 were discussed in Chapter 5. The primary differences between the experiments were the flow rates, which were maintained at 0.5 gpm (1.9 L/m) and 0.75 gpm (2.8 L/m) during Test 5 and 6, respectively. Because Test 6 had fewer experimental uncertainties than Test 5, it was chosen as the first system to model. Pressure drop was calculated using a steady state momentum balance and
neglecting gravitational effects (Wilkes, 1999)

\[
\Delta p = 32 f_F \frac{\dot{m}^2 \Delta z}{\rho n^2 D^5}
\]  

(6.3)

where \(\Delta p\) is pressure drop (Pa), \(f_F\) is the Fanning friction factor, \(\rho\) is the fluid density (kg/m\(^3\)), \(\Delta z\) is the axial distance (m) and \(D\) is the inner diameter of the flowloop (9.3E-3 m/0.37 in). The Fanning friction factor was fit to match the flowloop pressure drop as shown in Table 6.1.

<table>
<thead>
<tr>
<th>Distance (m)</th>
<th>Actual (\Delta P) (psi)</th>
<th>Calculated (\Delta P) (psi)</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>12.1</td>
<td>1.7</td>
<td>1.3</td>
<td>23%</td>
</tr>
<tr>
<td>24.2</td>
<td>2.6</td>
<td>2.6</td>
<td>0%</td>
</tr>
<tr>
<td>36.3</td>
<td>3.9</td>
<td>3.9</td>
<td>0%</td>
</tr>
<tr>
<td>48.4</td>
<td>5.5</td>
<td>5.3</td>
<td>3.6%</td>
</tr>
<tr>
<td>60.6</td>
<td>6.2</td>
<td>6.5</td>
<td>4.8%</td>
</tr>
<tr>
<td>72.7</td>
<td>7.7</td>
<td>7.8</td>
<td>1.3%</td>
</tr>
</tbody>
</table>

Table 6.1. Comparison of experimental and predicted pressure drop in the test section.

The pressure drop calculations shown in Table 6.1 were completed using a \(f_F\) value of 1.07E-2. This value was 18% greater than the predicted factory value of 9.1E-3. However, because the pressure drop calculation did not incorporate the various fittings used for the data acquisition probes and coupling the 14 heat exchangers, the fitted value is considered reasonable.

The temperature profile was calculated using an energy balance, assuming the cooling fluid was maintained at a constant temperature of 252.5 K (this assumption
was made because cooling fluid was supplied in parallel to each heat exchanger)

\[ T_{out} = T_{in} - \frac{q_r}{C_p \dot{m}} \]  \hspace{1cm} (6.4)

where \( T_{in} \) and \( T_{out} \) are the temperature of the fluid entering and exiting the control volume (K), \( q_r \) is the energy transferred from the condensate to the cooling fluid (W), \( C_p \) is the condensate specific heat capacity (J/kg-K), and \( \dot{m} \) is the condensate mass flow rate (kg/s). A series of convective resistances (neglecting conduction through the pipe wall) were used to calculate \( q_r \) as illustrated in Figure 6.3.

Figure 6.3 shows heat transfer through the pipe wall is a function of: \( T_B \) the bulk condensate temperature (K), \( T_c \) the cooling fluid temperature (K), \( r_w \) the inner radius of the flowloop (m), \( r_c \) the outer radius of the flowloop (m), \( h_B \) is the internal heat transfer coefficient (W/m²-K), and \( h_c \) is the external heat transfer coefficient (W/m²-K). The internal heat transfer coefficient, \( h_B \), was calculated using
the Chilton-Colburn analogy (Incropera and Dewitt, 1996)

\[ Nu_D = 0.023Re_D^{4/5}Pr^{1/3} = \frac{h_B D}{k} \]  

(6.5)

where \( Nu_D \) is the Nusselt number, \( Re_D \) is the Reynolds number, \( Pr \) is the Prandtl number and \( k \) is the thermal conductivity of condensate (assumed to be the properties of n-decane at 252 K and 1000 psi  0.14 W/m-K). The heat bare pipe internal heat transfer coefficient, \( h_B \), was calculated to be \( \sim 1300 \) W/m²-K.

Equation 6.4 was used to match the bare pipe temperature profile, as shown in Table 6.2, by fitting \( h_c \) to 360 W/m²-K.

<table>
<thead>
<tr>
<th>Distance (m)</th>
<th>Actual Temp (K)</th>
<th>Calculated Temp (K)</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>287.5</td>
<td>287.5</td>
<td>0%</td>
</tr>
<tr>
<td>12.1</td>
<td>258.9</td>
<td>258.9</td>
<td>0%</td>
</tr>
<tr>
<td>24.2</td>
<td>254.2</td>
<td>253.7</td>
<td>0.1%</td>
</tr>
<tr>
<td>36.3</td>
<td>252.6</td>
<td>252.7</td>
<td>0.03%</td>
</tr>
</tbody>
</table>

Table 6.2. Comparison of experimental and calculated temperature profiles.

6.2.2 Hydrate/Ice Deposition Model

As previously mentioned, hydrate/ice was modeled using a simplified version of the wax deposition model presented by Singh et al. (2000). The modeled geometry is shown in Figure 6.4. The subscript ‘i’ in Figure 6.4 denotes the radius, temperature, and concentration profiles at the condensate-solid interface. Several assumptions were used in modeling the flowloop data:
1. Water concentration at the solid-L$_{Cond}$ interface was in equilibrium with the interface temperature.

2. Hydrate/ice was assumed to be deposited uniformly, with respect to radius and distance, in each $\Delta z$ increment.

3. Heat transfer was assumed to be one dimensional (radial) and quasi-steady state.

4. Hydrate/ice was assumed to be constant density. The present model does not incorporate an ‘aging’ mechanism as discussed in Section 6.1. Because density, thickness, and morphology were not directly measured in the flowloop experiments, the accuracy of an aging model could not be tested. Thus, constant density was assumed to reduce computational complexity.
Change in hydrate/ice thickness was calculated using the following mass balance on the water phase

\[ \Delta \frac{\partial \ell}{\partial t} + \mathbf{Q} \cdot \nabla \ell = \text{Accumulation} \]

\[ 2\pi \Delta \tau_i h_m [C_B - C_i(T_i)] = \frac{d \Delta z(r_w^2 - r_i^2) \rho_s}{dt} \]

where \( \rho_s \) is the density of the solid deposit (kg/m\(^3\)), \( r_i \) is the radius of the solid front (m), and \( h_m \) is the mass transfer coefficient (m/s). The mass transfer coefficient was calculated analogous to the heat transfer coefficient

\[ Sh_D = 0.023 Re_D^{4/5} S_c^{1/3} = \frac{h_m D}{D_{WC}} \]

where \( Sh_D \) is the Sherwood number, \( S_c \) is the Schmidt number, and \( D_{wc} \) is the molecular diffusion coefficient of water in condensate. \( D_{wc} \) (cm\(^2\)/s) was calculated using the Wilke-Chang correlation (Seader and Henley, 1998)

\[ D_{wc} = \frac{7.4 \times 10^{-8} (\phi_c M_c)^{1/2} T}{\mu_c \nu_w^{0.6}} \]

where \( \phi_c \) is the association factor of the condensate (0), \( M_c \) is the molecular weight of the condensate (142 g/mol), \( T \) is the temperature (273 K), \( \mu_c \) is the viscosity of the condensate (2.64E-5 Pa-s), and \( \nu_w \) is the molar volume of water (18 cm\(^3\)/mol). Equation 6.8 yields a predicted diffusion coefficient for water in condensate of 1.6E-8 m\(^2\)/s. The predicted diffusion coefficient was then used to calculate a mass transfer coefficient (Equation 6.7) of 2.7 E-4 m/s for the bare pipe diameter.
The two unknowns in Equation 6.6 are \( r_i \) and \( T_i \). \( T_i \) was calculated using an energy balance across the control volume

\[
\text{In} - \text{Out} + \text{Generation} = \text{Accumulation}
\]

\[
2\pi\Delta z r_i h_B (T_B - T_i) - 2\pi\Delta z r_i u'(T_i - T_c) + 2\pi\Delta z r_i h_m [C_B - C_i(T_i)] \Delta H_f = 0
\]

