A STUDY OF HYDRATE DISSOCIATION IN PIPELINES BY THE METHOD OF
TWO-SIDED DEPRESSURIZATION: EXPERIMENT AND MODEL

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A STUDY OF HYDRATE DISSOCIATION IN PIPELINES BY THE METHOD OF
TWO-SIDED DEPRESSURIZATION: EXPERIMENT AND MODEL

by

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ABSTRACT

This thesis deals with dissociation of methane hydrate plugs by depressurization at both ends of the plug. One goal of this work was to identify if there were optimal conditions to depressurize a pipeline so that the hydrate plug could be removed as quickly as possible. The experimental portion of the research indicated that the optimal condition is to depressurize a pipeline to atmospheric pressure. This work revealed that the formation of ice during the dissociation of hydrate at atmospheric pressure aided the dissociation process.

The second goal of this work was to develop a computer model that simulates hydrate dissociation. A model was developed that acceptably simulated the experimental data with no fitted parameters. The model assumed that the hydrate dissociated radially inward and was heat transfer controlled. The only source of heat input to the system was the heat conducted through the pipe wall. All convective effects within the pipeline were assumed negligible.

One further important result was the qualitative verification of the model. The experiments indicated that the hydrate did shrink radially inward as it dissociated. This has important safety implications; when a hydrate dissociates, it will release from the
pipe wall first. If any pressure gradient exists along the plug, it could easily become a projectile with enough momentum to cause severe equipment damage and loss of life.
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Chapter 1

INTRODUCTION

Hydrate plugs in pipelines have been the source of much frustration since their discovery in 1934 (Hammerschmidt 1934). However, very little work has been done since then to determine how hydrates dissociate once they form inside a pipeline. The purpose of this research was to examine hydrate dissociation in pipelines. There were two goals at the start of the project. The first was to determine if there was any optimal way to depressurize a pipeline, from both ends of the plug, to achieve the fastest dissociation. The second goal was to develop a mathematical model that simulated hydrate dissociation in a pipeline. Both objectives have been achieved in this work.

Gas hydrates belong to a class of compounds called clathrates. The hydrate is composed of two components, the host water molecule and the guest hydrate forming gas. The host water molecules form a hydrogen-bonded crystal lattice filled with cavities. The guest molecules can fill these cavities and stabilize the crystal lattice through weak van der Waals interactions. These guest molecules include the lighter paraffinic molecules, such as methane, ethane, or propane, and some smaller gases, such as CO₂, N₂, or H₂S. For a more detailed description of hydrates, the reader is referred to the monograph by Sloan (1998a).
Hydrates usually form under conditions of high pressure and low temperature. Figure 1.1 shows an equilibrium curve for methane hydrate. The temperature of interest was assumed to be 277 K, an approximation of the deep ocean ambient temperature. The pressure needed for hydrate formation at this temperature is about 3 MPa, a pressure frequently exceeded in subsea pipelines. While the focus of this work was to simulate subsea conditions, the results were still applicable to plugs formed on land.

There are currently two conceptual pictures of hydrate formation in a pipeline (Lingelem et al. 1994). In one picture ofhydrate formation, the hydrates form at the gas/water interface. Due to the turbulent nature of the flow in the pipe, the interface is constantly disrupted, so there are many small hydrate particles present in the system. Eventually, enough small particles agglomerate to form a blockage in the line. The second scenario involves the formation of hydrate along the periphery of the pipeline. There is a gradual buildup and eventually the hydrate blocks the pipeline. Both of these scenarios have been observed in pipelines, but the agglomeration model is the most common method of blockage removal.

Once a hydrate plug has formed in a pipeline, there are limited options available to remove the plug. There are four methods currently used to remove a hydrate plug (Sloan 1998b). These possibilities include heating the hydrate plug, adding thermodynamic inhibitors to the system, using mechanical methods, or depressurizing the pipeline.
Figure 1.1: Methane Hydrate Equilibrium Curve
For various safety, economic, and physical inaccessibility reasons, thermal stimulation, inhibitor injection, and mechanical methods are not the preferred methods of hydrate removal. Heating a pipeline is often expensive and if the location of the end of the plug is unknown, heating can be dangerous because of the exponential dependence of pressure on temperature. A small increase in temperature can create a large increase in pressure, which may be enough to rupture the pipeline. Inhibitor injection and mechanical methods are not widely used because of difficulties in reaching the face of the hydrate plug.

Pressure reduction in the line is usually the most viable option. However, there are problems associated with this method, particularly when only one side of the plug can be depressurized (Borthne et al. 1996). Joule-Thomson cooling can occur when gas flows through a hydrate plug. The colder gas will stabilize the hydrate plug (Austvik et al. 1995). This can be represented on Figure 1.1 as a temperature decrease while the gas is expanded, or the pressure is decreased. The new temperature and pressure are within the hydrate stability region. The hydrate will not be dissociated until the upstream pressure is reduced below equilibrium condition.

The second problem that can occur with one-sided plug depressurization is of much greater concern, particularly to the people operating the pipeline. As the plug begins to melt, it releases from the pipe wall, and due to the pressure gradient across the plug ends, the plug begins to move within the pipeline. If the pressure gradient across the plug is sufficient, the plug may have enough momentum to do serious damage once it
reaches some obstruction such as an elbow or a valve. For example, in 1997 DeepStar field tests, a plug velocity was measured at 82.3 m/s (Hatton et al. 1997).

There have been several reported problems with pipeline depressurization (Kent and Coolen 1991). All cases involved the depressurization of the pipeline, from one end, and the subsequent release of the hydrate plug. All cases also resulted in either loss of life, equipment damage, or both.

Current research efforts revealed the following results. First, when hydrate plugs dissociated, they did so radially. The experiments described in this thesis provided the first visual confirmation of radial dissociation. Lysne (1995) first hypothesized this method of dissociation. When hydrate plugs dissociated, they released from the pipe wall first. If any pressure gradient existed across the plug, it would cause the plug to move, leading to the safety problems described earlier.

Another important result was the verification of hydrate temperature during dissociation. Previous work by Lysne (1995) indicated that the hydrate temperature was in equilibrium with the prevailing pressure. However, if the equilibrium temperature was below the ice point, the heat of fusion of ice would buffer the temperature during hydrate dissociation, and the temperature would not drop much below the ice point.

The research in the current thesis indicated the existence of an optimal dissociation pressure. It was determined that the hydrate dissociated fastest when the pressure was lowest, i.e. atmospheric pressure. This indicated that ice formation in the system upon depressurization helped the hydrate dissociate quicker. This observation
was contrary to the previous conception that ice formation hindered the dissociation of hydrate (Lysne 1995).

The hydrate dissociation model that was developed as a part of the current research assumed a best case scenario, wherein the system could be depressurized from both ends of the plug. The model predicts that the optimal dissociation pressure was as low as possible. This result was confirmed in the experiment.

The results of this work will aide the removal of hydrate plugs in the future. This work indicated the existence of an optimal dissociation pressure, atmospheric pressure. It also verified that hydrates dissociate radially in a pipeline. A model was developed to predict dissociation times in pipelines.
CHAPTER 2
LITERATURE REVIEW

The purpose of this work was to examine hydrate dissociation in pipelines. A review of the current, limited literature on hydrate dissociation served as the starting point.

The main focus of previous hydrate dissociation work was to create efficient methods to develop natural gas from hydrate reservoirs. This was due to the enormous amounts of naturally occurring hydrates that are believed to exist in permafrost regions and in ocean sediments. Recent estimates differ regarding the amount of gas present in hydrate form, but all agreed that the total amount was significant (Kvenvolden 1993 and Ginsburg and Soloviev 1995). The total amount of energy present in hydrated form is believed to be twice the total of all fossil fuels.

The work done on hydrate dissociation revealed that there were only a few options available to produce such hydrate reservoirs. These methods included thermal stimulation, inhibitor injection, and pressure reduction. Of these methods, only thermal stimulation has been widely explored. There was only a limited amount of work reported in the literature on the other methods.
For a review of the previous research and hydrate dissociation models that were developed to simulate production of hydrates from reservoirs, the reader is referred to the monograph by Sloan (1998a). In the review by Sloan, all modeling attempts were discussed in chronological order to indicate how the thinking about hydrate dissociation progressed. Also, Sloan discussed models that were developed to specifically address the three methods of hydrate production. It should be noted that the models were for the case of hydrate in porous media. In this chapter, only models that were developed specifically for pipeline situations will be discussed.

Lysne et al. (1992) and Kelkar et al. (1998) formulated the only models that specifically address hydrate dissociation in pipelines. The model by Lysne et al. (1992) was described in the thesis of Lysne (1995) as follows:

...a one-dimensional steady state model...Based on the properties of the fluids present, the hydrate phase and wall layers, the model calculated the propagation velocity of the dissociation boundary. The model assumed that the energy required to dissociate the plug was provided by heat flux through the pipe wall only. Convective heat transfer inside the pipe was neglected. It used an equivalent dissociation zone with a length that needed to be estimated. One of the parameters that had a significant impact on the length of the dissociation zone was hydrate porosity.

This model developed by Lysne (1992) was simplistic in its assumptions. The model assumed that all heat input to the hydrate, from the surroundings, went into dissociating the hydrate. The formation of ice in the system was not accounted for in this model. This model required knowledge of the plug length, which is a value not typically known. The model was also described in a later paper by Berge et al (1996).
The model by Kelkar et al. (1998) was a one-dimensional unsteady state model, which neglected the effect of curvature in the pipeline and solved the governing differential equations in rectangular coordinates and a semi-infinite media. It also assumed that the energy required to dissociate the plug was provided by heat flux through the pipe wall only. This work assumed that hydrate dissociated as a moving boundary, to provide a shrinking core model. An estimate of hydrate plug length was not needed in this model since the plug was assumed to dissociate radially. This model further assumed if the hydrate temperature was below the ice point, ice formed in the system as hydrate dissociated. The results of this work showed that it may be beneficial to have some ice present in the system during dissociation. Some ice actually helps the hydrate dissociate faster. This work will be further summarized in a later chapter.

Lysne (1995) performed experiments on the dissociation of ethane hydrates by pressure reduction. This work led to the following three hypothesis; (1) hydrate plugs can be porous (33% minimum). This porosity allowed for transfer of pressure throughout the plug. Note that most of the previous hydrate models assumed the plug was impermeable. (2) When depressurized, the hydrate temperature was below the ambient temperature and this caused heat to flow in radially from the surroundings, contrary to the previously held conception of plugs dissociating from the ends. (3) If the hydrate temperature was below the ice point, ice formed in the system. This formation of ice acted as a temperature buffer and prevented the hydrate from cooling much below the ice point.
There were two large-scale investigations of hydrate plugs in pipelines reported in the literature. One case was reported by Austvik et al. (1995). In this study, 17 hydrate plugs were intentionally formed in an 11.5-km, 6-inch test/service line at the Tommeliten Gamma Field in the North Sea. Six types of field tests were performed to form and dissociate the plugs. The plugs were dissociated using the various hydrate plug remediation techniques reported earlier. The important conclusion that came from this study was that hydrate plugs were permeable to flow. This permeability indicated that hydrate plugs formed in more realistic situations were also porous. This supported the work done by Lysne (1995). Hydrate porosity was an important parameter in dissociation models as reported by Lysne (1992), and supported by observations of the current modeling effort.

The other study of hydrate dissociation in pipelines was done in a Deepstar field trial to determine if one-sided depressurization could be done safely (Hatton et al. 1997). In this study several hydrate plugs were formed and then dissociated. After one side of the plug was depressurized, one of the plugs was able to withstand a pressure drop of 3.3 MPa before it dislodged. When the plug released and began to move, it reached a velocity of 82.3 m/s. However, in all cases, the plugs could be dissociated safely within the pipeline.

Kelkar et al. (1998) previously explored the modeling of hydrate plug dissociation in pipelines. However, this work was limited to hydrate dissociation in a semi-infinite
media with a constant surface temperature. The solution to this problem is presented in Carlsaw and Jaeger (1959).

The problem solved by Kelkar et al. (1998) is often referred to as a Stefan type problem. This type of problem is typified by a moving boundary and a change of phase. An example of this would be the fusion of ice to water. As the ice melts, it forms water and at the same time, the ice phase shrinks. The main difficulty in these types of problems is tracking the moving boundary, since it is incorporated as a nonlinear boundary condition.

Several review articles described different methods of solution to this type problem. There was only one numerical solution to the Stefan problem and that was for the conditions given above. All other methods of solution rely on some numerical technique. Bankoff (1964) gave a review of all work previous to 1964. Roberts (1982) gave a review of the Stefan-type problem, which was meant to serve as an extension of the review given by Bankoff.

A review of more current literature reveals that no further significant progress was made in this area. The problem must still be solved numerically. Most articles are extensions of previous methods that work on improving the accuracy of the solutions and decreasing the amount of computer time needed.

Also, a review of the current literature revealed that there were not any reported cases of modeling two moving boundaries. All previous cases dealt with one moving
boundary. The current modeling effort has two moving boundaries: (1) a water/ice moving boundary and (2) an ice/hydrate moving boundary.

This research was an extension of the work done by Lysne (1995) and Kelkar et al. (1998). The goal was to verify and extend the results obtained by Lysne (1995). His experiments were conducted over a limited pressure range with ethane hydrates. The current work extended that pressure range to give a more accurate picture of hydrate dissociation with methane or natural gas. In addition, the modeling effort in this work was an attempt to remove some of the assumptions used in the model by Kelkar et al. (1998).
CHAPTER 3
EXPERIMENTAL APPARATUS

3.1 Introduction

The purpose of the experiment was to collect data from a dissociating methane hydrate plug. The experiments were conducted in an unstirred batch reactor under isobaric and isothermal conditions. The formation experiments were conducted under variable temperature and pressure. Experimental conditions were limited to pressures between 0 and 21 MPa and temperatures between 263 K and 288 K. The upper limit on temperature was not 283 K, but all experiments were conducted below this temperature. The hydrates were prepared using technical grade methane and ice frozen from distilled water.

3.2 Experimental Equipment

A schematic view of the experimental equipment used to measure hydrate dissociation is detailed in Figure 3.1. The main section of the apparatus was a 0.2 m (8") long stainless steel reactor. The reactor had an internal diameter of 0.048 m (1 7/8"), a wall thickness of 0.003 m (1/8"), and an internal volume of 350 ml. The reactor had a threaded cap that needed to be screwed on during each experiment. Between the cell and
Figure 3.1: Diagram of Reactor
the cap was an end cap. A Rocket Seal® was used between the end cap and the reactor to prevent leaks during the experiment.