(6.9)

where \( \Delta H_f \) is the latent heat of solid formation. The value \( u' \) is the combined heat transfer coefficient, incorporating solid thermal conductivity and the external heat transfer coefficient in series

\[
u' = \frac{1}{\ln\left(\frac{r_{w}/r_i}{k_s} + \frac{1}{h_c r_c}\right)}
\]

(6.10)

where \( k_s \) is the thermal conductivity of the composite solid deposit (W/m-K).

The flowloop was divided into sections (\( \Delta z \)) as illustrated in Figure 6.5. In each section, Equation 6.9 was used to solve for the interface temperature, \( T_i \). The interface temperature was then used to calculate the equilibrium water concentration at the solid interface, allowing the change in radius (\( r_i \)) to be calculated with Equation 6.6. Energy and mass balances were then conducted on the exiting fluid and the process was repeated in the next section of pipe. After, solving Equations 6.6 and 6.9 for the entire flowloop, the model moved to the next time step and restarted at the flowloop inlet. Note that the variables changing with diameter, such as \( h_B \) and \( h_m \), were recalculated at each distance and time step.

After calculating thickness profiles of the solid deposits, pressure drop was calculated to compare with experimental data. Equation 6.3 was used to calculate pressure drop for each \( \Delta z \) using the effective radius of the solid deposit and assuming mass flow rate remained constant. The pressure drop calculations were then summed over the entire test section. The friction factor used, was the greater of two values: (1)
Figure 6.5. Illustration of the flowloop, which was divided into sections in the model.

the value used for fitting the bare pipe, or (2) the friction factor calculated using the Colebrook and White Correlation. The Colebrook and White correlation calculates the friction factor as a function of surface roughness (Wilkes, 1999)

$$f_F = \left\{ -1.737 \ln \left[ \frac{0.269 \varepsilon}{D} - \frac{2.185}{Re} \ln \left( \frac{0.269 \varepsilon}{D} + \frac{14.5}{Re} \right) \right] \right\}^{-2} \tag{6.11}$$

where $\varepsilon$ represents the surface roughness. The present work assumes that the deposit was rough as depicted in Figure 5.25 and the average hydrate thickness ($r_w-r_i$) was equal to $\varepsilon$.

6.3 Modeling Results

Flowloop experiments were modeled assuming the inlet concentration was 25 ppmw and the cooling fluid temperature ($T_c$) was constant at -21°C. A curve was fit to the predicted equilibrium points in Figure 5.11. The curve was then used to predict equilibrium water concentrations at the interface ($C_i$), after calculating the interface temperature (Equation 6.9). The time and distance steps were set to 120 s and 0.1 m, respectively (validation of the time and distance step is discussed in Appendix D.1).
6.3.1 Hydrate Base Case and Sensitivity Analysis

Test 6 was initially modeled using properties for pure structure II hydrate \((k_s = 0.5 \text{ W/m-K}, \rho_s = 900 \text{ kg/m}^3)\). The predicted hydrate deposit, formed from the dissolved water phase, qualitatively matched the expected trends as shown in Figure 6.6. The initial radius at 0 hours is the original pipe radius of 4.65E-3 m. The hydrate thickness increased with time, which is observed by the decreasing hydrate radius in Figure 6.6. Another encouraging aspect of Figure 6.6 is that the hydrate growth propagates downstream with time, similar to the observed experimental pressure drop trend. The propagating growth behavior is explained by the increased heat transfer resistance due to hydrate deposition, as shown by the temperature profiles in Figure 6.7.

Figure 6.7 shows the temperature profiles at varying distances in the test section. The step changes in the experimental temperature profiles resulted from increasing the pump speed. The pump speed was increased to maintain a constant flow rate, as pressure drop increased with solid deposition. The temperature profiles should be compared directly after the increase in pump speed (signified by the step change in temperature). Figure 6.7 shows that the predicted temperature profiles match the measured temperature increase at corresponding locations.

The final piece of information for comparing experimental data and predicted results was the pressure drop shown in Figure 6.8. Figure 6.8 shows that the calculated pressure drop profiles under predict the experimental pressure drop. Equation 6.3 shows the pressure drop was likely under predicted due to errors in the friction factor or the hydrate thickness. Appendix D.2 investigates the effects of an increased friction factor and a localized hydrate deposit. However, friction factor had to be multiplied by a factor of 7 and a more localized deposit still under predicted pressure drop.
Figure 6.6. Test 6 predicted hydrate radii from 0–120 hours, through the first 60 m of the flowloop test section.
Figure 6.7. Test 6 experimental and predicted temperature profiles assuming pure hydrate.
Appendix D.2 concluded that neither an increased friction factor nor a localized deposit explained the difference between the experimental and predicted pressure drop.

Figure 6.8. Test 6 experimental and predicted pressure drop profiles assuming pure hydrate.

A sensitivity analysis was conducted to further investigate sources of error related to experiments and transport correlations. Parameters investigated in the sensitivity analysis were: heat transfer coefficient (internal), mass transfer coefficient, inlet water concentration, and flow rate. The range of values tested were expected to encompass the range of error that may have been present in each variable. The results of this
sensitivity analysis are shown in Figures 6.9 and 6.10.

Figure 6.9. Tornado diagram summarizing the sensitivity analysis on the maximum hydrate thickness.

Figures 6.9 and 6.10 show how adjusting each variable affects the maximum hydrate thickness and pressure drop 35 m into the test section, respectively. The center line represents the base case thickness/pressure drop and the relative change is shown for the range of values tested. The experimental error of water concentration and flow rate was expected to between ± 5 ppmw and ± 0.25 gpm, respectively. The uncertainty surrounding the heat and mass transfer coefficients was ± 5x and the thermal conductivity of hydrate was adjusted ± 0.25 (W/m-K). Figure 6.9 shows
Figure 6.10. Tornado diagram summarizing the sensitivity analysis on the pressure drop at 35 m.
that the mass transfer coefficient and inlet water concentration have the greatest affect on the maximum thickness. However, the largest change in pressure drop was associated with flow rate and the inlet water concentration.

The pressure drop profiles for the 1.0 gpm flow rate and 30 ppmw inlet concentration are shown in Figure 6.11. These figures show the high flow rate and inlet water concentration still significantly under predict pressure drop. Given the results of this sensitivity analysis and Appendix D.2, another factor must be accounted for in the model.

![Figure 6.11. Comparison of Test 6 predicted and experimental pressure drop (a) with a flow rate of 1 gpm, and (b) with an inlet concentration of 30 ppmw.](image)

6.3.2 Porous Hydrate and Ice Deposits

The previous section explored a wide range of variables, yet the pressure drop was under predicted in each circumstance. Revisiting Equation 6.3 reveals that the pressure drop is inversely proportional to $D^5$, suggesting the experimental deposit must have been thicker than the predicted deposits. A thicker deposit could be explained by porous deposits. The frost and wax literature, previously discussed,
describe an initially porous deposit that anneals with time. The author hypothesizes that annealing is true of hydrate/ice deposits as well. The effect of porosity was tested by assuming the hydrate deposit had a void fraction of 73%. The composite thermal conductivity was calculated using a volumetric average of the hydrate and condensate fractions.

Figure 6.12 shows that the final pressure drop was matched to the same order of magnitude as the experimental data. However, the predicted temperature profiles significantly over predicted the data. A possible explanation for the temperature divergence in Figure 6.12b is that the composite thermal conductivity was too low. Revisiting Figure 5.11, it can be seen that the difference in equilibrium water concentrations between ice and hydrate is ~2 ppmw at -21°C. Given the uncertainty in formation kinetics at that temperature, the deposit may have been ice, rather than hydrate. This is significant because ice has a thermal conductivity of 2.23 W/m-K (Sloan and Koh, 2008) or approximately 4 times the value used for hydrate.

Figure 6.12. Comparison of Test 6 predicted and experimental values using a hydrate void fraction of 73% (a) pressure drop profiles, and (b) temperature profiles.
The results of modeling the flowloop deposit as a porous (67%) ice deposit are shown in Figure 6.13. Similar to the porous hydrate deposit, pressure drop was matched to the same order of magnitude. However, the temperature profiles of the porous ice deposit exhibited a much closer match to the experimental data. Note that the ice deposit required a less porous deposit than the hydrate deposit to match pressure drop. The lower porosity deposit is due to the increased thermal conductivity of the ice deposit, which resulted in a more localized deposit than the hydrate.

![Figure 6.13a](image1.png)  
Figure 6.13a. Comparison of Test 6 predicted and experimental values using an ice void fraction of 67% (a) pressure drop profiles, and (b) temperature profiles.

Figure 6.13a shows that the pressure drop profiles are still under predicted in the initial stages of the experiment. This can be attributed to the use of a constant density in the model. The experimental deposit was likely more porous than the 67% void fraction in the initial stages of the experiment, before annealing to an average value of 67% as the experiment progressed.
Test 5 Modeling

After fitting the Test 6 data, the Test 5 data (0.5 gpm) set was investigated. It is important to note that there was a major upset in the middle of Test 5, which was removed from the data set. Similar to Test 6, a friction factor and external heat transfer coefficient were fit to the bare pipe, which were determined to be 0.0134 and 328 W/m²-K, respectively. The flow rate was decreased from 0.75 gpm to 0.5 gpm and the remaining parameters were identical to the Test 6 model.

Comparable to Test 6, a porous hydrate deposit over predicted the temperature profile (Figure D.4). But encouragingly, the porous ice deposit (67% void fraction) used in Test 6, reasonably predicted the Test 5 temperature and pressure drop profiles. Figure 6.14 shows the predicted pressure drop and temperature profiles qualitatively match the experimental data.

Figure 6.14. Comparison of Test 5 predicted and experimental values using an ice void fraction of 67% (a) pressure drop profiles, and (b) temperature profiles.

The Test 5 predicted pressure drop profile is slightly delayed in relation to the experimental data. Possible explanations for this difference are the experimental
procedure and the flowloop leak (Appendix C.7). Prior to conducting the long term deposition study in Test 5, rapid pressure drop was investigated, which was then followed by running the dehydration unit. An unknown amount of solid was likely deposited in the test section prior to running the long term deposition test. Thus, the model would under predict the total volume of hydrate in the flowloop and under predict the pressure drop as shown in the first 120 hours of the comparison.

The final portion of experimental data to be modeled was the Test 5 dissociation. Experimentally, a dehydrator was placed in line with condensate flow, effectively lowering the inlet water concentration to a value of 3±1 ppmw. The under saturated stream then dissociated the deposit. The dissociation experiment was modeled with the same model used in the deposition, except the inlet concentration was reduced from 25 ppmw to 3 ppmw. Figure 6.15 shows the ice thickness decreased with time and slowly propagated downstream as was illustrated experimentally in Figure 5.33.

Figure 6.16a shows the predicted pressure drop decreases and matches the final experimental pressure drop. Likewise, the temperature profile (Figure 6.16b) shows the predicted temperature profile matches the relative change observed in the experiment. However, upon further examination, the predicted pressure drop profile does not match the initial time delay before pressure drop began to decrease. Figure 5.39 shows that a slight pressure drop increase and flow rate decrease was observed after initially running the dehydrator. The initial pressure drop behavior was matched by adjusting the diffusion coefficient ($D_{wc}$), which was proportional to the mass transfer coefficient.

Figure 6.17 probes the effect of the diffusion coefficient on the pressure drop profiles. It can be observed that increasing $D_{wc}$ by a factor of 2 or 2.5, yields a closer match between the predicted and experimental pressure drops. Two possible
Figure 6.15. Test 5 predicted deposit profile while running the dehydrator.
Figure 6.16. Comparison of Test 5 predicted and experimental values while running the dehydrator (a) pressure drop profiles, and (b) temperature profiles.

Explanations for this behavior are (1) an incorrect value of $D_{wc}$ was used, or (2) portions of the deposit were sheared off the wall and became entrained as the deposit dissociated. These results show that the deposition and dissociation mechanisms are mass transfer limited in the current model, which is further discussed in Appendix D.4.
Figure 6.17. Comparison of Test 5 predicted and experimental pressure drop profiles while running the dehydrator (a) increasing $D_{wc}$ by 2x, and (b) increasing $D_{wc}$ by 2.5x.
6.4 Conclusions of Flowloop Modeling

A deposition model was derived from a mass and energy balance. The same modeling parameters were used to model three experiments (Test 5 and 6 deposition and Test 5 dissociation) with reasonable accuracy. The model used an ice deposit with a 67% void fraction. Ice dissociation was successfully modeled by decreasing the inlet concentration in the deposition model.

The comparison of the model and experimental data suggests that the deposit annealed (became denser) with time, as observed in both frost and wax literature. However, additional experiments capable of measuring the actual thickness and density of the deposits are required to further refine the current model.
Chapter 7

FIELD SENSITIVITY ANALYSIS

Chapter 6 developed a heat and mass transfer model which was used to model the Chapter 5 flowloop data. The model was based on fundamental transport properties and is expected to yield order of magnitude predictions for solid deposition in dissolved water hydrocarbon systems. The first portion of the present chapter extrapolates the condensate model to an arctic pipeline geometry. The second section in this chapter extrapolates the model to a more typical offshore gas export line, assuming the line is 100% methane.

7.1 Condensate Pipeline

This section investigates the effect of scaling the flowloop model to a larger pipeline. The majority of the properties used in modeling the flowloop data (Chapter 6) were also utilized in the present work. However, several of the modeling parameters were changed as shown in Table 7.1.