The main reactor was located in a temperature controlled ethylene glycol/water bath. The bath temperature was controlled with a Neslab immersion cooler, and a 1000 Watt immersion heater controlled by a Precision Instrument Controller (Bayley Instrument Company). The voltage input to the heater was adjusted by the controller to maintain the desired temperature set point. The control unit and cooler were capable of heating the bath at a rate of either 3.5 K/hr or 0.35 K/hr, depending on the cooler setting. The temperature bath fluctuations using this system were approximately ±0.2 K. This effect was too small to have any effect on the interpretation of the experimental results.

All other parts of the apparatus (Figure 3.2) were connected with 0.006 m (¼”) stainless steel tubing connected with Swagelock fittings. An Omega pressure transducer, with a pressure range between 0 and 21 MPa, was used to continuously monitor the pressure in the reactor. The temperature inside the reactor was determined with the use of five type T (Copper–Constantan) thermocouples. The location of the thermocouples is also detailed in Figure 3.1. Figure 3.1 also indicates the name of each thermocouple as it is used in the discussion of results in later chapters. The temperature of the gas just outside each end of the cell was also measured using type T thermocouples. The temperature of the bath was monitored using a platinum resistance temperature detector (RTD).
Figure 3.2: Schematic Diagram of Experimental Apparatus
Refer to Figure 3.2 for a diagram of the experimental apparatus. The pressure and all the temperature measurements were continuously measured using a Keithley DAS 802 data acquisition card with an EXP-800 external board. Connected to the EXP-800 were an FWA-EXP, which measured the thermocouples, and an FWA-37U, which measured signals from the RTD and pressure transducer. Voltage readings from the EXP-800 were sent to a PC and recorded into a data file for later analysis. The data acquisition program was written exclusively for this experiment and was capable of simultaneously recording all desired values and the time that the data point was taken. The end result was a data file with temperatures of hydrate versus time, bath temperature versus time, and pressure in the system versus time.

The reactor was attached to a methane gas supply through valves V1, V2, and V3 (Figure 3.2). The methane gas used in all experiments was technical grade purity (99% purity). Before valve V1 was a Ruska high-pressure pump that was capable of increasing the system pressure to 41.4 MPa. The valves downstream of the reactor, V4 and V5, could be closed to prevent gas from flowing through the reactor. During the depressurization portion of the experiment, valves V4, V5, V6, and V7 could be opened to reduce the pressure in the reactor at both ends of the plug.

In the case when the system was depressurized to atmospheric pressure, the pressure relief valves were not used. In the experiments when the hydrate was dissociated at a pressure higher than atmospheric, the pressure relief valves were used to
control the pressure in the reactor. The pressure relief valves were Swagelock model R34 Proportional Pressure Relief Valve. These pressure relief valves were adjustable in the pressure range between 2.4 and 5.2 MPa. These pressures allowed the hydrate to be dissociated at temperatures greater then the melting point of ice.

In several experiments, a gas mixture was used instead of the methane. The gas mixture is referred to as a pseudo-Qatar gas mixture. The gas mixture was originally designed to have the same equilibrium conditions as a natural gas sample from a gas field in Qatar. This mixture was designed such that there would not be a liquid phase present at pressures below 21 MPa. The gas was prepared by Scott Specialty Gases, and had the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>MolePercent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>83.8</td>
</tr>
<tr>
<td>Ethane</td>
<td>7.01</td>
</tr>
<tr>
<td>Propane</td>
<td>1.6</td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.05</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.02</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.02</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.003</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.003</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>4.85</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>1.84</td>
</tr>
</tbody>
</table>
3.3 Calibration Procedures

The thermocouples were calibrated against a known standard mercury thermometer. The mercury thermometer had a temperature range of 265 K to 303 K. The accuracy of the thermometer was ± 0.1 K. The main area of interest for this work was in the temperature range of 271 K to 278 K. The melting temperature of ice was verified on the mercury thermometer using an ice bath. The thermocouples and RTD were calibrated such that they all read 273 K at the ice point. The calibration for other temperatures was done by adjusting the bath temperature, measuring the bath temperature with the mercury thermometer, and then correlating the voltage output of the thermocouple and RTD to that temperature.

In order to get an accurate value of temperature for the thermocouples, a reference temperature had to be specified. For these thermocouples, the reference temperature was measured on the EXP-800 and was equal to the ambient temperature. The problem that arose during the experiments was a change in ambient temperature between day and night, which caused oscillations in the thermocouple readings. An additional modification was needed for the thermocouple calibration to account for the change in the reference junction temperature. The modification included adding or subtracting some percent of the change in ambient temperature relative to the ambient temperature at the time of the calibration.

The calibration plot for two of the thermocouples is included as Figure 3.3. All other thermocouple calibrations were very close to the two shown. The slope varied
Figure 3.3: Calibration Curve for Thermocouples
between 0.243 and 0.246 K/mV and the intercepts varied between 297.7 and 299.5 K. The average error in all thermocouple measurements was no more than 0.2 % of the reading. This translated to a maximum error in the temperature measurement of ± 0.5 K. The RTD calibration is included as Figure 3.4. The maximum error in the RTD is slightly smaller than the thermocouple values and was just under 0.2%. This corresponded to a maximum error in the RTD readings of about ± 0.4 K.

The pressure transducer was calibrated in a manner similar to the thermocouples. However, the standard measurement of pressure was two Heise pressure gauges, with a pressure range of 0-33 MPa. These pressure gauges had been previously factory calibrated and had an accuracy of ±1% of full scale. The system was pressurized to some pressure and measured on both pressure gauges. In all cases the pressures matched on both gauges. The pressure transducer was calibrated to the pressures measured with the pressure gauges.

A calibration plot for the pressure measurements is included as figure 3.5. Note that this calibration curve is fitted with the intercept set to zero. The maximum error in the pressure is about 1%. This corresponded to a maximum error of about ±0.1 MPa.
Figure 3.4: Calibration Curve for RTD

\[ y = 0.0946x + 273.14 \]

\[ R^2 = 0.9995 \]
Figure 3.5: Calibration Curve for Pressure Transducer
CHAPTER 4

HYDRATE FORMATION EXPERIMENTS

4.1 Introduction

The process of making a large, reproducible sample of hydrate proved to be one of the most difficult challenges of the entire project. The method of making hydrates that was the most reliable was adapted from the method used by Stern et al. (1996) to make hydrate samples that were suitable for materials property testing. The idea behind this method, for the formation of hydrates, was to begin with small ice particles (<850 μm) surrounded by a hydrate forming gas. The temperature and pressure conditions were maintained in the hydrate formation region for the duration of the experiment.

The ice was kept below the ice point for the initial part of the experiment to prevent premature melting. To initiate hydrate formation, the bath temperature and consequently, the temperature of the ice was increased above the melting point. As the ice melted, hydrate began to form. The temperature of the bath remained at these conditions for some time to allow for almost complete conversion of ice to hydrate. This was the procedure followed in the formation experiment, but each individual run was a variation on this general idea.
There were several reasons why ice made a better precursor to hydrate formation than water (Hwang et al. 1990). Ice had a hydrogen-bonded structure that was similar to hydrates and melted ice had more residual hydrogen bonds than did free water, which had never frozen. The use of small ice particles increased the surface area available for hydrate formation. And, ice was able to better absorb the hydrate heat of formation.

To initiate hydrate formation from ice, the ice must first begin to melt. As the ice melted, there was a lot of residual structure present in the water near the ice/water interface. Since hydrates are another form of structured water, this residual structure was helpful in forming the hydrate cages.

In order to achieve a high percent conversion, the ice particles must be very small. The smaller the ice particles, the more surface area they will have per unit volume. With more surface area, there was a larger gas/liquid interface present for the hydrate to begin growth. As the ice was melted during formation, a new surface was generated for the hydrate to continue growing. The rate of hydrate formation is proportional to the area available (Hwang et al. 1990).

When the Stern group synthesized hydrate, they began with 200 μm size particles of ice. One of the differences between the procedure used in this work and the procedure reported by Stern et al. (1996) was the size of ice particles used to form the hydrates. Due to limitations in the lab, only ice particles that were about 850 μm could be used. Attempts to use smaller ice particles failed because the ice melted too fast.
An additional benefit provided by ice over water during hydrate formation was the ability of ice to better absorb the hydrate heat of formation. As hydrates were formed, they released their heat of formation to the surrounding medium. When hydrates form in water, the heat tends to accumulate at the water/hydrate interface, which in turn increases the surface temperature (Chalmers 1964). This increase in temperature tends to decrease the rate of hydrate growth because the driving force for hydrate growth is decreased. If the temperature is increased enough, the hydrate stops growing because the hydrate interface is no longer in the hydrate forming region. Conversely, if hydrates are grown from ice, the ice absorbs the heat of formation. When ice absorbs this heat, it melts rather than increasing the temperature of the interface.

4.2 Conceptual Picture of Hydrate Formation

A conceptual mechanism as to how hydrates are formed from ice is presented schematically in Figure 4.1. As the ice began to melt, a layer of water was formed around the periphery of the ice particle. The first hydrate was formed as a shell around the ice particle. In order to convert all of the ice to hydrate, the hydrate forming component must diffuse through the hydrate shell to the inner, unconverted ice. The diffusion of gas through hydrate is very slow, much slower than the observed formation rates. This indicated a different mechanism than gas diffusion through the hydrate layer. The most reasonable explanation would be the presence of fissures and cracks in the
hydrate shell that allowed gas to diffuse through easily. Given adequate time, enough gas
could diffuse through the hydrate shell to convert all the ice to hydrate.

4.3 Hydrate Formation Procedure

4.3.1 Ice Preparation:

The first step of the hydrate synthesis was to make the ice. The process of making small grained ice included the freezing of distilled water. Distilled water was used to eliminate any possible effects that would result from impurities in tap water. For many of the initial runs, ice made from tap water was used without any significant changes in the results. In later experiments, distilled water was used in case tap water presented some unnoticed differences and to provide consistency between the ice used in all experiments.

The water was frozen in a gallon size stainless steel container. To freeze the water, it was placed in a freezer at 253 K overnight. Once the water was frozen, the crushing process began. The first step was to break the solid mass of ice into pieces that were small enough to go into a blender (Hamilton Beach Model 936-2).

The grinding of the ice was done in several stages. Initially, ice was loaded into the blender and crushed to a fine powder. This process was continued until enough ice was crushed to be used in an experiment. This experimental system required roughly 200 grams of ice. The crushed ice was returned to the stainless steel container and placed back into the freezer to refreeze any ice that melted. After the powdered ice was
refrozen, it was put back into the blender to be crushed again. This time liquid nitrogen was used to ensure the ice would not melt.

After the ice was crushed again, it was separated using a sieve with an 850 μm opening. The sieve was precooled to liquid nitrogen temperatures to prevent any further ice melting. Once the ice was crushed and sieved to the desired size, it was transferred to an insulated container also at liquid nitrogen temperatures. The ice was then stored in the freezer until it was needed for an experiment.

It was best to use the ice immediately after crushing. As the ice remained in the freezer, it began to anneal. It was not a solid mass and broke apart easily in the blender, but it did not work as well in the formation part of the experiment. Any ice that was not used in the experiment was put back into the stainless steel container for later use. This crushing process was repeated prior to every experiment to ensure a uniform size and consistency of the ice.

4.3.2 Loading the Reactor with Ice

When the reactor was loaded with ice, it was very important that the ice and the reactor remained as cold as possible. It was critical that the ice did not melt during this step. In many of the early experiments, liquid nitrogen was not used, and much of the ice was melted as it was loaded into the reactor. In these experiments, it was difficult to form any hydrates.
In the final experiments, liquid nitrogen was used to keep the system below the ice point. The reactor was filled with liquid nitrogen and allowed to cool. Once the liquid nitrogen evaporated, the reactor was filled again. This process was repeated several times to ensure that the reactor was close to liquid nitrogen temperatures. The ice was also cooled using liquid nitrogen prior to loading in into the reactor.

The reactor was loaded as quickly as possible with the cooled ice. Once the reactor was filled with the ice, the end cap was placed on the reactor, and then the cap was screwed on to the reactor. Then two additional pieces of 0.006 m (¼”) tubing were also attached because the ends of the reactor were submerged when the reactor was placed into the temperature bath.

The porosity of the ice and consequently of the hydrate can be controlled by the amount of ice that was packed into the reactor. The porosity in these experiments only varied between 0.3 and 0.5. There was an effort for all the experimental runs to be consistent. Porosity was not the variable of interest in these experiments. A future direction these experiments might take would be to vary porosity and measure the effect it has on dissociation. As evidenced by Lysne (1992) and later by the current model, porosity has a large effect on dissociation times.

4.3.3 Transferring Reactor to Temperature Bath

Once the reactor was filled with the desired amount of ice and all the necessary piping attached, it was transferred to the temperature-controlled bath. Prior to loading the
reactor with ice, the bath was cooled down to at least 268 K. In some of the later experiments, the bath was cooled down to 263 K. These temperatures were chosen because 268 K is the lower limit of the temperature controller and 263 K was close to the lower limit of the liquid in the temperature bath. At lower temperatures, freezing of the bath became a problem.

The reactor was taken from the loading area to the bath as quickly as possible to prevent any melting of the ice. The time between loading the reactor and placing it into the temperature bath was no longer than a couple of minutes. Since the reactor was made of stainless steel and had just been cooled to almost liquid nitrogen temperatures, this amount of time did not allow the reactor to heat up significantly. Consequently, little ice melted during this time.

After placing the reactor into the temperature bath, it needed to be connected to the rest of the unit. The gas supply line and the gas vent lines were all attached. During the formation portion of the experiment, the valves leading to the vent were closed so that the pressure in the system could be monitored using a pressure transducer.

4.3.4 Formation of Hydrates

After the reactor was placed in the temperature bath and all necessary equipment was attached, the temperature in the reactor was much colder than the temperature of the bath due to the liquid nitrogen used in the loading step. As shown of Figure 4.2, the ice was ~230 K when first loaded into the reactor, while the bath temperature was closer to
263 K. An attempt was made to pressurize the reactor right away in order to take advantage of this colder temperature. The gas used to pressurize the reactor was at room temperature prior to pressurizing the reactor. This was believed to introduce very little error in the actual measurement. Since gas has a very low heat capacity, it quickly decreased to the bath temperature.