Table 7.1 shows that the field system was chosen to be a 24 in pipeline with an ambient temperature of -15°C. The equilibrium water concentration at -15°C is ~10 ppmw. The first step was to investigate the effect of ice vs. hydrate and porosity, which were determined to significantly affect deposition in Chapter 6. Pure ice and hydrate were compared with 67% void fraction ice and 73% void fraction hydrate. The porosities chosen are the values required to match flowloop pressure drop in Chapter 6. Figure 7.1 shows that the ice and hydrate deposits have similar final
Model Parameter | Value
--- | ---
Condensate Velocity | 2 m/s
Inlet Concentration | 25 ppmw
Inlet Temperature | 2°C (275 K)
Ambient Temperature | -15°C (258 K)
Pipe i.d. | 24 in (0.61 m)
External Heat Transfer Coef | 22 W/m²-K (4 Btu/ft²-hr)
Pipe Length | 100 km

Table 7.1. Parameters used to scale flowloop model to field geometry (100% condensate).

thickness profiles at 100 days. The similarity in deposition profiles is contrary to the flowloop models, which observed the ice deposit to be more localized than the hydrate deposit. The hydrate and ice deposition profiles suggest that the model is limited by external heat transfer through the pipe wall, rather than heat transfer through the deposit. If the model was limited by heat transfer through the deposit, the ice deposit would have been more localized as observed in Chapter 6 (due to the increased thermal conductivity of ice). Figure 7.1 shows that the hydrate deposit with a 73% void fraction had the greatest thickness of the four deposits investigated. Therefore the hydrate deposit with a 73% void fraction was used for the remainder of this chapter.

Figure 7.2 shows the predicted hydrate (73% void) growth in an arctic pipeline with an ambient temperature of -15°C (10 ppmw equilibrium concentration). This simulation was designed to model a scenario in which the dehydrator went out of the 10 ppmw specification and increased to 25 ppmw. Figure 7.2 shows that the hydrate deposit thickness would increase to a maximum of 4.5 mm over ~100 days. The deposit would also begin to propagate downstream with time, as the deposit began
Figure 7.1. Comparison of predicted deposit profiles after 100 days of growth.
to act as insulation.

Figure 7.2. Predicted hydrate deposition profiles (73% void) in condensate field geometry.

The next simulation tests the deposit’s response to changing the inlet concentration to 10 ppmw. This scenario assumes that the dehydrator malfunction was corrected, but the ambient temperature remained the same. Figure 7.3 shows that the deposit would be redistributed further downstream, but only a minute amount of the deposit would be removed from the pipeline.

The final simulation investigates how the final deposit in Figure 7.2 would change if the inlet concentration was lowered to 10 ppmw and the ambient temperature
Figure 7.3. Effect on hydrate deposit formed in Figure 7.2, after lowering inlet concentration to 10 ppmw.
was increased to -5°C. The temperature and water concentration were chosen to simultaneously simulate a change in seasons (summer) and repairing the dehydrator. Figure 7.4 shows that over the course of 100 days, the deposit would decrease to a thickness less than 1 mm thick and would be almost completely removed from the pipeline.

Figure 7.4. Effect on hydrate deposit formed in Figure 7.2, after lowering inlet concentration to 10 ppmw and increasing ambient temperature to -5°C.

Figures 7.2 and 7.4 show that in the event of a dehydrator upset, operations may be able to continue, as long as free water is not condensed into the system. A hydrate deposit formed from the dissolved water phase is expected to grow extremely slowly.
in a condensate system. The results also suggest that the deposit can be removed in a similar time frame that the deposit occurred, if the water concentration is lowered below the equilibrium concentration associated with the ambient temperature (which can also result from seasonal temperature increases).

7.1.1 Sensitivity Analysis

A sensitivity analysis was conducted on the condensate system to determine what parameters warrant further investigation in developing an accurate field model. The following parameters were investigated: inlet water concentration (20 and 30 ppmw), external heat transfer coefficient (±5x), internal heat transfer coefficient (±5x), mass transfer coefficient (±5x), and hydrate thermal conductivity (0.25, 0.75 W/m-K). Figure 7.5 shows the how these range of variables affect the maximum thickness of the hydrate deposit.

Figure 7.5 shows that the inlet water concentration and external heat transfer coefficient have the largest impact on the maximum hydrate thickness. The importance of the inlet water concentration is intuitive, because increasing the inlet concentration also increases the amount of water that can deposit in the pipeline. The effect of the external heat transfer coefficient confirms that the results in Figure 7.1 were limited by the external heat transfer, suggesting that the pipeline insulation or surrounding medium plays a significant role in the deposition thickness. The third most significant variable is the mass transfer coefficient, which is proportional to the diffusion coefficient. The sensitivity to the diffusion coefficient illustrates the importance of experimentally measuring the diffusion coefficient of water in specific field condensates.
Figure 7.5. Tornado diagram illustrating which variables have the greatest impact on maximum thickness.
7.2 Gas Systems

The previous section investigated hydrate deposition from a dissolved water phase in a condensate system. Because the solubility of water in a liquid hydrocarbon is extremely low, the previous section was only applicable to extremely low temperatures such as arctic environments. This section investigates a subsea methane pipeline, which is a more typical industrial scenario. In this section, the condensate model was extrapolated to a gas system and the fluid properties were adjusted appropriately. The basic heat and mass transfer phenomena are expected to be similar to the condensate system and should scale accordingly with the updated fluid properties. Three major assumptions in the methane model are (1) methane is considered to be constant density throughout the pipeline, (2) pressure is assumed constant throughout the pipeline, and (3) Joule-Thompson effects are neglected.

A major difference between the condensate and methane systems is that the methane holds significantly higher concentrations of water. The concentrations are illustrated in Figure 7.6, which depicts the water vapor concentration in equilibrium with either liquid water or hydrate. The incipient hydrate formation temperature at 3000 psia is 19°C (292 K) and the corresponding equilibrium water vapor concentration is 263 ppmw. The experimental results in Chapter 5 suggest that at 3000 psia, a dehydrator upset greater than 263 ppmw would result in liquid water condensing and the formation of a localized plug. However, an upset below 263 ppmw, but still above the hydrate equilibrium water concentration (94 ppmw at 4°C) would result in a dispersed hydrate deposit.

The same system geometry used in Section 7.1 was utilized in the present analysis. Besides switching to a methane system, the primary difference is that the ambient temperature was held at 4°C, which is typical of most offshore pipelines. As illus-
Figure 7.6. Methane water vapor concentrations in equilibrium with liquid water and hydrate at 3000 psia (predicted using Multi-Flash CPA model). If the methane is cooled below the saturation curve above 263 ppmw, free water will coalesce and form a localized deposit. Crossing the saturation line below 263 ppmw would result in a dispersed deposit.
trated in Figure 7.6, the methane gas holds significantly more water and the inlet concentration was assumed to be 250 ppmw. This water concentration is the upper limit that would still result in a dispersed deposit and is significantly greater than the 92 ppmw equilibrium concentration at 4°C. The methane simulation assumes that the dehydrator normally operates at 50 ppmw, but there has been an upset and water concentration increased to 250 ppmw. Additional properties used in the methane model are listed in Table 7.2.

<table>
<thead>
<tr>
<th>Model Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane Velocity</td>
<td>4 m/s</td>
</tr>
<tr>
<td>Inlet Concentration</td>
<td>250 ppmw</td>
</tr>
<tr>
<td>Inlet Temperature</td>
<td>300 K</td>
</tr>
<tr>
<td>Methane Viscosity</td>
<td>1.96E-5 Pa-s</td>
</tr>
<tr>
<td>Methane Thermal Cond</td>
<td>0.0629 W/m-K</td>
</tr>
<tr>
<td>Methane Density</td>
<td>150 kg/m^3</td>
</tr>
<tr>
<td>Methane Cp</td>
<td>3550 J/kg-K</td>
</tr>
<tr>
<td>Diffusivity Coef</td>
<td>9E-8 m^2/s</td>
</tr>
<tr>
<td>Ambient Temperature</td>
<td>4°C (277 K)</td>
</tr>
<tr>
<td>Pipe i.d.</td>
<td>24 in (0.61 m)</td>
</tr>
<tr>
<td>External Heat Transfer Coef</td>
<td>22 W/m^2-K (4 Btu/ft^2-hr)</td>
</tr>
<tr>
<td>Pipe Length</td>
<td>100 km</td>
</tr>
</tbody>
</table>

Table 7.2. Parameters used to scale flowloop model to field geometry using 100% methane.

Figure 7.7 shows the hydrate deposition profile assuming a 73% void fraction. The hydrate thickness is approximately 4 times greater than the condensate system over the same time period (Figure 7.2). The increased thickness is primarily due to the increased water concentration that can be carried in the vapor phase. The driving force from the inlet concentration to ambient temperature is \(~150\) ppmw in the methane phase compared to \(~15\) ppmw in the condensate phase.
Figure 7.7. Predicted deposition profile in a methane system assuming a hydrate deposit with a 73% void fraction.
Another major difference between the condensate and methane system is that the methane system was operated at twice the velocity as the condensate simulation. (Although the density of the condensate system is 4 times greater than the methane). Figure 7.8 compares the deposition profiles of the methane system using a gas velocity of 2 m/s and 4 m/s. Interestingly, the maximum deposition thickness is comparable between the two velocities. The 4 m/s deposit is dispersed throughout a greater distance of the pipe, which is expected because twice the amount of water was added to the system. However, the comparable maximum thickness suggests that the system is heat transfer limited in the upstream portions of the deposit.

Figure 7.8. Comparison of final hydrate deposit profile using 2 m/s and 4 m/s.
Similar to the condensate field investigations, the feasibility of dissociation via dehydration was investigated. The final deposit in Figure 7.7 was used as the initial condition and the inlet water concentration was decreased to 50 ppmw (assuming the dehydrator was brought back into specification). Figure 7.9 shows the deposit propagates downstream and a portion of the water is removed from the pipeline. However, a large deposit still exists after 100 days. The lingering deposit is intuitive because the driving force for hydrate dissociation was only ~50 ppmw (92 ppmw - 50 ppmw), while the deposition driving force was ~150 ppmw (250 ppmw - 92 ppmw) over the same time period.

Figure 7.9. Hydrate profile in methane system after changing inlet water concentration to 50 ppmw.
7.2.1 Sensitivity Analysis

Similar to the Section 7.1.1, a sensitivity analysis was conducted on the methane field geometry model. Because the model was already run at the upper boundary for moisture content, this parameter was eliminated from the analysis. Figure 7.10 illustrates the relative change in maximum thickness by using the same range of values used in Section 7.1.1. The figure shows that the external heat coefficient and thermal conductivity are the most sensitive parameters. This is in agreement with Figure 7.8, which indicated the system was heat transfer limited.

![Tornado diagram illustrating how various model parameters affect the maximum deposit thickness in a methane system.](image)

Figure 7.10. Tornado diagram illustrating how various model parameters affect the maximum deposit thickness in a methane system.
Thermal conductivity was significantly more important in the methane system than in the condensate system (Figure 7.5), because the increased water concentration in the methane system developed a thicker deposit. The thicker deposit increases the importance of thermal conductivity as the system becomes heat transfer limited. This also indicates that the porosity of the deposit is very important. Because the thermal conductivity is calculated using a volumetric average of gas and hydrate, the porosity greatly effects the composite thermal conductivity.

7.3 Conclusions of Field Sensitivity

The flowloop model from Chapter 6 was extrapolated to field geometries to investigate the relative effect of the model parameters. Both a pure condensate and pure methane system were investigated. The combination of the experimental results in Chapter 5 and the modeling results in the present chapter indicate there is a range in which operators can continue to produce fluids in the event of a dehydrator upset. The author hypothesizes that an inlet water concentration which reaches the hydrate equilibrium line (as the fluid is cooled) before reaching the dewpoint curve (Figure 7.6) will result in a dispersed deposit.

The results in this chapter suggest that a hydrate deposit formed from a dissolved water phase would have a growth rate less than millimeter/week. Because methane carries more dissolved water than condensate, a greater deposit thickness is expected in the methane system. However, in both systems it was predicted that hydrates could be dissociated via dehydrating the gas and/or seasonal increases in the ambient temperature.

In both model systems, the external heat transfer coefficient was found to be the most significant variable. In the condensate system, the diffusion coefficient was
the second most important variable; whereas thermal conductivity was found to be
the second most important variable in the methane system. Because the thermal
conductivity is closely tied to the porosity of the deposit, the effect of changing
porosity must be accounted for in future deposition models for gas systems.

The simulation results propose that a model can be used to predict hydrate
thickness in the event of a dehydrator upset. Experimental results suggest that con­
densation of a free water phase will result in rapid plugging and should be treated
with chemicals or depressurization. However, inlet concentrations that cool past the
hydrate saturation curve, prior to the liquid saturation curve, will result in a gradual
hydrate build up. The modeling approach in this chapter will allow operators to plan
pigging schedules and/or dehydration solutions to remedy hydrate deposits.
A key uncertainty in oil and gas pipelines is whether or not hydrates deposit on the pipe wall. This work primarily investigated the feasibility of hydrate deposition within liquid condensate, in the absence of free water, via two mechanisms (1) hydrate deposition from particles formed in the bulk phase, and (2) hydrate deposition via hydrates formed on the steel or the existing deposit itself.

Hydrate deposition from particles formed in the bulk phase was investigated by measuring adhesive forces between preformed cyclopentane (CyC5) hydrates and carbon steel (CS). These forces were found to be significantly lower than CyC5-CyC5 measurements and slightly lower than ice-CS forces. The measured force of 2 mN/m* was used in a particle removal force balance assuming the hydrate particles were within the viscous boundary layer. The force balance calculations predicted hydrates, 3 microns or larger, would be removed during typical pipeline operating conditions.

These predictions suggest that entrained particles will not deposit on the pipe wall in the absence of free water. However, experimental observations demonstrated that hydrates formed on the steel surface had a significantly higher force than the preformed particles and would likely remain on the pipe wall under normal operating conditions. Because the pipe wall is the coldest point in the system and provides the most nucleation sites, it is probable that deposition via hydrate formation at the steel/hydrate interface occurs in pipelines.

Hydrate deposition via formation at the steel/hydrate interface was investigated
using a single pass flowloop with a dissolved water condensate. Hydrate/ice was found to nucleate on the pipe walls with a driving force of 1 – 3 ppmw above the equilibrium water concentrations in condensate. Equilibrium water concentrations in the presence of hydrate/ice were measured using the test section outlet water concentrations. Four deposition experiments were conducted, in which two different hydrate/ice plugging mechanisms were observed:

1. A rapid pressure drop increase (>1 psi/hour) was observed when the condensate was cooled past the liquid water (L_w) saturation curve. Crossing the L_w saturation curve resulted in free water coalescing and forming a localized hydrate/ice restriction in the flowloop.

2. Uniform/dispersed deposition from a dissolved water phase resulted in a slow pressure drop increase (<1 psi/hour) throughout the first 40–120 ft of the flowloop. During uniform/dispersed deposition it was found that the hydrate/ice deposit acted as insulation on the pipe wall, resulting in the solid deposit propagating downstream.

The uniform hydrate/ice deposits were removed using two approaches: (1) dehydrating the inlet condensate stream and (2) injecting MeOH. Dehydrating the condensate stream reduced the inlet water concentration below the 2-phase equilibrium concentration, while the outlet concentration remained at the equilibrium concentration. This behavior was accompanied by a decrease in pressure drop as water was removed from the test section. MeOH was similarly effective at removing solid deposits.