Figure 4.2: Low Initial Temperature of Ice Due to Liquid Nitrogen

However, a possible error introduced at this time was the warm gas may have initiated melting of the ice and this melted ice may have converted to hydrate. This effect was an observed problem in most of the experiments. It did not make the determination of total conversion difficult because a pressure drop was still observable.
Figure 4.3 shows the effect of an initial pressure drop. The bath temperature was held below the freezing point after initially pressuring the system. There should be very little hydrate formation when the temperature was below the ice point, but as shown on Figure 4.3, there was a definite pressure drop at the beginning of the experiment. The pressure dropped at the rate of 0.1 MPa/hr. This was initially attributed to a leak in the system. However, at the end of the experiment, the pressure stopped decreasing and the pressure drop was only 0.02 MPa/hr. If there was a leak in the system, the pressure drop would still be observable at the end of the experiment. Thus, the initial pressure drop could be attributed to hydrate formation.

Once the reactor was pressurized with gas, the reactor was allowed to equilibrate with the bath temperature. The amount of equilibration time varied with each experiment, but was usually on the order of several hours. This time allowed for any melted ice to refreeze and for the gas to decrease to the bath temperature. As shown in Figure 4.2, the initial temperature of the system was well below the ice point. Consequently, very little ice should have melted. In the later experiments, when the system was pressurized at 263 K, the bath temperature setpoint was immediately changed to 267.5 K and the sample was allowed to equilibrate at that temperature. In these runs, the experiment was ready to begin as soon as the bath temperature reached the setpoint.

In almost all experiments, the initial equilibration temperature was the same, 267.5 K. It was found that equilibration time was not very important to the final results
of the experiment. A time of several hours was chosen because it eliminated much of the problem of the initial hydrate formation due to pressurizing with warm gas.

![Graph showing temperature and pressure over time]

Figure 4.3: Initial Pressure Drop Due to Hydrate Formation

Once the system was given enough time to equilibrate, it was necessary to start melting the ice and begin the conversion of ice to hydrate. The bath temperature setpoint was changed from 267.5 K to a value just above the freezing point, usually about 273.5 K. This portion of the experiment was tried in many different ways. The best way found
to achieve the highest conversion was to increase the bath temperature quickly and to stop at a temperature just above the ice point.

Refer to Figure 4.3 for a description of the following hydrate formation case. The fastest hydrate formation occurred when the bath temperature was increased above the ice point, as indicated by pressure drop. Then the rate of conversion began to decrease slowly. Note that all formation graphs show this trait. The pressure stopped decreasing significantly after about 12 hours. To increase the rate of hydrate formation, the system was repressured to ~21 MPa.

Several ways were attempted to speed up this portion of the experiment. The bath temperature could either be decreased to 267.5 K, as in Figure 4.3, or it could be left at the current temperature, which was just above the melting point, as in Figure 4.4. Note the increase in ice/hydrate temperatures during pressuring. This effect was not as prominent in the other method of pressurizing (Figure 4.3). In most cases, the temperature was decreased to 267.5 K, although there was not any observable benefit to either method. By decreasing the bath temperature back below the freezing point, any ice that did melt was given a chance to refreeze. Since the melting ice had the highest conversion rate, this method should have been more beneficial. Although it provided no observed benefit, this method was used for consistency.

After the reactor was repressurized, the bath temperature was increased to the final bath temperature of about 277 K and allowed to remain at this temperature for the remainder of the formation process, as shown in Figure 4.3. There were several
experiments in which the hydrate was allowed to finish forming at temperatures other than 277 K, but this had little effect on the results. The hydrate was allowed to continue forming until the pressure in the system had stopped decreasing. At this time, the rate of hydrate formation was extremely slow and the system had converted virtually all the ice to hydrate. The fastest pressure drop in the system, when hydrate formation was highest, the rate of pressure drop was ~0.32 MPa/hr. The rate of pressure drop at the end of the experiment, when the hydrate was assumed to be done forming, was ~0.02 MPa/hr.

Figure 4.4: System Repressurized Without Lowering Bath Temperature
One of the failed experiments attempted to begin with 200 μm size ice particles. These particles were prepared in a cold room at the Denver Federal Center and then transferred to this laboratory, where they were stored in a freezer prior to use. When the container holding the 200 μm size ice particles was removed from the freezer, the ice began to melt almost immediately. It was extremely difficult to keep this ice frozen even when using liquid nitrogen. The ice melted quickly and became slushy as it was loaded into the reactor. By the time the reactor was loaded and transferred to the temperature bath, too much of the ice had melted. As a result, there was very little hydrate formation during this experiment and this run was considered a failure. No further attempts were made to use this size ice particle.

4.4 Discussion of Results

During the trial stages of this experiment, many different techniques were attempted in forming the hydrate. Two major results came from these trials. First, hydrates did not form in any significant amount when there was bulk water present in the system. Secondly, hydrates formed from ice more readily when the ice was melted quickly.

4.4.1 Initial Formation Experiments

All of the early attempts to make hydrates were unsuccessful. The ice used in the early experiments was not kept at liquid nitrogen temperatures and consequently most of
the ice had melted by the time it was loaded into the reactor. In the best of the early experiments, the ice and the reactor were cooled in the freezer until just before the experiment began. The reactor heated to room temperature rather quickly and the ice melted to a slushy consistency by the time it was loaded into the reactor and placed in the temperature bath. In these experiments, very little hydrate formation took place. Figure 4.5 shows the formation experiment that achieved 19% conversion, which was much more successful than any previous attempts. This was the first experiment in which the reactor was also cooled before loading with ice. Consequently, more of the ice remained frozen during the loading step.

Figure 4.5: Early Formation Experiment with Many Temperature Cycles
Conversion calculations for these initial experiments were done differently than for the later experiments. A small piece of the hydrate was removed from the reactor after formation and stored in the freezer to freeze any water that was present due to hydrate dissociation. This only amounted to a small amount of ice around the edge of the sample. This had the additional benefit of freezing the water as a shell around the hydrate. This ice shell stabilized the hydrate against further dissociation by preventing dissociated gas to be released and in turn setting up an internal pressure within the ice shell. A recent paper (Tulk et. al. 1999) suggests that it was not a good idea to rely on self-preservation when storing hydrate samples. This paper suggested that the measured conversion was an underestimate of the actual amount. However, due to the time between sample storage and measurement, these errors were believed to be minimal, but there was no way of verifying this.

The hydrate sample was removed from the freezer for analysis. The sample was weighed, allowed to dissociate/melt, and then was weighed again. The difference in mass could be attributed to the methane gas that was present in the hydrate. Using the amount of methane present, a percent conversion to hydrate could be calculated, once the cage occupancy was determined. The value for cage occupancy was determined using CSM Hydrate, a hydrate equilibrium prediction program that was developed at the Colorado School of Mines.

The calculation of conversion for all future experiments was done differently. The pressure drop during the experiment was used as an indication of percent conversion
of ice to hydrate, together with the knowledge of how much ice was initially present. An explanation of the conversion calculation is included in Appendix A.

In the initial experiments, when the reactor was taken apart after formation, it was noticed that the hydrate had mainly formed around the edges of the reactor, as shown in Figure 4.6. The hydrates were noticeable because they were cloudy in appearance whereas the ice was clear. Hydrate presence could also be verified by placing a sample in a cup of water. If hydrates were present, the piece would bubble and fizz as the methane gas was released. The reason for this type of hydrate formation was the ice loaded into the system was partially melted and when it was placed into the temperature bath, which was below the ice point, it froze into a solid block. The edges of the ice melted first because all heat transfer to the reactor contents was from the temperature-controlled bath. Consequently, the edges were converted to hydrate first. These experiments would be the equivalent of trying to form hydrates from a single large piece of ice.

During these initial trials, many different formation procedures were attempted. The main variable that was changed was the bath temperature. Figures 4.5 and 4.7 illustrate how the bath temperature was varied. In the Figure 4.5 experiment, the bath temperature was varied relatively often and between large extremes. The lowest temperature was around 271 K and the highest temperature was about 288 K. The long duration of the experiment suggested that this rate was much too slow to provide efficient formation of hydrates.
Cross Sectional View of Reactor

Hydrates and Ice

Pipe Wall

Ice

Figure 4.6: Conceptual Picture of Hydrate Formation with Only a Single Block of Ice Present in Reactor

Figure 4.7: Early Formation Experiment with a Few Temperature Cycles
In the second experiment, shown in Figure 4.7, the bath temperature was only varied a few times. The percent conversion to hydrates in this case was only about 2%. Both experiments suffered from other difficulties that inhibited hydrate formation, such as the presence of large amounts of bulk water in the reactor. However, it was determined from these and other initial experiments that cycling the bath temperature did not have any significant effect on hydrate formation. Consequently, for many of the later experiments, the bath temperature was only varied slightly.

4.4.2 Hydrate Formation Using Stern Method

After this initial trial period, the method used by Stern et al. (1996) was followed. This method called for only ice to be present in the system and to begin at low temperatures. These experiments met with much more success. This method led to the almost complete conversion of ice to hydrate. In most cases the conversion of ice to hydrate was greater than 90%.

Table 4.1 provides a summary of results for all formation experiments done since the implementation of the Stern method. This table shows values for conversion in each experiment. Note that several experiments report a conversion of greater than 100%. This was impossible and was attributed to leaks in the system. This table shows that there were also mass balances done between the hydrate formation and dissociation. This mass balance provided a good check on how much gas was incorporated into the hydrate. These mass balances will be discussed in the next chapter.
Table 4.1 Summary of Experiments

<table>
<thead>
<tr>
<th>file</th>
<th>mass ice used</th>
<th>ice porosity</th>
<th>hydrate porosity</th>
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<th>% conversion</th>
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One problem in these experiments was the amount of time required for a typical experiment. Many different ideas were tried in the cycling of the temperature bath in hopes of increasing hydrate formation rates. Previous experience showed that many temperature cycles had no benefit over a few temperature cycles. Therefore, most of the changes were made to heating rate and the temperature to which the bath was increased.

Figures 4.8 and 4.9 show experiments conducted with the two possible heating rates. Figure 4.8 shows the fastest heating rate possible, 3.5 K/hr and Figure 4.9 shows the slowest heating rate, 0.35 K/hr. Both experiments began with essentially the same amount of ice but the conversion was much different. In the case of the faster heating rate, Figure 4.8, the conversion was 94% while in the case with the slower heating rate, Figure 4.9, the conversion was only 79%. In this work, experiments with the faster heating rate consistently increased the amount of ice conversion to hydrate.

This result may be due to the hydrate shell that was formed around the ice particle. In case of the slower heating rate, the hydrate had ample time to form at the rate of the melting ice and the resulting hydrate shell that was formed was much more solid. Conversely, in the case of the faster heating rate, the hydrate could not form as rapidly as the ice melted and the resulting shell that formed had many cracks and fissures, which allowed for higher conversion rates. This hypothesis has not been verified by any experiments and is subject to debate.
Figure 4.8: Heating Rate of 3.5 K/hour

Figure 4.9: Heating Rate of 0.35 K/hour
The results of these experiments indicate that it was best to heat the temperature bath quickly, or at least as quickly as the equipment allowed. It should be kept in mind that heating too fast could be worse than heating too slowly. If the ice was melted too fast, the hydrate would not be able to form quickly enough to prevent bulk melting.

It was also found that cycling the temperature was unnecessary. However, for consistency, the temperature was cycled in these experiments. It was only necessary that the experiment begin the formation process below the ice point and then relatively quickly, heat the system to a value just above the ice point.

Another variable tested during the formation procedure was the number of times that the system was pressurized. This was varied between one and three times during the experiment. Figure 4.10 shows a case when the pressure was increased once. The pressure began to level off and stopped decreasing around 60 hours. Figure 4.11 shows the case when the pressure was increased twice and formation occurred after each time the pressure was increased. The time for complete hydrate formation in this case was around 40 hours.

Figure 4.12 shows the case when the system pressure was increased three times. Here the total formation time was around 65 hours. In these experiments, the highest conversion was achieved for the case when the system was pressurized three times and the lowest conversion for the case when the pressure was only increased once.
Figure 4.10: Hydrate Formation Experiment with a Single Pressure Increase

Figure 4.11: Hydrate Formation Experiment with Two Pressure Increases
The conversion was very close for the cases when the pressure was increased two and three times, 94% and 97% respectively. The real benefit was in the time required for hydrate formation. The case when the pressure was increased twice had the shortest conversion time. This was the procedure that was used for the rest of the experiments. As shown on some of the figures, the formation time took longer than 40 hours although the pressure was increased twice. The length of these runs were the result of leaving the temperature too long at the initial temperature below the freezing point or when the bath temperature was heated too slowly. These practices were subsequently changed to methods that were more efficient.
4.4.3 Hydrate Formation with Gas Mixture

There were several experiments done with a different gas mixture. The gas mixture used was the pseudo-Qatar gas mixture as described earlier. This gas mixture was a structure II former while the methane experiments were a structure I former. These experiments were tried in order to see how differently the methane hydrates would behave from a structure II forming gas. There was very little difference observed between the two formation experiments. Both the methane hydrate and the natural gas hydrate formed similarly. They both exhibited the same type of temperature and pressure profiles. Figure 4.13 shows the formation curve for the pseudo-Qatar gas mixture while all other figures in this chapter show structure I hydrate formation for a methane gas.

There was some difference between the two formation experiments. The initial formation rate for the structure II experiment was faster, but subsequent pressurization did not increase the formation rate. In fact, after the system pressure was increased again, the formation rate was much slower than the experiments with methane gas (Figure 4.3). The calculation of conversion had to be modified slightly to account for the different gas mixture and the different hydrate structure. A description of this calculation is also included in Appendix A. The experimental conditions were the same for the formation of the structure II hydrate and the methane structure I hydrate. The structure II difference may be explained by the fact that less gas was needed for complete conversion, so in the initial part, most of the ice was already converted to hydrate. After the second
pressuring, the formation rate was slower because there was a larger hydrate shell the gas needed to penetrate.

![Figure 4.13: Hydrate Formation with Pseudo-Qatar Gas Mixture](chart)

### 4.4.4 Temperature Deviations Between Reactor Contents and Bath

One interesting thing to note from all the formation experiments was the deviation of hydrate temperature from bath temperature during hydrate formation. This can be noted on all formation curves that include both the bath temperature and the hydrate
temperatures. Figure 4.14 shows this trend nicely; as the bath temperature was increased, the sample temperatures match the bath temperature until the bath reached the melting point of ice. At this temperature, ice began to melt and as the ice melted it had a cooling effect on the system, since the melting ice is endothermic. This showed up on the figure, at point A, as a temperature lag in the thermocouples.

Hydrate formation also occurred during this time. Hydrate formation is an exothermic process and released heat to the surroundings. Initially, the ice was melting faster than the hydrate could form so the temperature remained below the bath temperature. Eventually the hydrate formation rate surpassed the melting ice, this is shown on the graph at point B as an increase in temperature, and the hydrate temperature actually overshot the bath temperature. Hydrate formation then began to slow down and the temperature within the reactor equilibrated to the bath temperature.