A mass and energy balance was used to model the uniform/dispersed deposit from dissolved water. The same modeling parameters were used to model three experiments (Test 5 and 6 deposition and Test 5 dissociation) with reasonable accuracy.
assuming an ice deposit with a 67% void fraction. Test 5 dissociation was successfully modeled by decreasing the inlet concentration in the deposition model to 3 ppmw.

The comparison of the model and experimental data suggests that the deposit annealed (became denser) with time, as observed in both frost and wax literature. However, additional experiments capable of measuring the actual thickness and density of the deposits are required to further refine the current model.

The flowloop model was extrapolated to field geometries to investigate the relative effect of the model parameters. Both a pure condensate and pure methane system were investigated. The combination of the experimental and modeling results indicate there is a range in which operators can continue to produce fluids in the event of a dehydrator upset, while the system is quickly corrected. It is hypothesized that an inlet water concentration which reaches the hydrate equilibrium line (as the fluid is cooled), before the appearance of a free water phase, will result in a dispersed deposit.

In both the condensate and methane systems, the external heat transfer coefficient was found to be the most significant variable. In the condensate system it was determined that the diffusion coefficient was the second most important variable; whereas thermal conductivity was found to be the second most important variable in the methane system. Because the thermal conductivity is closely tied to the porosity of the deposit, the effect of changing porosity must be accounted for in future deposition models for gas systems.
The work in this thesis primarily investigated hydrate deposition in the absence of free water. The work initially investigated adhesive forces between steel and hydrates, and then moved towards deposition from a dissolved water phase. The author proposes a recommendation for each of those topics.

Chapter 4 determined that hydrates formed in the bulk phase are not expected to deposit on the pipe wall. However, hydrates formed on the steel exhibited high adhesive forces and are expected to deposit on the pipe wall. The experiments in this thesis were conducted in absence of any surfactants.

Recently, Aspenes et al. (2008) measured the angle of wettability on various surfaces with different surfactants. Aspenes hypothesizes that oil wet surfaces will not promote hydrate deposition; however, Apenes’ hypothesis was never tested in their work. The author recommends combining the work in the present thesis with the work of Aspenes et al. (2008). The micromechanical force apparatus is a unique tool that could be used to investigate Aspenes’ hypothesis. The force between hydrates and steel can be measured after the particles are formed directly on the steel. The measurements should be completed using materials and surfactants with various angles of wettability to determine the effect on adhesion. Knowledge of the relationship between wettability and hydrates formed on steel may eventually lead to innovations in pipeline surfaces that are capable of reducing hydrate deposition.

The second recommendation pertains to the wall growth model. The model in
this thesis assumes a constant void fraction; however, the comparison of the data and the model suggests that the deposit likely 'ages' (anneals) with time. A more detailed experimental setup is required to measure the parameters (density, heat transfer, height) required to validate a model that incorporates aging. Several bench top apparatus' have been used in literature to measure frost properties as frost deposited across a flat plate (Lee et al., 1997; Mao et al., 1992; Besant et al., 1990). A similar apparatus could be developed to measure hydrate formation from saturated methane. A bench top methane deposition experiment would help (1) validate the current deposition model using gas input parameters, and (2) provide information on the aging mechanism. If the aging phenomenon proves significant, then a more robust model should be developed to incorporate the correct physics.
REFERENCES

Ardis, M. 2007. Phone conversation with GE Applications Engineer (July 6, 2007).


INFOCHEM. 2007. MULTIFLASH, Version 3.7.05. Infochem Computer Services Ltd, 13 Swan Court, 9 Tanner Street, London SE1 3LE, UK.


Flow regime prediction is a critical parameter in predicting pressure drop behavior during pipeline design. Additionally, as discussed in Chapter 2, flow regime prediction is an important parameter for a hydrate prediction model. In particular, the flow regime plays an important role in predicting surface area of the hydrocarbon-water interface and therefore, predicting the plugging mechanisms. Slug, stratified, stratified-wavy, and annular-mist are the dominant flow regimes for the oil and gas pipelines as discussed in Chapter 2.

Figure A.1. Illustration of stratified, slug, and annular-mist flow (reprinted from Gomez et al. (2000)).
Figure A.1 shows three of the four flow regimes discussed above. Stratified flow occurs at low liquid and gas flow rates. During stratified flow, gas flows along the top section of pipe, while liquid flows on the bottom. As gas velocity increases, stratified flow moves to stratified wavy flow. Although not illustrated in Figure A.1, stratified wavy flow is similar to stratified flow, except the liquid has waves across the surface. As liquid velocity increases, slug flow begins to occur. Slug flow occurs when gas pockets, termed Taylor bubbles, separate plugs of liquid (Brill and Mukerjee, 1999). Slug flow is limited to systems with high liquid loading and is generally not observed in gas systems. The final flow regime depicted in Figure A.1 is annular-mist. Annular-mist flow occurs in low liquid systems, under conditions of high gas velocity. During annular mist flow, a thin film of liquid encompasses the circumference of the pipe and water droplets become entrained in the center of the pipe. A number of papers have been published regarding flow regime prediction in two-phase flow. Taitel and Dukler proposed one of the first analytical methods of predicting flow regime changes for two-phase flow in gas-liquid systems. The proposed mechanisms were based on physical concepts and were fully predictive in that no flow regime data was used in developing the predictive criteria (Taitel and Dukler, 1976). Numerous studies, resulting in a plethora of engineering correlations, have been completed since Taitel and Duklers work; however, Taitel and Duklers work remains one of the more prominent predictive models for two phase flow (Brill, 2006).

Many flow regime studies have produced flow regime maps, providing a convenient visual reference for understanding flow regime boundaries. An example of a flow regime map is shown in Figure A.2.

Figure A.2 shows superficial gas velocity on the abscissa and superficial liquid velocity on the ordinate. As discussed earlier, low liquid and gas flow rates result in
Figure A.2. Flow regime map, showing flow regimes versus liquid (ordinate) and gas superficial velocities (abscissa) (Laurinat et al., 1984).
stratified flow. As gas velocity increases, stratified flow progresses to stratified-wavy and then annular (annular-mist) flow. Likewise, as liquid velocity increases from the stratified flow regime, plug (slug) flow is encountered.
APPENDIX B

CONDENSATE COMPOSITION

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Percent</th>
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<tbody>
<tr>
<td>n-C4</td>
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</tr>
<tr>
<td>i-C4</td>
<td>0.43</td>
</tr>
<tr>
<td>i-C5</td>
<td>13.25</td>
</tr>
<tr>
<td>n-C5</td>
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</tr>
<tr>
<td>2,2 Dimethylbutane</td>
<td>1.1</td>
</tr>
<tr>
<td>n-hexane</td>
<td>8.35</td>
</tr>
<tr>
<td>Fractional C6</td>
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</tr>
<tr>
<td>Methylcyclopentane</td>
<td>4.58</td>
</tr>
<tr>
<td>Benzene</td>
<td>3.27</td>
</tr>
<tr>
<td>Cyclohexane</td>
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</tr>
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<td>n-heptane</td>
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<td>Fractional C7</td>
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<td>Methylcyclohexane</td>
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<td>Fractional C8</td>
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<td>o-xylene</td>
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<td>C10</td>
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<td>C11</td>
<td>0.18</td>
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<tr>
<td>C12</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>98.9</strong></td>
</tr>
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Table B.1. Composition of condensate used in flowloop experiments
APPENDIX C

ADDITIONAL INFORMATION PERTAINING TO FLOWLOOP EXPERIMENTS

C.1 Discussion of GE Moisture Probe Readings and Limitations

The GE moisture probes represent the best industrial instrument available, at the time of this work, for measuring dissolved water concentrations in gas or condensate. The GE moisture probes contain an aluminum oxide probe, which adsorbs water and measures impedance. Each probe has a unique calibration curve relating impedance to dew point. The dew point represents the equivalent raw data between probes. The probes also measure temperature.