In Figure 4.14, when the bath temperature was decreased at point C, the reactor and bath temperatures match until the water in the system began to refreeze. At point D, the rate of reactor temperature decrease slows relative to the bath temperature. Both ice and hydrate formation, are exothermic so it was difficult to determine which process resulted in the temperature excursion.

Similar trends were observed on subsequent cycling, (A=E and G) and (D=F), of the bath temperature, but each time the heat effect was smaller in magnitude. This was another indication that hydrate formation was taking place. In the final temperature
Figure 4.14: Deviations Between Reactor Temperatures and Bath Temperature
cycle, the temperature deviations were very small, which indicated that very little ice remained and most of the reactor contents were hydrate.

4.5 Recommended Formation Method

In conclusion, the best method found for making hydrates is the following procedure. The ice particles used should be as small as possible without melting before formation. If a cold room is available, then 200 μm particles should be used. When only liquid nitrogen is available, 850 μm particles are easy enough to work with. Once the reactor is loaded and placed into the temperature bath, the system pressure should be increased right away to a value well into the hydrate formation region. The initial bath temperature is not extremely important, but it does need to be below the freezing point.

Only a matter of several hours is necessary for equilibration at this temperature. Then the bath temperature should be increased quickly to a temperature just above the ice melting point. There were only two heating rates available in this experiment, 3.5 K/hr or 0.35 K/hr. In this work, the faster the heating rate resulted in the higher conversion. There may be some optimal heating rate, but this was not discovered in this research.

The system is then left at these conditions overnight for at least twelve hours. The bath temperature is decreased to below the ice point and the system pressure is increased back up to the original pressure. The system is allowed to equilibrate at this condition for several hours before the bath temperature is increased to the final desired temperature.
The system is then left at these conditions until the pressure stops decreasing. At this point, all of the ice has been converted to hydrate.
CHAPTER 5

HYDRATE DISSOCIATION EXPERIMENTS

5.1 Introduction

After the hydrate had been formed, as described in the previous chapter, then the dissociation process could begin. The temperature of the bath was set in the final stage of the formation portion of the experiment and in most cases the reactor was allowed to equilibrate at this temperature for at least twelve hours.

There were two different types of dissociation experiments done during this research. In the majority of the cases, the system pressure was dropped rapidly from the final formation pressure to atmospheric pressure. In the other type of experiment, the pressure was dropped from the final formation pressure to a pressure above atmospheric, but still low enough to be below the equilibrium curve and allow for hydrate dissociation at a temperature above the ice point.

The goal behind these dissociation experiments was twofold. The first goal was to find if there was any optimal way to depressurize a hydrate plug such that it would dissociate the fastest. The second goal was to provide data for and to verify a mathematical model that simulated hydrate dissociation.
5.2 Depressurization Procedure

The hydrates in this experiment were dissociated by the method of pressure reduction on both sides of the plug. The depressurization of the system was done as quickly as possible in all experiments. This required simply opening the valves on each end of the reactor and venting the gas until the pressure in the system was at the desired set point. In the case when the pressure was reduced to atmospheric pressure, the pressure relief valves were bypassed. The time necessary to depressurize in this manner required about a minute.

The other case was when the system was depressurized to a pressure greater than atmospheric. In these experiments, the time to depressurize was about ten minutes. In this case, the pressure relief valve was used to maintain the pressure at a given set point. The idea behind the pressure relief valve was that it would vent gas until the pressure dropped below the set point. At this point, the gas flow would stop, but the hydrate would continue to dissociate because the system was below the hydrate equilibrium condition. It was presupposed that the dissociating hydrate would release methane gas, which would increase the system pressure until the pressure increased above the pressure relief valve set point and gas would vent again. This process would continue until all of the hydrate dissociated. However, in the actual experiments, gas was continuously vented for the duration of the experiment. The cycling of pressure was not observed as was expected. This made the analysis of flow data much easier in these experiments.
5.3 Gas Evolution

After the system had been depressurized and the new pressure set point was achieved, then the flow rate of gas from the system could be measured using an inverted cylinder (see Figure 5.1). The process of measuring flow rates was done using an inverted 1000 ml graduated cylinder, filled with water. The cylinder was inverted over a five-gallon bucket that was also filled with water. The gas venting from the dissociating hydrate was fed into the inverted cylinder and gas flow rates were measured. The volume of water displaced as a function of time was used to determine the flow rate. There were two vent lines and both were fed into the same inverted cylinder. A plot of flow rate versus time could be generated (see Figure 5.2). The area under this curve could be integrated to obtain a plot of total moles of gas evolve versus time (Figure 5.3).

Both vent lines were fed to the same inverted cylinder. One experiment was attempted in which each vent line was fed to a separate inverted cylinder and flow rates were measured independent of one another. However, it was difficult to measure both flow rates at the same time due to the variability in individual flow rates and the inability to measure both flow rates continuously. The final curve of total moles evolved versus time (Figure 5.4) was not nearly as smooth as other runs, a typical run is shown in Figure 5.3.

The difficulties in venting the gas were determining two conditions: (1) when the dissociated gas became measurable and (2) when all of the excess gas in the system finished venting. The system was depressurized as quickly as possible so that much of
Figure 5.1 Schematic of Experimental Apparatus with Only Vent Lines Shown

- Pressure Relief Valve
- Gas Outlet
- Thermocouple Inlet
Figure 5.2: Flow Rate of Methane Gas Released from Dissociating Hydrate

Figure 5.3: Experiment When Mass Balance Worked Out to within 2%
this error was reduced. If the system was depressurized quickly enough, very little hydrate dissociated during this step. There was a noticeable break when the gas slowed venting and was no longer audible. This was assumed the point when the gas finished venting and the dissociating gas became measurable. This was a very tenuous assumption, but necessary in order to quantify the amount of hydrate dissociated.

![Graph](image)

**Figure 5.4: Curve Generated Using Two Inverted Cylinders**

### 5.4 Temperature Measurements

In addition to measuring the flow rate of gas evolved during hydrate dissociation, it was also possible to continuously measure the temperature at the center of the hydrate
plug at five different axial positions. These temperature measurements were very helpful in determining what was happening during the dissociation process. Unfortunately, the position of the thermocouples for many of the runs was oriented in such a way as to give false temperature readings, but valuable information was still obtained.

![Diagram of Reactor with Thermocouples](image)

*Figure 5.5 Diagram of Reactor when Thermocouples are Inserted from Top of Reactor*

Some discussion about the thermocouples is necessary. Realistic temperature readings in the hydrate plug were difficult to obtain. For many of the initial runs, the thermocouples were oriented in the reactor from the top and extended down into the center of the hydrate sample (see Figure 5.5). The problem with this setup was that the thermocouples provided a site for the hydrate to dissociate. When the hydrate
dissociated, it melted away from the thermocouple and formed a hole around the thermocouple (Figure 5.6).

Figure 5.6 shows a dissociation experiment that was stopped before the hydrate completely dissociated. This picture indicated the formation of holes in the remaining hydrate section. Each hole was located where there was a thermocouple. All the water that was formed from this dissociating hydrate collected in these holes and accumulated at the bottom. The actual temperature of the hydrate was low enough that the accumulated water would refreeze and form ice.

There were also some observations made from Figure 5.6 that were not photographed. There was very clearly a small block of ice at the bottom of the hole, below where the thermocouple tip was located. This piece of ice was very clear, indicating that it was refrozen from water.

The initial temperatures that the thermocouples measured were accurate, but soon they began to measure the temperature of the water, ice, or gas instead. In Figure 5.7, the hydrate temperature dropped below the ice point as the pressure was lowered. Figure 5.8 shows the complete dissociation curve for Figure 5.7. The temperatures began to rise right away until they reached about 272 K and then slowly increased to 273 K where they remained at that temperature for several hours. Some thermocouple temperatures began to diverge from 273 K and showed large temperature jumps during the dissociation
Figure 5.6: Dissociating Hydrate Plug with Holes Caused by Thermocouples
Figure 5.7: Hydrate Temperature Drop as Pressure is Decreased
Figure 5.8: Dissociation Experiment with the Channel 4 Thermocouple Inverted
process. These large temperature variations were most likely because the temperature of the gas was now being measured. The gas was the only phase capable of changing temperature this quickly in the system. In addition to the water freezing to ice, it also accelerated the dissociation of the hydrate due to higher thermal diffusivity, relative to the gas phase, as shown by experimental evidence. Therefore, the tip of the thermocouple did not remain in the hydrate as long as it should.

The thermocouples used in the experiment had a 0.003 m ($\frac{1}{8}$") stainless steel sheath around the thermocouple wires. It was believed that the metal sheath was conducting heat from the temperature bath and accelerating the melting in that vicinity. To eliminate this problem, several ideas were tested. Different types of insulation were used around the metal sheath to minimize the amount of heat conducted through the thermocouple and into the hydrate. This had no effect on the temperature results. In addition, thermocouples of different radii were used. This also did not meet with any success.

Different types of thermocouples were used, including Teflon coated thermocouple wires. These Teflon coated thermocouples also caused the problem of melting near the thermocouples and resulted in holes similar to the metal-sheathed thermocouples, as shown in Figure 5.6. It was this observation that led to the realization that the thermocouples themselves were not the problem.

In order to finally achieve a better measurement of the hydrate throughout an entire dissociation experiment the orientation of the original thermocouples was altered.
The thermocouples were inserted from the bottom of the reactor up into the hydrate (see Figure 5.9). Now the temperature measurements gave a more accurate picture of what was happening during the dissociation process. Figures 5.10 shows a dissociation experiment in which one thermocouple, channel 4, was inverted. It is apparent that the temperature of the hydrate did increase up to 273 K relatively quickly but it remained constant at this temperature. There were no erratic fluctuations in temperature as observed in some of the other thermocouples, such as channel 1.

This orientation of the thermocouples was thought to be better because as the hydrate dissociated to water, the water simply drained away and did not accumulate in a
pool around the thermocouple. Now that the water was not around the thermocouple, there was not the increased driving force to melt the hydrate as in the case of Figure 5.6 where the holes were formed. The tip of the thermocouple remained imbedded in the hydrate and thus measured the actual hydrate temperature longer.

The smaller diameter thermocouple did not improve the accuracy of measuring the hydrate temperature. However, in one experiment where the reactor was pressurized without any ice present and then depressurized, the smaller diameter thermocouple did give a different reading than the other thermocouples, as shown in Figure 5.10. The 0.0016 m ($\frac{1}{16}$") thermocouple recorded a low temperature of 223 K whereas the 0.003 m ($\frac{1}{8}$") thermocouples all consistently recorded a low of about 238 K. The smaller diameter thermocouple was only more accurate in the case of very rapid temperature changes. During all other dissociation experiments, there was no noticeable difference in the temperature measurements.

5.5 Results

5.5.1 Temperature Results

The results of the temperature measurements during hydrate dissociation provided an interesting view of hydrate dissociation. The following results will be discussed for the case when the system is depressurized to atmospheric pressure. Figure 5.7 shows how the temperature of the hydrate and gas change as the system was depressurized. The gas temperatures were recorded on channels zero and six. These two temperatures
Figure 5.10: Reactor Depressurized with No Ice Present
initially decreased at the same rate as all the other temperatures but they did not drop as low. These two temperatures very quickly rise back up to the bath temperature.

The temperatures of the hydrate, channels one through five, all followed each other fairly closely. The only exception is channel 5, which decreased much further. This was most likely due to non-uniformity in the hydrate. It should not be expected that the hydrate would be evenly distributed in the reactor in all experiments. The trends in this experiment were typical of any dissociation experiment. The gas phase temperatures dropped as the pressure was decreased but then very quickly returned to the bath temperature. The hydrate temperatures usually dropped at the same rate to a value below the freezing point. Occasionally one of the thermocouples recorded a lower temperature than the other ones.

As time progressed, the hydrate temperatures still followed each other well, as seen in Figure 5.8. The temperatures dropped to their lowest value just after depressurization and then slowly over the course of dissociation, the temperatures all rose to about 273 K and remained at this temperature until most of the hydrate had dissociated. Note the temperature excursions, in particular channel one, it shows a large deviation just prior to complete dissociation. This deviation was the result of the thermocouple alignment, discussed earlier. These deviations were not actually the hydrate temperature, but more likely the gas phase temperatures. The initial temperature measurements in the experiment could still be considered correct; it was only after these temperature deviations occurred that the temperature results were less meaningful.
Later experiments, after the thermocouple position was changed, showed that the hydrate temperature remained at the ice point for the duration of the experiment (see Figure 5.11). It was not until the ice began to melt that the temperatures inside the reactor began to increase. Note Figure 5.8, which shows an experiment in which only one thermocouple, channel four, was inverted. The temperature profile for this thermocouple is dramatically different than the others. The temperature for channel 4 remained at the ice point until the very end and then there was a sudden, dramatic temperature increase up to the bath temperature. This temperature rise indicated the complete melting of any ice present during the experiment. Once the ice finished melting, then the water in the system began to increase in temperature. All other thermocouples show a premature departure from the ice point and actually increased slowly up to the ice point.

In Figure 5.11, channel 1 shows a large temperature jump just prior to dissociation. This could be an indication of longitudinal dissociation occurring within the reactor. Channel 1 was at the end of the reactor and if longitudinal dissociation were occurring, it would be expected to show up as a temperature rise on either channel 1 or 5. The unusual thing to note about the temperature jump is that it returns to the original temperature. If longitudinal dissociation were the cause, the temperature would be expected to remain at an elevated temperature. It was difficult to explain the temperature channel 1 deviation in Figure 5.11 and a satisfactory answer has not been determined.
Figure 5.11: Dissociation Experiment with All Thermocouples Inverted
A difficult parameter to quantify in each experiment was how low the temperature would drop once the pressure was lowered. The minimum temperature reached in each experiment was different. Figure 5.11 shows a low temperature of 271 K. There were other experiments run where the temperature dropped more than this and some where they dropped less. However, in all experiments, the temperatures rose quickly after the initial temperature drop, and then slowly rose to the ice point where they stayed for some time. The discrepancy in initial temperatures is most likely due to inhomogeneity in hydrate throughout the reactor and between runs.

There were also several hydrate plugs dissociated at bath temperatures other than 277 K. Figure 5.12 shows an experiment when the bath temperature was held below the ice point at 270 K. This experiment shows a rapid decrease in temperature and then a quick rise back up to the bath temperature. There was some initial dissociation, but once the hydrate temperature reached the bath temperature, hydrate dissociation stopped as evidenced by the end of gas evolution (see Figure 5.13). The hydrate stopped dissociating because there was no longer any temperature driving force for dissociation. The hydrate was no longer being supplied with the heat needed to dissociate.