The dew point is converted to partial pressure of water ($P_w$) by assuming the partial pressure is equal to the water vapor pressure in equilibrium with water ($> 0^\circ$C) or ice ($< 0^\circ$C) corresponding to the respective dew point temperature (see Figure C.1)

Water content in the gas phase is calculated using the partial pressure of water, total system pressure, and assuming an ideal gas. This calculation yields parts per million by volume (ppmv).

Water concentration in the liquid phase is found using a saturation curve for the fluid. Figure C.1 shows the saturation curve (parts per million by weight) predicted by Multi-Flash (CPA-model), which was employed in these experiments.
Figure C.1. Water saturation curve for condensate and illustration of dew point vs. partial pressure curve.
Water concentration in liquid phase is calculated using the following expression:

\[
ppmw = P_w(DP) \frac{\text{Saturated water conc}(T_P)}{P_w(T_P)}
\]  

where ppmw is parts per million by weight, \(P_w(DP)\) is partial pressure at the probe dew point reading, saturated water conc \((T_P)\) is the saturated water concentration at the probe temperature, and \(P_w(T_P)\) is the partial pressure of water vapor at the probe temperature. According to GE’s specialist, the accuracy of predicted saturation curves is 30% (Ardis, 2007). Consequently, the highest order of accuracy for the moisture probes in a liquid phase is ±30%.

It should be noted that the probes will show a reliable relative change in moisture readings when probe temperatures remain constant. However, a change in probe temperature can greatly affect the multiplication factor, saturated water conc \((T_P)/P_w(T_P)\). In the situation where probe temperature is changing, it is best to compare dew point readings and monitor relative change.

A final limitation of the moisture probes is that they must be operated at temperatures greater than 10°C above the dew point. When operating at temperatures less than 10°C above the dew point the probes become saturated and must be removed and dried in an oven.
C.2 Tabulated Experimental and Equilibrium Values

Table C.1 summarizes the comparison of the experimental and predicted equilibrium water concentrations in this work.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Flowloop Measurements (ppmw)</th>
<th>Multi-Flash CPA Ice/Water Saturation Predictions (ppmw)</th>
<th>Multi-Flash CPA Hydrate Predictions (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-21.5</td>
<td>7.0±2.1</td>
<td>8.5</td>
<td>6.3</td>
</tr>
<tr>
<td>-16.7</td>
<td>9.5±2.9</td>
<td>12.1</td>
<td>9.3</td>
</tr>
<tr>
<td>-9.7</td>
<td>13.5±4.1</td>
<td>19.7</td>
<td>15.9</td>
</tr>
<tr>
<td>-4.7</td>
<td>17.0±5.1</td>
<td>27.9</td>
<td>22.5</td>
</tr>
<tr>
<td>2.6</td>
<td>28.0±8.4</td>
<td>43.2</td>
<td>37.2</td>
</tr>
</tbody>
</table>

Table C.1. Experimental measurements compared with Multi-Flash predictions (INFOCHEM, 2007).
C.3 Additional Figures for Test 3

![Graph showing flow rate and moisture readings for Test 3]

Figure C.2. Test 3 flow rate and moisture readings. Probe 3 showed a spike when flow rate increased.

Flow rate through the probe sampling ports was sensitive to valve position and loop flow rate. It is possible that flow through the sampling port decreased during (Figure C.2) 10/1/07 14:00 and 10/2/07 14:00, with the exception of a sudden increase when loop flow rate was manually increased.

Figure C.3 shows a rapid restriction formed in the cool down section. This decreased the loop flow rate, thereby decreasing pressure drop across the test section.
Figure C.3. Test 3 pressure drop and flow rate during rapid plugging, associated with free water condensing out of condensate.
C.4 Test 3 Water Mass Balance

Figure 5.13 shows that water was injection was started at a rate of 15 micro­liters/min and the inlet concentration (Probe 6) increased 12 ppmw. The following calculation illustrates that this was the expected increase.

\[
\frac{\text{Water}}{\text{Condensate}} = \frac{15 \mu L}{1 \text{ min}} \times \frac{1 E - 6 \text{ kg}}{1 \mu L} \times \frac{1 \text{ gallon}}{0.5 \text{ gallon}} \times \frac{3.785 E - 3 \text{ m}^3}{1 \text{ gallon}} \times \frac{660 \text{ kg}}{1 \text{ m}^3} \times 1 \text{E}6 = 12 \text{ ppmw} \quad (C.2)
\]
C.5 Additional Figures for Test 4

Figure C.4. Test 4 pressure drop profiles across the test section. Each line represents pressure drop over an additional 40 ft in the test section. The pressure drop was calculated by subtracting the pressure at a given point in the test section from the test section inlet (Figure 5.1).

Figure C.4 shows that the nucleation event occurred between 40 ft and 80 ft. This is elucidated by the pressure drop increase between 0–40 ft and the lack of pressure drop increase between 0–80 ft. Likewise, the pressure restriction during the rapid pressure drop increase also occurred between 40–80 ft.

Figure C.5 shows the flow rate increased as the localized pressure restriction was
Figure C.5. Test 4 pressure drop and flow rate response to shutting off cooling fluid to heat exchangers 4 and 5.
dissociated and deposited uniformly downstream. The resulting flow rate of 0.82 gpm was reduced back to approximately 0.5 gpm, thereby reducing the loop pressure drop.

Figure C.6 shows the pressure drop response while attempting to reproduce a rapid pressure drop increase. The figure shows that a rapid pressure drop was not achieved and the deposit was forming between 40 – 80 ft. It is hypothesized that the presence of hydrates buffered the condensate water concentration and prevented free water from coalescing. This is conceptually illustrated on a phase diagram in Figure C.7.
Figure C.7. Measured and predicted phase equilibrium from Test 4. The gray arrows illustrate the possible path for rapid pressure drop increase during the initial injection in Test 4. The brown arrow shows the hypothesized deposition mechanism while attempting to reproduce a rapid pressure drop increase.
C.6 Additional Figures for Test 5

Figure C.8 shows the moisture probes were much more consistent after Probe 6 was replaced at 10/31/07 7:10. This suggests the probe divergence in Figure 5.26 was a result of probe inaccuracies, rather than a physical phenomenon.

Figure C.9 shows that water injection was increased to 45 microliters/min and the inlet concentration climbed to as high as 53 ppmw.

Figure C.10 shows that the restriction in the first 40 ft of the test section was displaced downstream as the test section temperature was increased. The restriction
Figure C.9. Test 5 water injection rates and matching moisture readings during the rapid pressure drop study.
Figure C.10. Test 5 test section temperature (208) and pressure drop profiles during the initial dehydrator test.
was further reduced when the dehydrator was installed at 11/5/07 18:00.

Figure C.11. Test 5 temperature and moisture profiles while decreasing the loop temperature, after running the dehydrator, in preparation of the long term deposition testing. The fluid temperatures represent the temperature in the cool down section and test section respectively.

Figure C.11 shows the condensate water content decreased as the flowloop temperature was decreased. This trend is consistent with the expected hydrate/ice equilibrium behavior (Figure 5.10).