There were some experiments done where the bath temperature was between the ice point and 277 K (see Figure 5.14). There was also an experiment done where the bath temperature was above 277 K (Figure 5.15). In both cases, the hydrate temperatures dropped below the ice point and then slowly returned to the ice point. The end of these data is not included due to experimental difficulties. In all cases, the temperature profiles
Figure 5.12: Dissociation Experiment When Bath Temperature was Below the Ice Point
were very similar to the 277 K case.

Figure 5.13: Dissociation Experiment When Bath Temperature was Below the Ice Point-Gas Evolution

5.5.2 Dissociation Experiment with Gas Mixture

Another type of experiment performed was the use of a gas mixture, pseudo-Qatar gas, other than methane. This gas mixture formed a structure II hydrate while the methane formed a structure I hydrate. In general, the trends observed for these experiments (see Figure 5.16) were similar to the methane hydrates. The one noticeable
Figure 5.14: Dissociation Experiment when Bath Temperature was Between the Ice Point and 277 K
Figure 5.15: Dissociation Experiment when Bath Temperature was Greater Than 277 K
Figure 5.16: Dissociation Experiment with Psuedo-Qatar Gas Mixture
difference from these experiments was that the dissociation time was on the order of 30% less. The model developed predicted the structure II hydrate to take longer to dissociate, which is the opposite of the trend observed in the experiment.

An explanation for this will only briefly be comment on. The goal of this research was to simulate the dissociation of methane hydrate. It was expected that the results would also be applicable to different hydrate structures. It was assumed in the model that the dissociation process was heat transfer controlled. It is possible that dissociation at this pressure also has some kinetic limitation. The equilibrium condition for the two hydrate structures is different and it is reasonable to assume that the kinetics of dissociation would also be different for different structures. Work previously done by Jamaluddin et al. (1989) indicated that by changing the system pressure the system could go from a heat transfer controlled regime to a regime where both heat transfer and kinetics are important. This idea will be left for discussion during the comparison with the computer model.

One very unusual result occurred during one of the experiments with the pseudo-Qatar gas mixture and has not been able to be reproduced. The temperatures of the hydrate dropped to 238 K (see Figure 5.17). The temperatures very quickly rose to the ice point, quicker than the other experiment. The other unusual thing to note was in the time for dissociation to occur, it was much less than any of the previous runs. There is currently no explanation for this run.
Figure 5.17: Anomalous Experiment with Very Low Initial Temperature Drop
5.5.3 Dissociation Experiments at Pressures Greater than Atmospheric

The second part of this work considered the effects when the system was not depressurized to atmospheric pressure. All of these experiments were done at pressures such that the equilibrium temperature was between 273 K and 277 K. With any temperatures below zero the results would have been similar to the previous experiments and at hydrate equilibrium temperatures above 277 K and there would have been no hydrate dissociation.

Upon depressurization, the temperature dropped rapidly, but remained above the ice point (Figure 5.18). The temperatures then increased to the equilibrium temperature at the prevailing pressure. The hydrates remained at this temperature until all the hydrate had dissociated and then increased to the bath temperature. There were oscillations in the bath temperature, so an average value was used for the analysis. Figure 5.18 also included the pressure profile during the dissociation experiment and indicated that the pressure relief valves did a good job of maintaining a constant system pressure.

The time necessary for these plugs to dissociate was considerable more than when the plug was dissociated at atmospheric pressure. As shown in Table 4.1, the times increased dramatically as the hydrate dissociation temperature approached the bath temperature. Since the dissociation of hydrate requires the input of heat, it is expected that as the temperature driving force decreased, the dissociation rate also decreases.

The pressure and temperature profiles were analyzed as an indication of whether or not the hydrate was in equilibrium with the prevailing pressure. Figure 5.19 shows the
Figure 5.18: Dissociation Experiment Conducted at a Pressure Greater Than Atmospheric
results of this analysis. Figure 5.19 indicates that in each experiment, the hydrate was in equilibrium with the pressure as predicted by CSM Hydrate. The maximum deviation in temperature from the equilibrium value was about 5%.

Figure 5.19: Methane Hydrate Equilibrium Curve with Experimental Data Points

5.5.4 Gas Flow

The only means available to discern how the hydrates dissociated were temperature and pressure measurements and the amount of gas evolved. Measuring the gas evolution proved to be invaluable in determining how the hydrates dissociate.
A difficulty in determining gas evolution was the possibility that pockets of gas could be trapped somewhere in the hydrate and only after some of the hydrate has dissociated, does this gas in the pocket vent. If anything, the gas evolved should be more than the number of moles consumed. In these experiments, it was not possible to measure the total volume of gas present in the system, due to the large volume of gas present in this study. It was a very difficult task to determine when to start measuring flow rates and, as expected, the mass balances do not always match.

However, in most cases the mass balance between number of moles consumed and evolved were within about 20% (Table 4.1) and in most cases there were more moles of gas evolved than consumed. The mass balances in Table 4.1 show that when more moles of gas were evolved than consumed, the value is negative and the value is positive when more moles were consumed than evolved. However, in some cases the amount consumed was more than evolved due to other experimental difficulties. These difficulties usually included leaks that were not detected right away. Figure 5.3 shows an almost ideal case when the moles consumed was nearly identical to the amount evolved, while Figure 5.20 shows the more usual situation when the moles evolved was noticeably more than the amount consumed.
Figure 5.20: Typical Dissociation Curve When More Gas was Evolved Than Consumed

In the cases of the experiment when the final pressure was above atmospheric, the same types of errors were present, but it was much more difficult to know when to begin measuring flow rates. There was no distinct break in sound to indicate that venting finished. However, since the flow rates in this part were much less than the previous case, the error was minimized. The gas evolution from these experiments was only recorded for a few experiments. The total time it took to completely dissociate the hydrate was very long and in most cases, it was more than a full day (see Figure 5.21). There was no way to record all of the flow data using the inverted cylinder for the duration of the experiment as indicated by the gap in Figure 5.21. However, it was safe to interpolate between these points since the gas flow rate was slow and did not vary
much between the end points in the gap. Early experiments attempted to use an electronic flow meter, but the flow meters were not sensitive enough to measure the necessary flow rates.

![Graph showing the total amount of methane consumed during formation over time (hours)](image)

**Figure 5.21: Dissociation Experiment That Took More Than 24 Hours**

### 5.5.5 Pictures

Some of the most important experiments done were those where the hydrate was not allowed to completely dissociate. The experiment was run normally, but after some
predetermined time the experiment was stopped and the reactor was taken apart so the remaining hydrate could be observed and photographed. These observations lent a great deal of verification to the simplicity of the model that was developed as part of this research. The hydrate was observed to dissociate radially. Figure 5.22 a, b, and c show the results from three different dissociation experiments. Each experiment was allowed to dissociate for a different amount of time. In each successive photograph, it is apparent that the hydrate plug continued to shrink radially. The hydrate released from the pipe wall first and then shrunk inwards. There was very little, if any, dissociation in the axial direction. Figure 5.22 c and d show that the plug recedes very little from the end of the reactor. The small space that is present was due to the end cap extending into the reactor.

Another interesting idea to note from these pictures is that the bottom of the plug was flattened (Figure 5.22). This observation could have a significant impact on any future modeling done on hydrate dissociation. As the hydrate dissociated or as the ice melted to form water, the water drained and accumulated on the bottom of the reactor. Water has a much higher thermal diffusivity than the methane gas at the top of the remaining hydrate plug. The hydrate in contact with the water will melt faster than the hydrate in contact with the gas, thus providing the flattening on the bottom of the hydrate.

It has been previously mentioned that all the temperature profiles in the dissociating hydrate plug remained around 273 K for much of the dissociation process when the pressure was atmospheric. This is an indication that ice was present in the system. Further verification of ice formation in the system was obtained from some of
a) Dissociating Hydrate Plug After 1 Hour  

b) Dissociating Hydrate Plug After 2 Hours

c) Dissociating Hydrate Plug After 3 Hours  

d) Very Little Axial Dissociation Taken Place

Figure 5.22: Pictures of Hydrate Dissociation
experiments which were stopped early to view the remaining sample inside the reactor. Figure 5.22c shows the remains of a sample after approximately 95% of the hydrate had dissociated. What is remaining in the picture is essentially an ice core. Another picture was of the remaining sample after some hydrate was allowed to dissociate (Figure 5.23). This picture shows a small piece that was broken off from the remaining core. When water was slowly dropped on the sample, bubbling was observed, which indicated the presence of hydrates. The interesting thing about this test was that bubbling only occurred in the center of the sample. Along the edges there was not any bubbling, which indicated that the solid present was ice.

5.6 Conceptual Picture of Hydrate Dissociation

A great deal of experimental data were taken during the dissociation experiments. The difficulty comes in trying to develop a cohesive picture of hydrate dissociation that is capable of combining all of the observed results. The following description of hydrate dissociation attempts to pull together all of these results and develop such a picture.

One important result found in this work was that when hydrates dissociate in a pipeline, they do so radially. This idea was first hypothesized by Lysne (1995) but this research is the first to provide visual confirmation of radial dissociation. When hydrates dissociate, they do so at the surface as opposed to within the bulk. Since all of the hydrates formed in this research were porous, it might be expected for that hydrate would dissociate everywhere within the hydrate mass. However, pictures revealed that the
Figure 5.22: Piece of Dissociating Hydrate Surrounded by an Ice Layer
hydrate clearly dissociated from the pipe wall inward and that there is very little axial dissociation.

Even though the hydrate may be in the dissociation region, it cannot dissociate until the necessary heat is supplied to the hydrate surface. Sources of heat input into the system were either from the pipe wall or the ends of the plug. The heat transfer through the pipe wall is much greater than from the ends of the plug, due to larger heat transfer area, and it would be expected for the hydrate to dissociate radially faster.

There are important safety implications to the fact that hydrates dissociate radially. When a plug is depressurized and begins to dissociate, it will melt at the wall first and then shrink inwardly. If there is any pressure gradient across the plug then when the plug releases, it may turn into a projectile. This hydrate projectile can have serious safety implications for people working near hydrate plugs. There are several cases of either loss of life, equipment damage, or both that have been reported (Kent and Coolen 1994).

Another important result was the formation of ice. When the system was depressurized such that the hydrate equilibrium temperature, at the prevailing pressure, was below the ice point, ice formed in the system. This leads to the possibility of turning a hydrate plug into an ice plug. However, based on these experiments, the time required to remove all solids, hydrate and ice, was less than the time to remove the hydrate when no ice was present.
Ice may increase the dissociation rate for two reasons. When ice was formed, temperatures in the system were lower and this increased the temperature driving force for heat transfer, for a constant external temperature. The second reason was that ice has an order of magnitude higher thermal diffusivity ($\alpha$) than water. Thermal diffusivity ($\alpha = k/\rho C_p$) is a measure of the materials ability to conduct thermal energy relative to its ability to store thermal energy. Materials with a large thermal diffusivity respond more quickly to changes in their thermal environment (Incropera and De Witt 1990). The thermal conductivity ($k$) for ice is five times greater while the specific heat ($C_p$) for ice is about half that of water. This implies that the heat will be transferred much faster through the ice phase than it will through the water phase.

The following discussion was adapted from the thesis by Lysne (1995). It is repeated here because it discusses an important issue, hydrate temperatures during dissociation. This research was able to experimental verify Lysne’s conclusions. When the system was depressurized, there were several different scenarios that were possible. These different scenarios depended upon the rate at which the system was depressurized and the final pressure of the system. The following discussion refers to Figure 5.24. The hydrate plug was initially at 277 K, the ocean ambient temperature, and some high pressure, point A. The pressure was then reduced infinitely slowly from point A to point $B_{1a}$. By slowly reducing the pressure, one can assume that the hydrate remained at a constant temperature equal to the starting temperature. The rate of cooling due to gas expansion was slow and the hydrate would have sufficient time to equilibrate with the
Figure 5.24 Conceptual Picture of Hydrate Temperatures During Depressurization
surrounding temperature. Hydrate would begin to dissociate at point $B_{1a}$. As the pressure was further reduced, the temperature decreased in order for the hydrate to remain in equilibrium with the pressure.

At the other extreme was the case when the pressure was reduced very rapidly. Now the gas cools due to a Joule-Thomson type expansion and the hydrate would cool as well. The hydrate cooled to a temperature below its equilibrium value ($B_{1b}$) at the new pressure, $P_1$ but then the hydrate temperature increased to reach equilibrium with the new pressure, point $C_1$. This second case was observed most often in these experiments (see Figure 5.18). The hydrate temperature would cool below the equilibrium temperature and then quickly rise up to the equilibrium temperature.

There was also the case when the equilibrium temperature at the prevailing pressure was below the ice point. The same scenarios still occurred as mentioned above, but now there was the additional presence of ice in the system. The ice would tend to buffer the temperature of the hydrate. When the system was depressurized slowly, the pressure dropped isothermally until it reached the equilibrium point, $B_{1a}$. At this point, it followed the equilibrium curve until is reached the ice point, $Q_1$, where it remained until all the hydrate had dissociated. The other case, when the pressure was dropped rapidly, the temperature decreased below the ice point, but only slightly below, before it increased back up to the ice point, point $Q_1$. When this ice point is reached, any water released during dissociated was converted to ice and absorbed most of the heat of dissociation. The hydrate temperature did not drop much below the ice point or increase much above
the ice point until all of the hydrate dissociates. The important idea here is that when the
equilibrium temperature is below the ice point, the temperature of the hydrate will not be
in equilibrium with the pressure. The temperature of the hydrate will always tend toward
the ice point.

There was an experiment where the initial temperature drop of the hydrate was
238 K (Figure 5.17). The current model does not explain this temperature drop. As
mentioned before, this experiment currently does not have an explanation and does not fit
this current explanation.

The results of this work provide information into the nature of hydrate
dissociation. The results of the dissociation experiments provided insight into the hydrate
dissociation phenomena and provide the necessary verification of the model developed as
part of this research. The data were also able to provide a basis to determine when the
model will fail and how future modeling efforts need to account for these observations.
CHAPTER 6

THE EXISTING MODEL

6.1 Introduction

This research had two main objectives. The first was to find an optimal way to depressurize a pipeline such that hydrate will dissociate the fastest. The second goal was to create a computer model that simulates hydrate dissociation in a pipeline.

Previously, hydrate dissociation had been modeled in this laboratory by Kelkar et al. (1998). Much of the following discussion is taken directly from that work and will be summarized here to provide the reader with the necessary knowledge base to understand and appreciate the modeling that was done for this research.

6.2 Modeling Assumptions

As with any model, there were certain assumptions that were needed before the situation could be modeled effectively. This set of assumptions served to make the problem relatively easy to model. These assumptions appear to be fairly well supported by other research and field evidence.

Typically the time it takes to depressurize a pipeline is small compared to the time it takes to dissociate the hydrate plug (Sloan 1998b p.78). This case study revealed that it
took on the order of several days to depressurize the pipeline and 23 days for the hydrate to dissociate. This was an example of a system that was slowly depressurized. There were also some results from OLGA (Figure 6.1), a pipeline simulation program, which indicated it took roughly 2 hours to depressurize a pipeline. One of the assumptions in the model was that the pressure was step changed on both sides of the plug to a final pressure so that the hydrate would begin to dissociate.

Figure 6.1: OLGA Simulation Results for Time Needed to Depressurize a 12'' Pipeline with a 2'' Vent Line
Recent laboratory data have shown that hydrate plugs were porous (Lysne 1995). Additionally, there have been field tests, where hydrate plugs were purposely formed (Austvik et al. 1995). These tests also indicate that hydrate plugs were porous. Since the plugs were porous, they were able to transmit pressure throughout the plug while acting to block the flow of liquids.

To set up this model, the hydrate temperature was assumed to be in equilibrium with the pressure of the gas surrounding the plug. It was already assumed that the plug was porous and able to easily transmit pressure throughout the plug. It stands to reason that the pressure was uniform throughout the plug. Since the pressure was constant, it seemed reasonable to assume that the temperature would also be constant throughout.

Since the hydrate was in equilibrium with the pressure, it was possible to decrease the system pressure such that the hydrate equilibrium temperature would be below the ice point. When the temperatures were low, there was the possibility of ice formation in the system. For the case of methane hydrates, the pressure only needed to be below about 2.5 MPa before ice formed in the system.

In addition, only the radial dissociation of hydrate was considered important. Typically, when a plug is formed in a pipeline, the length of the plug is orders of magnitude greater than its diameter (Sloan 1998b and Hatton et al. 1997). The typical length to diameter ratio, based on these results, was on the order of 100 to 1000.

Additionally, it was assumed that the flow of gas in the system, due to dissociating hydrate was small. This assumption implied that the dominant method of
heat transfer would be conduction both through the pipe wall and inside the pipeline. The equations governing the system were defined by Fourier's law of heat conduction.

The final assumption that was used to model this system was defining the system in terms of rectangular coordinates, which neglected the effects of curvature in the pipeline. This may not be a valid assumption and will be corrected in the next chapter. Initially, this system was solved in this manner since there was an analytical solution to the equations in rectangular coordinates (Carslaw and Jaeger 1959). This made the analysis easier and provided a convenient starting place before the system was solved in cylindrical coordinates.

6.3 Description of the Below Ice Point Model

Figure 6.2 is included as a representation of the dissociation process when ice was present in the system. Figure 6.2a shows a cross-sectional view of a pipeline with water, ice, and hydrate present. Initially, the pipe was filled with hydrate. As the hydrate dissociated, it shrunk inward, away from the pipe wall. Since the equilibrium hydrate temperature was below the ice point, the water formed from dissociating hydrate was converted to ice. The ice formed a shell around the hydrate. When the ice melted, it formed liquid water. The water made up the outer layer of the system. It was assumed that the hydrate and ice core remained centered in the pipe at all times and the water was
Figure 6.2: Hydrate Dissociation Schematic with Water, Ice and Hydrate Present, Semi-Infinite Case

a) Cross-sectional view of pipeline with all three phases present, heat flow radially into system
b) Representation of the temperature profile in each phase and moving boundary motion
in contact with all of the ice. The water did not drain and accumulate on the bottom of the pipe.

Figure 6.2b is an illustration of the temperature profiles in each of the phases. The water temperature decreased from the wall temperature, \( T_0 \), at the pipe wall, \( x=0 \), to the melting point of ice, \( T_M \), at the water/ice moving boundary, \( x=X_1 \). Similarly, the ice temperature decreased from the melting point of ice, at water/ice moving boundary, \( x=X_1 \) to the to the hydrate temperature, \( T_H \), at the ice/hydrate moving boundary, \( x=X_2 \). The hydrate temperature was assumed uniform throughout.

With the assumptions defined, it was possible to set up the defining differential equations and boundary conditions. For the case when the dissociation temperature was less than 273 K and all three phases, water, hydrate, and ice, were present, the governing differential equations were as follows:

\[
\frac{\partial T_w}{\partial t} = \alpha_w \left[ \frac{\partial^2 T_w}{\partial x^2} \right] \quad 0 < x < X_1 \quad t > 0 \quad (6.1)
\]

\[
\frac{\partial T_i}{\partial t} = \alpha_i \left[ \frac{\partial^2 T_i}{\partial x^2} \right] \quad X_1 < x < X_2 \quad t > 0 \quad (6.2)
\]

The boundary conditions for the system were:

\[
T_w = T_0 \quad x = 0 \quad t > 0 \quad (6.3)
\]

\[
-k_w \frac{\partial T_w}{\partial x} = -k_i \frac{\partial T_i}{\partial x} + (1 - \varepsilon) \rho_i \lambda_i \frac{dX_i}{dt} \quad x = X_i \quad t > 0 \quad (6.4)
\]

\[
T_w = T_i = T_M \quad x = X_1 \quad t > 0 \quad (6.5)
\]
\[-k_i \frac{\partial T_i}{\partial x} = (1 - \varepsilon) \rho_i \lambda_i \frac{dX_i}{dt} \quad x = X_2 \quad t > 0 \quad (6.6)\]

\[T_f = T_D \quad x = X_2 \quad t > 0 \quad (6.7)\]

Boundary conditions (6.3), (6.5) and (6.7) were due to constant temperatures at the pipe wall, the ice-water interface, and the ice-hydrate interface, respectively. At the ice-water boundary, condition (6.4) indicated that heat conduction through the water layer was equal to heat conducted into ice, as well as heat to melt the ice. At the ice-hydrate boundary, condition (6.6) requires the heat conducted through the ice was made to dissociate the hydrate.

The previous set of equations had the following analytical solution (Kelkar et al. 1998):

\[
\frac{T_w - T_0}{T_M - T_0} = \frac{\text{erf} \left( \frac{x}{\sqrt{4\alpha_w t}} \right)}{\text{erf} \left( \xi_1 \right)}
\quad (6.8)
\]

\[
\frac{T_i - T_M}{T_D - T_M} = \frac{\text{erf} \left( \frac{x}{\sqrt{4\alpha_i t}} \right) - \text{erf} \left( \xi_1 \sqrt{\alpha^*} \right)}{\text{erf} \left( \xi_1 \sqrt{\alpha^*} \right)}
\quad (6.9)
\]

\[
\xi_1 = \frac{X_1}{\sqrt{4\alpha_w t}}
\quad (6.10)
\]

\[
\xi_2 = \frac{X_2}{\sqrt{4\alpha_i t}}
\quad (6.11)
\]
The following transcendental equations needed to be solved to find the constants $\xi_1$ and $\xi_2$:

\[
\frac{e^{-\xi_1^2}}{\text{erf}(\xi_1)} = T_D^* \text{erf}(\xi_1^2) - \frac{e^{-\xi_1^2}}{\text{erf}(\xi_1^2)} + \left(1 - e^{\frac{\pi}{\xi_1^2}}\right) \lambda_i^* \lambda_H \xi_1^2
\]  

(6.12)

\[
\frac{e^{-\xi_2^2}}{\text{erf}(\xi_2^2) - \text{erf}(\xi_1^2)} = \left(1 - e^{\frac{\pi}{\xi_1^2}}\right) \lambda_H \xi_2^2
\]  

(6.13)

The dimensionless groups were defined as follows:

\[
\alpha^* = \frac{\alpha_w}{\alpha_i} \quad T_D^* = \frac{k_i}{k_w} \frac{T_M - T_D}{T_0 - T_M} \quad \rho^*_i = \frac{\rho_i}{\rho_w}
\]

\[
\rho^*_H = \frac{\rho_H}{\rho_i} \quad \lambda_i^* = \frac{\lambda_i}{C_{p_i}(T_0 - T_M)} \quad \lambda_H^* = \frac{\lambda_H}{C_{p_H}(T_M - T_D)}
\]

To begin the solution process, equations (6.12) and (6.13) need to be solved for $\xi_1$ and $\xi_2$. These equations can be solved iteratively using a Newton-Raphson technique (Stark 1970). Once these roots are solved, $\xi_2$ can be used to find the time it would take for the ice/hydrate moving boundary, $X_2$, to retreat to a given position, assumed to be the pipe radius, using equation (6.11). Once the ice/hydrate front had receded a distance of the pipe radius, it was equivalent to removing all the hydrate from a pipeline with that given radius. Using the time found to remove the hydrate, the distance the water/ice moving boundary can be found using equation (6.10).

Once the hydrate was removed, then the ice needed to be removed from the system (see Figure 6.3). A similar system of equations could be written for this case.
Figure 6.3: Hydrate Dissociation Schematic with Water and Ice Present, Semi-Infinite Case
1) cross sectional view of pipeline with water and ice present, heat flow radially into system
2) representation of the temperature profile in each phase and moving boundary motion
The governing differential equation, 6.1, would remain the same. Only the differential equation describing the ice temperature and the boundary conditions would be changed.

The new differential equation and boundary conditions were as follows:

\[
\frac{\partial T_l}{\partial t} = \alpha_w \left[ \frac{\partial^2 T_l}{\partial x^2} \right] \quad \text{for} \quad X_1 < x < \infty \quad t > 0 \quad (6.14)
\]

\[T_w = T_0 \quad \text{for} \quad x = 0 \quad t > 0 \quad (6.15)\]

\[-k_w \frac{\partial T_w}{\partial x} = -k_i \frac{\partial T_i}{\partial x} + (1 - \varepsilon) \rho \lambda \frac{dX_1}{dt} \quad \text{for} \quad x = X_1 \quad t > 0 \quad (6.16)\]

\[T_w = T_i = T_M \quad \text{for} \quad x = X_1 \quad t > 0 \quad (6.17)\]

\[T_i = T_D \quad \text{for} \quad x = \infty \quad t > 0 \quad (6.18)\]

The final analytical solution was as follows (Kelkar et al. 1998):

\[
\frac{T_w - T_0}{T_M - T_0} = \frac{\text{erf} \left( \frac{x}{\sqrt{4\alpha_w t}} \right)}{\text{erf} \left( \xi \right)} \quad (6.19)
\]

\[
\frac{T_i - T_D}{T_M - T_D} = \frac{\text{erfc} \left( \frac{x}{\sqrt{4\alpha_i t}} \right)}{\text{erfc} \left( \xi \sqrt{\alpha_i} \right)} \quad (6.20)
\]

\[
\xi = \frac{X_1}{\sqrt{4\alpha_w t}} \quad (6.21)
\]

The following transcendental equation needed to be solved for the constant \(\xi\):
\[
\frac{e^{-\xi}}{\text{erf} (\xi)} = T_d \sqrt{\alpha} \left( \frac{e^{-\xi' \alpha'}}{\text{erf} \left( \frac{\xi'}{\sqrt{\alpha'}} \right)} \right) + (1 - \varepsilon) \sqrt{\pi \rho \lambda' \xi} \tag{6.22}
\]

To begin this solution, equation (6.22) was solved for \( \xi \) using a Newton-Raphson technique (Stark 1970). The value of \( \xi \) was used in equation (6.21) to find the time necessary to remove all the ice in the system.

6.4 Description of the Above Ice Point Model

If the pipeline was depressurized such that the equilibrium temperature of the hydrate was above the ice point, then no ice would be formed in the system upon dissociation. This is shown schematically in Figure 6.4. For this case there was only one differential equation, 6.1. The boundary conditions would change to the following:

\[
T_w = T_0 \quad x = 0 \quad t > 0 \tag{6.23}
\]

\[
-k_w \frac{\partial T_w}{\partial x} = (1 - \varepsilon) \eta \lambda h \frac{dx}{dt} \quad x = X_1 \quad t > 0 \tag{6.24}
\]

\[
T_w = T_D \quad x = X_1 \quad t > 0 \tag{6.25}
\]

The solution for this case was as follows (Kelkar et al. 1998):

\[
\frac{T_w - T_0}{T_D - T_0} = \frac{\text{erf} \left( \frac{x}{\sqrt{4 \alpha_w t}} \right)}{\text{erf} (\xi)} \tag{6.26}
\]
Figure 6.4: Hydrate Dissociation Schematic with Water and Hydrate Present, Semi-Infinite case
a) cross sectional view of pipeline with water and hydrate present, heat flow radially into system
b) representation of the temperature profile in each phase and moving boundary motion
\[ \xi = \frac{X}{\sqrt{4\alpha_w t}} \]  
(6.27)

\[ \frac{e^{-\xi^2}}{\text{erf}(\xi)} = (1 - \varepsilon)\sqrt{\pi} \rho^* \lambda^* \xi \]  
(6.28)

The dimensionless groups were defined as follows:

\[ \rho^* = \frac{\rho_u}{\rho_w}, \quad \lambda^* = \frac{\lambda_u}{C_{pu} (T_o - T_D)} \]

The same solution strategy could be used in this case as with the below ice point model. Equation (6.28) was solved for \( \xi \) using a Newton-Raphson technique. The value of \( \xi \) is then used in equation (6.27) to find the dissociation time.

### 6.5 Results of Rectilinear Models

The goal of this work was to find an optimal depressurization condition. When these equations were solved for dissociation times, in the rectilinear coordinates, an optimal dissociation pressure was found. This optimal pressure occurs at about 2.5 MPa, which corresponds to an equilibrium temperature at the ice point. Figure 6.5 shows the results from this model.
Figure 6.5: Rectilinear Model Predictions
CHAPTER 7

MODELING HYDRATE DISSOCIATION

7.1 Introduction

The last chapter defined the basic tenets of the mathematical model developed to simulate hydrate dissociation in a pipeline. The model made the assumption of rectilinear coordinates, perceived to be the weakest of its assumptions. This new model removed this assumption and solved the system in cylindrical coordinates.

However, when the system of equations was written in cylindrical coordinates, there was no longer an analytical solution, and the system of equations had to be solved numerically. This chapter redefines all the equations in terms of cylindrical coordinates, sets up the numerical algorithm needed to solve the equations, and then presents the results of these simulations.