Figure C.12 shows the temperature 40 ft into the test section increased as hydrate/ice deposited in the same section, indicating hydrate/ice was acting as insulation.
Figure C.12. Test 5 pressure profiles and condensate temperature 40 ft into the test section throughout the uniform deposition testing.
C.7 Test 5 Flowloop Leak and Remediation

The water injection system consisted of an ultrasonic horn which fed through a machined fitting in the flowloop. This fitting was sealed with two o-rings which were placed around the ultrasonic horn. During the uniform deposition portion of Test 5, the o-rings degraded, resulting in a pressure leak at 11/10/07 23:00.

Following the failure of the ultrasonic o-rings the methane tank was able to maintain flowloop pressure until 11/11/07 18:45 when the methane tank pressure dropped below 1000 psi. At this point in time the flowloop pressure began to decrease.

Figure C.13. Test 5 pressure drop profile and loop pressure after ultrasonic o-ring failure.
below 1000 psi. Figure C.14 shows that a new methane tank and 4L of condensate were added at 11/11/07 22:00.

As a result of the condensate lost in the leak, flowloop circulation was lost for approximately 6 hours as illustrated in Figure C.14. Figure C.15 shows that circulation stopped around 11/11/07 15:15 and was resumed around 11/11/07 21:40. Although flow was still being measured, it is believed that the signal was just a result of noise. Evidence for lost circulation is shown by the pressure drop in Figure C.14, which dropped to 0 psi and the temperature profiles shown in Figure C.15.

Figure C.14. Test 5 pressure drop and flow rate profiles during the flowloop leak.

Figure C.15 shows that the temperature readings increased when the pressure
Figure C.15. Test 5 temperature and pressure profiles during the flowloop leak.
drop dropped to 0 psi. This occurred because the thermocouples were located in ~2 ft long sections connecting the heat exchangers together. As a result, the temperatures in these sections increased when circulation was lost at 11/11/07 15:15. The same behavior was recorded between 11/12/07 12:15 and 11/12/07 15:10 when flowloop circulation was stopped to repair the ultrasonic o-rings.

It is important to note that although temperature profiles increased, this only occurred in the jumpers between heat exchangers. Because the chiller was running throughout this time period, the temperature within the 14, twenty feet long, heat exchangers remained virtually constant at -21°C. Figure C.14 also shows that the hydrate deposit was shifted slightly down stream once circulation was resumed at 11/11/07 21:40. The hydrate deposits were re-deposited downstream because water was not being injected and the condensate was below the hydrate equilibrium concentration in the upstream (warm) sections of the flowloop.

Because the majority of the test section remained cool during the lost circulation, the decision was made to continue on with the experiment. Additionally, it can be observed that the pressure drop profiles essentially reached an equilibrium condition at 11/12/07 15:09, which was nearly identical to the pre-leak pressure drop profiles (Figure C.14).
C.8 Additional Figures for Test 6

Figure C.16. Test 6 water injection rate and resulting concentrations during uniform deposition testing.

Figure C.16 shows the water injection rate was increased to 28 microliters/min, which resulted in an inlet concentration of approximately 24–25 ppmw.

Figure C.17 shows the water concentration profiles after water injection was stopped at 12/12/07 7:50. The plot shows that the inlet water concentration (Probe 6) dropped back to the initial equilibrium concentration of 7 ppmw. This indicates that the sudden decrease in Probe 3’s reading at 12/9/07 6:30 was due to a probe error, rather than a change in equilibrium concentration. Had Probe 6’s reading
Figure C.17. Test 6 water concentration profiles after ceasing water injection, following uniform deposition.
dropped to 5 ppmw after stopping water injection then it would have been suggested that the system’s equilibrium concentration had changed.

Figure C.18. Test 6 water concentration profiles and MeOH injection rates.

Figure C.18 shows the MeOH injection rate and the change in moisture readings that accompanied the onset of injection.
APPENDIX D

ADDITIONAL INFORMATION PERTAINING TO FLOWLOOP MODELING

D.1 Validation of Time and Distance Steps

Figure D.1 compares the hydrate thickness profile at 120 hours using three combinations of time and distance steps. The time and distance steps used in this work were 120 s and 0.1 m, respectively. Figure D.1 shows that doubling either of these values had no effect on the results, indicating the time and distance steps employed in this work were sufficiently small.
Figure D.1. Comparison hydrate thickness at 120 hours using different time and distance steps.
D.2 Adjusting Friction Factor and Hydrate Distribution

It was determined that the friction factor had to be multiplied by a factor of 7 to match the order of magnitude observed in the experiments. The pressure drop profiles are illustrated in Figure D.2a. This figure elucidates that although the final pressure drop is matched by an order of magnitude, the qualitative trends do not appear to be correct. Additionally, using the hydrate thickness and the Colebrook and White correlation (Equation 6.11) to predict friction is already expected to yield an upper limit on the friction factor. This implies that friction factor is not responsible for the discrepancy between experimental and predicted pressure drop.

![Figure D.2a](image1.png)

**Figure D.2.** Effect of multiplying the friction factor by 7 (a) experimental and predicted pressure drop comparison, and (b) comparison of base case and multiplied friction factor.

Because the pressure drop is inversely proportional to $D^5$ (Equation 6.3), a localized deposit would yield an increased pressure drop. This was investigated by increasing the mass transfer 100x and the external heat transfer 30x. Figure D.3, shows that the deposit is significantly more localized, but the pressure drop is still
under predicted.

Figure D.3. Effect of multiplying the mass transfer coefficient by 300 and the external heat transfer coefficient by 30 (a) comparison of hydrate distribution with base case, and (b) comparison of experimental and predicted pressure drop.

Figures D.2 and D.3, indicate that neither the friction factor or hydrate distribution was responsible for the discrepancy between the predicted and experimental pressure drop.
D.3 Test 5 Modeling - Additional Figures

Figure D.4 shows the Test 5 predicted pressure drop and temperature profiles associated with a 73% porous hydrate deposit. Similar to the Test 6, the temperature profiles were overpredicted.

Figure D.4. Comparison of Test 5 predicted and experimental values using a hydrate void fraction of 73% (a) pressure drop profiles, and (b) temperature profiles.


D.4 Transport Limitations in the Model

The model incorporates both heat and mass transfer limitations. The hydrate/ice interface temperature is calculated, which is used to calculate the equilibrium water concentration at the interface. The concentration gradient between the bulk fluid and the interface is then used to predict convective diffusion from the bulk phase to the hydrate/ice surface. The mass transfer limitations are compared at 0 hours and 120 hours for the Test 6 deposition using ice with a 67% void fraction. Figure D.5 shows the equilibrium water concentration at the interface temperature, which is compared to bulk fluid water concentration. If the model was heat transfer limited, the concentration curves would lie on top of each other. The gap between the curves indicates the model was mass transfer limited.

Figure D.5. Test 6 predicted interface temperature, interface equilibrium concentration, and bulk fluid water concentration while using ice with a 67% void fraction (a) at 0 hours, and (b) at 120 hours.

The mass transfer limitations in the Test 5 dehydration runs are illustrated in Figure D.6a. This figure compares the interface equilibrium concentration and the
bulk condensate water concentration after starting dehydration. It can be seen that the increased diffusion coefficient results in a quicker increase in condensate water concentration. Subsequently, the water is re-deposited after crossing the equilibrium concentration. The effect of this behavior is shown in Figure D.6b, which shows the deposit initially shifts downstream before dissociating. This explains why an increased diffusion coefficient results in the pressure drop time lag observed in Figure 6.17.

Figure D.6. (a) Predicted condensate water concentrations during Test 5 dehydration using varying values of $D_{wc}$, and (b) ice deposit profile in Test 5 dehydration using $D_{wc} \times 2.5$. 