7.2 Hydrate Dissociation Model-Below the Ice Point

Consider the dissociation of a hydrate plug in a cylindrical region $r_0 \geq r \geq 0$ initially at a uniform temperature, which is above the hydrate formation temperature at a given pressure. Dissociation begins when the pressure is decreased so that the hydrate temperature is now below the equilibrium temperature. When the pressure is decreased,
the temperature of the hydrate is also decreased. If the hydrate equilibrium temperature is below the ice point, ice will form around the hydrate as it dissociates. When the hydrate is above the ice point, ice will not form in the system and only water and hydrate will be present. The case with only water and hydrate present is the simpler of the two cases and will be discussed after the case when all three phases are present.

After depressurization of the pipeline, the hydrate temperature, $T_D$, is less than the pipe wall temperature, $T_0$. Heat begins to flow radially into the system and dissociate the hydrate. As the hydrate dissociates, it retreats from the pipe wall and shrinks inward (Figure 7.1). Since the hydrate temperature is below the ice point, an ice shell is formed around the hydrate. As the ice melts, it is surrounded by a water layer. The ice/hydrate moving boundary, $r_{F2}$, is assumed to be at a constant temperature, $T_D$. The water/ice moving boundary, $r_{F1}$, is also assumed to be at a constant temperature, $T_M$.

The appropriate differential equations are determined from Fourier’s law of heat conduction and written in cylindrical coordinates:

$$\frac{\partial T_w}{\partial t} = \alpha_w \left[ \frac{1}{r} \frac{\partial T_w}{\partial r} + \frac{\partial^2 T_w}{\partial r^2} \right] \quad r_{F1} < r < r_0 \quad t > 0 \quad (7.1)$$

$$\frac{\partial T_i}{\partial t} = \alpha_i \left[ \frac{1}{r} \frac{\partial T_i}{\partial r} + \frac{\partial^2 T_i}{\partial r^2} \right] \quad r_{F2} < r < r_{F1} \quad t > 0 \quad (7.2)$$

The associated boundary conditions are given by:

$$T_w = T_o \quad r = r_0 \quad t > 0 \quad (7.3)$$
Figure 7.1: Hydrate Dissociation Schematic with Water, Ice and Hydrate Present, Cylindrical Case

a) cross sectional view of pipeline with all three phases present, heat flow radially into system

b) representation of the temperature profile in each phase and moving boundary motion
\[-k_w \frac{\partial T_w}{\partial r} = -k_l \frac{\partial T_l}{\partial r} + (1 - \epsilon) \rho_l \lambda_l \frac{dr_{f1}}{dt} \quad r = r_{f1}, \quad t > 0 \quad (7.4)\]

\[T_w = T_i = T_M \quad r = r_{f1}, \quad t > 0 \quad (7.5)\]

\[-k_l \frac{\partial T_l}{\partial r} = (1 - \epsilon) \rho_H \lambda_H \frac{dr_{f2}}{dt} \quad r = r_{f2}, \quad t > 0 \quad (7.6)\]

\[T_i = T_D \quad r = r_{f2}, \quad t > 0 \quad (7.7)\]

This problem is cast into a more convenient form by defining the following dimensionless variables:

\[R = 1 - \frac{r}{r_0} \quad (7.8)\]

\[R_{f1} = 1 - \frac{r_{f1}}{r_0} \quad (7.9)\]

\[R_{f2} = 1 - \frac{r_{f2}}{r_0} \quad (7.10)\]

\[\tau = \frac{\alpha_w l}{r_0^2} \quad (7.11)\]

\[U = \frac{T_w - T_M}{T_0 - T_M} \quad (7.12)\]

\[V = \frac{T_i - T_M}{T_M - T_D} \quad (7.13)\]

\[\alpha^* = \frac{\alpha_w}{\alpha_i} \quad (7.14)\]
\[ T_D^* = \frac{k_I T_M - T_D}{k_w T_0 - T_M} \]  
(7.15)

\[ \rho_I^* = \frac{\rho_I}{\rho_w} \]  
(7.16)

\[ \rho_H^* = \frac{\rho_H}{\rho_I} \]  
(7.17)

\[ \lambda_I = \frac{\lambda_I}{C_{P,I}(T_0 - T_M)} \]  
(7.18)

\[ \lambda_H = \frac{\lambda_H}{C_{P,H}(T_M - T_D)} \]  
(7.19)

Equations (7.1)-(7.7) expressed in terms of the dimensionless variables are given by:

\[ \frac{\partial U}{\partial \tau} = \frac{\partial^2 U}{\partial R^2} + \frac{1}{R - 1} \frac{\partial U}{\partial R} \quad 0 < R < R_{F1} \quad \tau > 0 \]  
(7.20)

\[ \frac{\partial V}{\partial \tau} = \frac{1}{\alpha} \left( \frac{\partial^2 V}{\partial R^2} + \frac{1}{R - 1} \frac{\partial V}{\partial R} \right) \quad R_{F1} < R < R_{F2} \quad \tau > 0 \]  
(7.21)

\[ U = 1 \quad R = 0 \quad \tau > 0 \]  
(7.22)

\[ \frac{\partial U}{\partial R} = T_D^* \frac{\partial V}{\partial R} \quad (1 - \varepsilon) \rho_I^* \lambda_I^* \frac{dR_{F1}}{d\tau} \quad R = R_{F1} \quad \tau > 0 \]  
(7.23)

\[ U = V = 0 \quad R = R_{F1} \quad \tau > 0 \]  
(7.24)

\[ \frac{\partial V}{\partial R} = -(1 - \varepsilon) \chi^* \rho_H^* \lambda_H^* \frac{dR_{F2}}{d\tau} \quad R = R_{F2} \quad \tau > 0 \]  
(7.25)

\[ V = -1 \quad R = R_{F2} \quad \tau > 0 \]  
(7.26)
7.3 Finite Difference Formulation

7.3.1 Finite Difference Grid
To obtain a solution to this parabolic system of differential Equations, (7.20)-(7.21), a typical finite-difference grid was constructed. The grid had spatial increments of equal size in the R-direction and time steps of equal size in the \( \tau \)-direction (Figure 7.2). The nomenclature used with the finite difference grid was such that \( U_{i,j} \) and \( V_{i+1,j} \) denoted the values of the water and ice temperatures at the grid points \( i\Delta R, \tau_0 + j\Delta \tau \) and \( (i+1)\Delta R, \tau_0 + j\Delta \tau \), respectively. The subscript \( i \) referred to position and the subscript \( j \) referred to time. The grid was set up such that \( R=0 \) corresponded to \( i=1 \) and \( \tau=\tau_0 \) corresponded to \( j=1 \). Note that the time did not begin at zero since the numerical solution required an initial solution to start the computations. A value \( \tau_0 \) for was obtained from the analytical solution presented in the previous chapter.

7.3.2 Temperature Distributions
The standard explicit scheme (hereafter referred to as the SE scheme) can be used to calculate the temperature at each grid point. The SE scheme requires values from only one previous time level, as illustrated in Figure 7.3. Equations (7.20) and (7.21) expressed in the SE scheme are given by

\[
\frac{U_{i,j+1} - U_{i,j}}{\Delta \tau} = \frac{U_{i+1,j} - 2U_{i,j} + U_{i-1,j}}{\Delta R^2} + \frac{1}{(i\Delta R-1)^2} \frac{U_{i+1,j} - U_{i-1,j}}{2\Delta R}
\]

\( i=2,3,\ldots,\text{mb}\) point-1

(7.27)
Figure 7.2: Finite Difference Grid
Figure 7.3: Graphical Depiction of the Standard Explicit Finite-Difference Scheme
\[
\frac{V_{i,j+1} - V_{i,j}}{\Delta \tau} = \frac{1}{\alpha^*} \left\{ \frac{V_{i+1,j} - 2V_{i,j} + V_{i-1,j}}{\Delta R^2} + \frac{1}{(i\Delta R - 1)} \frac{V_{i+1,j} - V_{i-1,j}}{2\Delta R} \right\}
\]

\[i = \text{mb1point+2,mb1point+3,\ldots,mb2point-1} \quad (7.28)\]

where mb1point indicates the nearest grid point to the left of the water/ice interface and mb2point indicates the nearest grid point to the left of the ice/hydrate interface.

Equations (7.27) and (7.28) can be rearranged and solved for the unknown dimensionless temperatures, \(U_{i,j+1}\) and \(V_{i,j+1}\), at the new time level to give

\[
U_{i,j+1} = U_{i,j} (1 - 2\lambda) + \lambda \left[ U_{i+1,j} \left( 1 + \frac{\Delta R}{2(R-1)} \right) + U_{i-1,j} \left( 1 - \frac{\Delta R}{2(R-1)} \right) \right] \quad (7.29)
\]

\[
V_{i,j+1} = V_{i,j} (1 - 2\lambda) + \frac{\lambda}{\alpha^*} \left[ V_{i+1,j} \left( 1 + \frac{\Delta R}{2(R-1)} \right) + V_{i-1,j} \left( 1 - \frac{\Delta R}{2(R-1)} \right) \right] \quad (7.30)
\]

where \(\lambda = \Delta \tau/(\Delta R)^2\).

The SE scheme was convergent as \(\Delta R\) and \(\Delta \tau \to 0\) and was stable for \(\lambda < 0.5\), for Equation (7.29), and \(\lambda/\alpha^* < 0.5\), for Equation (7.30). In the computer program used to solve this set of equations, the value of \(\Delta R\) was set to a value of 0.01. This meant that the value for \(\Delta \tau\) was fixed based on the above stability criterion. When \(\Delta R\) was set to a value smaller than 0.01, the corresponding value for \(\Delta \tau\) was very small and the resulting computations took a prohibitive amount of time. Also when a small value of \(\Delta R\) or \(\Delta \tau\) was used, the total number of computations in the program became large and the resulting roundoff error began to become a factor in the final result.
7.3.3 Moving Boundaries

The movement of the moving boundaries is also calculated using a finite difference scheme. Written in finite difference form, Equation (7.23) and (7.25) are as follows:

\[
R_{F_1}|_{r+\Delta r} = R_{F_1}|_r + \Delta r \frac{T_D}{(1-\epsilon)\rho_i \lambda_i} \left( \frac{\partial V}{\partial R} \bigg|_{R=\frac{R_1}{R}} - \frac{\partial U}{\partial R} \bigg|_{R=\frac{R_1}{R}} \right) \tag{7.31}
\]

\[
R_{F_2}|_{r+\Delta r} = R_{F_2}|_r - \Delta r \frac{\partial V}{\partial R} \bigg|_{R=\frac{R_1}{R}} \tag{7.32}
\]

Discussion of the determination of these temperature gradients, \( \partial U/\partial R \) and \( \partial V/\partial R \), will follow shortly.

7.3.4 Computations at End of Hydrate Dissociation

Once the ice/hydrate moving boundary had reached the last grid line (i.e. the center of the pipe), there was no longer any hydrate present in the system, only water and ice. The differential equations governing the water and ice temperatures remained the same as do all the boundary conditions except Equations (7.25) and (7.26), which were replaced by the following

\[
\frac{\partial V}{\partial R} = 0 \quad R = 1 \quad \tau > 0 \tag{7.33}
\]
An alternate means was needed in finding the temperature of the ice at the last grid line because Equation (7.30) was undefined at R=1. This difficulty was overcome by using l'Hopital's rule with Equation (7.30) and taking the limit as $R \to 1$ to obtain the following

$$\frac{\partial V}{\partial \tau} = \frac{2}{\alpha^2} \frac{\partial^2 V}{\partial R^2}$$

(7.34)

This equation written in SE form is given by

$$\frac{V_{i+1,j} - V_{i,j}}{\Delta \tau} = \frac{2}{\alpha^*} \frac{\left(V_{i+1,j} - 2V_{i,j} + V_{i-1,j}\right)}{(\Delta R)^2}$$

(7.35)

Equation (7.34) written in SE form is

$$\frac{V_{\text{point } s+1,j} - V_{\text{point } s-1,j}}{2\Delta R} = 0$$

(7.36)

In order to solve for the temperature at center of the pipeline, one needs to combine Equation (7.35) with (7.36) to obtain the following

$$V_{\text{point } s+1,j} = \left(1 - \frac{4\lambda}{\alpha^*}\right)V_{\text{point } s,j} + \frac{4\lambda}{\alpha^*}V_{\text{point } s+1,j}$$

(7.37)

7.3.5 Lagrangian Interpolation Scheme

The values of the unknown temperatures adjacent to the moving boundaries, (Figure 7.4), were calculated using a three-point Lagrangian interpolation except in the cases where noted. Figure 7.4 only shows the case for the water/ice moving boundary, but the approach was readily applicable to the ice/hydrate moving boundary as well. The general three point Lagrangian scheme was represented as a system of three equations
Figure 7.4: Three-point Lagrangian Interpolation for the Unknown Temperatures $U_{mb1point}$ and $V_{mb1point+1}$ Adjacent to the Water/Ice Moving Boundary
and three unknowns, a, b, and c. For this situation, the x's corresponded to a dimensionless distance, R, and y’s corresponded to a dimensionless temperature, either U or V.

\[
\begin{align*}
ax_1^2 + bx_1 + c &= y_1 \\
ax_2^2 + bx_2 + c &= y_2 \\
ax_3^2 + bx_3 + c &= y_3
\end{align*}
\] (7.38)

Solving for a, b, and c, the following equations were obtained

\[
a = \frac{y_1 - y_3 + y_3 - y_2}{x_1 - x_3} \times \frac{x_2 - x_3}{x_1 - x_2}
\] (7.39)

\[
b = \frac{y_3(x_2^2 - x_1^2) + y_2(x_1 - x_3)(x_1 + x_3) + y_1(x_3^2 - x_2^2)}{x_1 - x_2}(x_1 - x_3)(x_2 - x_3)
\] (7.40)

\[
c = \frac{y_2x_1x_3(x_1 - x_2) + x_3[y_1x_2(x_2 - x_3) + y_2x_1(x_3 - x_1)]}{x_1 - x_2}(x_1 - x_3)(x_2 - x_3)}
\] (7.41)

This interpolation scheme was very versatile. Once three temperatures and their corresponding distances were known, a, b, and c could be solved using Equation (7.39), (7.40), and (7.41). With values for a, b, and c, they could be used to solve for an unknown temperature at any given location, between \(x_1\) and \(x_3\), by solving for \(y_1\) in Equation (7.38).

This Lagrangian method had an additional benefit, besides the ability to find temperatures. This method could also be used to find temperature gradients. Once a and
b are known, they can be used to calculate a temperature gradient at a given location, between \( x_1 \) and \( x_3 \), using the equation:

\[
\frac{dy}{dx} = 2ax + b
\]  

(7.42)

There were situations where the above formulas could not be used to find a particular temperature or temperature gradient. When the water/ice interface was within the first grid space (Figure 7.5) a linear interpolation scheme was necessary to find this temperature gradient.

\[
\left. \frac{\partial U}{\partial R} \right|_{R_{s1}} = \frac{U_0 - U_{R_{s1}}}{0 - mb1}
\]  

(7.43)

\( U_0 \) is the dimensionless temperature at the pipe wall \( (R=0) \) and is given by Equation (7.22). \( U_{R_{s1}} \) is the dimensionless temperature at the water/ice moving boundary \( (R=R_{s1}) \) and is given by Equation (7.24). And \( mb1 \) is the dimensionless location of the water/ice moving boundary.

### 7.3.6 Temperature and Temperature Gradient Calculations using Linear Scheme

When the water/ice moving boundary was within the second grid space (Figure 7.6) then an alternate method is needed to find the temperature.

\[
U_2 = \frac{U_0 - U_{R_{s2}}}{0 - mb1} \Delta R + U_0
\]  

(7.44)

Once \( U_2 \) was known the temperature gradient could be found using Equation (7.42), provided that \( a \) and \( b \) had been determined first.
Figure 7.5: Graphical Depiction when Water/Ice Moving Boundary Is within the First Grid Space
- Known Temperature
- Temperature Calculated Using Equation 7.44

Figure 7.6 Graphical Depiction When the Water/Ice Moving Boundary Is within the Second Grid Space
Similar situations arose when finding \( V \) and \( \partial V/\partial R \). When the difference between the two moving boundaries was one grid space (Figure 7.7), the temperature, \( V \), cannot be solved using the SE scheme and must be found using the equation

\[
V_{mb2,point} = \frac{V_{RF1} - V_{RF2}}{mb1 - mb2} \left[ (mb2 \text{ point} - 1) \Delta R - mb1 \right] + V_{RF1}
\]  

(7.45)

The following equation could be used for the gradient at \( R=RF1 \)

\[
\frac{\partial V}{\partial R}_{RF1} = \frac{V_{RF1} - V_{RF2}}{mb1 - mb2}
\]  

(7.46)

Where \( V_{RF1} \) was the dimensionless ice temperature at the water/ice moving boundary and \( V_{RF2} \) was the dimensionless ice temperature at the ice/hydrate moving boundary. Similarly, the dimensionless temperature gradient at the ice/hydrate moving boundary was given by

\[
\frac{\partial V}{\partial R}_{RF2} = \frac{V_{RF1} - V_{RF2}}{mb1 - mb2}
\]  

(7.47)

When there were two grid spaces between the two moving boundaries (Figure 7.8), neither of the temperatures could be found using the SE method and again a linear equation was required. The temperature \( V_{mb2,point} \) could be found with Equation (7.45) and the temperature \( V_{mb2,point-1} \) could be found using

\[
V_{mb2,point-1} = \frac{V_{RF1} - V_{RF2}}{mb1 - mb2} \left[ (mb2 \text{ point} - 2) \Delta R - mb1 \right] + V_{RF1}
\]  

(7.48)

When the difference between the two moving boundaries goes from two to three, (Figure 7.9) none of the temperatures can be solved using the SE method and all must be
Figure 7.7: Graphical Depiction When There Is Only One Grid Line between the Two Moving Boundaries
- Known Temperature
- Temperatures Calculated Using Equations (7.45) and (7.48)

Figure 7.8: Graphical Depiction When There Are Two Grid Lines between the Moving Boundaries
Figure 7.9 Graphical Depiction When the Difference between the Two Moving Boundaries Changes From Two to Three
found using a linear interpolation scheme. This result caused many problems in the numerical solution, so the initial value of mb2 was set so that this situation arose very rarely. In the cases when this situation arose a linear interpolation between the two moving boundaries was needed to find all three temperatures. Equation (7.45) and (7.48) could be used to find two of the temperatures, but the third, \( V_{mb2point-2} \) required an equation similar to (7.48) except (mb2point-2) was replaced by (mb2point-3).

When the water/ice moving boundary moved to second to last grid spacing, (Figure 7.10), a linear interpolation scheme must be used to find the dimensionless temperature and temperature gradient

\[
V_{npoint, t-1} = \frac{V_{R_{t1}} - V_N}{mb1 - 1} \left[ (npoint - 2)\Delta R - mb1 \right] + V_{R_{t1}} \tag{7.49}
\]

\[
\frac{\partial V}{\partial R}_{R_{t1}} = \frac{V_{R_{t1}} - V_N}{mb1 - 1} \tag{7.50}
\]

Where \( V_N \) is the temperature at the center of the pipeline (R=1).

When the water/ice moving boundary moves into the last grid space, the ice temperature, \( V_N \), is set equal to zero, as per boundary condition (7.24). The temperature gradient is still found using Equation (7.50).

7.3.7 Calculation of Final Dissociation Times

A three-point Lagrangian interpolation formula was used to extrapolate the time when a moving boundary would just reach the final grid line. This approach was
Figure 7.10: Graphical Depiction of the Time Step Just after the Water/Ice Moving Boundary Reached the Second to Last Grid Space
applicable to both moving boundaries and was used to find the time necessary to
dissociate the hydrate and melt the ice.

\[
\tau_F = \frac{(1 - R_{F2})(1 - R_{F3})}{(R_{F1} - R_{F2})(R_{F1} - R_{F3})}\tau_1 + \frac{(1 - R_{F1})(1 - R_{F2})}{(R_{F2} - R_{F1})(R_{F2} - R_{F3})}\tau_2 + \frac{(1 - R_{F1})(1 - R_{F2})}{(R_{F3} - R_{F1})(R_{F3} - R_{F2})}\tau_3
\]

(7.51)

where \( R_{F1}, R_{F2}, R_{F3} \), were the last three computed values of the moving boundary position
just before the moving boundary reached the last grid line. The values of \( \tau_1, \tau_2, \tau_3 \) were
the dimensionless times corresponding to the above values of the moving boundary
positions.

### 7.4 Computational Algorithm

A Digital Visual FORTRAN computer program was produced which implements
the finite-difference scheme described previously. All calculations were performed in
double precision arithmetic. The computer program is included on disk. The program
consists of several subroutines, which allows for a versatile program that may be altered
relatively easily to modify the program as necessary. For instance, the finite-difference
scheme could be changed to model the semi-infinite solution and this was done to verify
the validity of the model (Figure 7.11). It can be seen in this graph that the numerical
solution does quite well to fit the exact analytical solution. Note that this graph only
shows the results for the above 273 K case.
Figure 7.11: Comparison of Analytical Solution with Numerical Solution in Rectangular Coordinates-Above Ice Point

For the below ice point model, the program and the analytical solution give very close to the same hydrate dissociation times (Figure 7.12). However, considerable modification would be needed on the below ice point program to simulate the semi-infinite media and reproduce the ice melting results. A problem arose in the determination of the water/ice boundary once the hydrate was gone. At this time, the ice phase extended to infinity in the semi-infinite model, but the program was only able to simulate a finite media. The computer program was unable to match the analytical
solution for the water/ice boundary (Figure 7.12). It should also be noted that the two solution methods indicate different trends.

![Graph showing comparison of analytical and numerical solutions](image)

**Figure 7.12: Comparison of Analytical Solution with Numerical Solution in Rectangular Coordinates-Below Ice Point**

### 7.4.1 Starting Solution

To initiate the program, the moving boundaries must be at some finite value, they cannot start at R=0 and τ=0, and some initial temperature profile in all phases must be specified. The analytical solution, presented as Equations (6.8)-(6.13), provided a convenient starting solution. The analytical solution to the semi-infinite case introduces
very little error into the final solution in cylindrical coordinates if the initial position of
the moving boundary has not progressed too far into the spatial domain.

The value of the ice/hydrate moving boundary, $R_{F2}$, was set such that it was
located between the 9th and 10th grid lines. This grid space was chosen because of the
problem discussed earlier about when the distance between the two moving boundaries is
less four. With this as a starting value for mb2, these problems arose only for extreme
conditions. Once this value of $R_{F2}$ was set, the position of the water/ice boundary could
be calculated from the analytical solution (Equation 6.10), as well as, the time when the
numerical solution would begin, $\tau_0$. The temperature distribution was calculated at this
initial time for both the water and ice phase using the analytical result, Equations (6.8)
and (6.9). This grid spacing, $\Delta R$, was taken to be 0.01, which meant there were 101
temperature grid points at each time level.

The computer program carried out these steps as follows. The computer prompts
the user for the hydrate temperature, the porosity of the hydrate, and the temperature of
the pipe wall (or ambient temperature). For all subsequent discussions, it was assumed
that the wall temperature was 277 K. Once these values were entered, the computer
could begin all calculations.

The first step was to find the roots of the transcendental Equations (6.12) and
(6.13). The determination of these roots was very dependent upon the initial guesses and
the computer provided much error checking so that it always converged to the correct
values of the roots. The value of $R_{F2}$ was set in the program and with the values of the
roots, both \( R_{F_1} \) and \( \tau_0 \) were calculated. The initial temperature profile of all phases was determined from the analytical solution, Equations (6.8) and (6.9). The temperatures were calculated at all grid points for the \( j=1 \) (\( \tau=\tau_0 \)) time level (Figure 7.13). The number of grid points that represent the water phase depend on the input values and the resulting roots of the transcendental equation.

The movement of the ice/hydrate moving boundaries was calculated from Equation (7.32) and the water/ice moving boundary from Equation (7.31). The new temperature profile in the water phase was calculated using Equation (7.29) and the ice temperatures were found with Equation (7.30). The temperature gradients within each phase could now be calculated. The value of \( \partial U/\partial R \) at \( R=R_{F_1} \) and the value of \( \partial V/\partial R \) at \( R=R_{F_1} \) and \( R=R_{F_2} \). With these temperature gradients, a new value of \( R_{F_1} \) and \( R_{F_2} \) could be calculated.

The computational process continued, in this fashion, until the ice/hydrate moving boundary reached the center of the pipe. At this time, there was a slight modification in the calculation of the ice temperature but this will be discussed later.

### 7.4.2 Time Step \( \Delta \tau \)

The size of the time step \( \Delta \tau \) is bounded by the fact that the ratio \( \lambda = \Delta \tau/\Delta R^2/\alpha^* \) must be less than 0.5. The value of \( \Delta R \) was already set at 0.01. The value of lambda can be arbitrarily chosen provided it is less than 0.5. For the calculations done in this
Figure 7.13: Graphical Depiction of the Computation at $\tau = \tau_0$
program, lambda was chosen to be 0.4. This value provided a good balance between numerical accuracy and computational time. Many runs were tried with varying values of \( \lambda \) and the results were different by no more than 1%.

7.4.3 Computations at the Time Level \( \tau_0 + \Delta \tau \)

The value of \( \Delta R_{F1} \) and \( \Delta R_{F2} \) were both known at the initial time level, \( \tau_0 \) (Figure 7.14). Both moving boundaries can be incremented by this amount. The calculations of the temperatures of the water and ice phase can now proceed at the \( \tau_0 + \Delta \tau \) time level. The temperatures that could be calculated using the finite difference scheme, were solved. This included all points except those at the gridlines adjacent to the two moving boundaries. For instance, in the water phase the temperature at some arbitrary grid point is \( U_{ij} \) and this value can be calculated provided the temperatures \( U_{i-1,j-1}, U_{i,j-1}, \) and \( U_{i+1,j-1} \) are all known. Situations in which the temperatures cannot be calculated using the finite difference method will be discussed in subsequent sections.

7.4.4 Water-Ice Interface Moves into the Second Grid Spacing

The case when the water/ice moving boundary starts in the first grid spacing was rare, but it did occur, particularly when the hydrate temperature was low, less than 266 K. Since the ice-hydrate moving boundary was fixed, the water/ice moving boundary was dependent upon the roots of the transcendental equation solved for in the semi-infinite solution. When the water-ice moving boundary was within the first grid spacing, the only
Figure 7.14: Graphical Depiction of the Computation at $\tau = \tau_0 + \Delta \tau$
two available grid points to determine the water temperature gradient were at \( R=0 \) and at the moving boundary. Now the simple Equation (7.43) was used to determine this gradient.

When the water-ice moving front crossed into the second grid spacing there were now three grid points available to determine the water phase temperature gradient and the Lagrangian interpolation formula, Equation (7.42) could be used. First the temperature at \( i=2 \) needed to be determined using Equation (7.44). This equation could now be used to calculate the temperature for all subsequent temperature gradient calculations in the water phase.

### 7.4.5 Calculation of the Ice Phase Temperature Gradient

The determination of the ice-phase temperature gradient was rather straightforward except for certain conditions. Problems arose when the water/ice moving boundary was located less than three grid spaces away. When this occurred, there were not enough grid points to use the Lagrangian method and an alternate means was necessary to calculate this temperature gradient. This problem only arose in the first few time steps. After that time, the difference between the two moving boundaries increased because the ice/hydrate moving front always moved faster than the water/ice moving front. There was also a problem when the water/ice moving front moved into the last grid space. When this occurred, there was not enough known ice temperatures to use the Lagrangian method and Equation (7.50) was needed to find the temperature gradient.
7.4.6 When a Moving Boundary Crosses a Grid Line

An additional problem occurred during the first time step after a moving boundary crossed a gridline (Figure 7.15). The two gridlines to the left of the moving boundary could not be calculated using the SE method. Both of these points needed to be found using the Lagrangian interpolation method, provided that there were enough known values of the temperatures before the moving front. The only time this became an issue was when the moving boundary moved from the second grid space to the third. Neither \( U_2 \) nor \( U_3 \) can be found using the SE method or the Lagrangian interpolation method so a linear interpolation scheme was used to find both temperatures. The point after a moving boundary could still be calculated using the SE scheme. This analysis is valid for both of the moving boundaries.

7.4.7 When a Moving Boundary Crosses the Last Grid Line

There were two important events marked by the moving boundaries crossing the final grid line. When the ice/hydrate moving boundary crosses the last grid line, it was the time it took to remove the hydrates from the pipeline. It also marked a change in the solution scheme. Two of the boundary conditions were replaced and the ice temperature, \( V_N \), was calculated differently for the remainder of the simulation using Equation 7.37.
Figure 7.15: Graphical Depiction of When the Water/Ice Moving Boundary Crosses a Grid Line
The other important event occurred when the water/ice moving boundary crosses the final gridline. This marked the total amount of time it took to remove all the solids, hydrate and ice from the system. In both cases, the final time was found using the three-point Lagrangian formula, Equation 7.51.

7.5 Hydrate Dissociation Model Above the Ice Point

The analysis for the case of hydrate dissociation above the ice point was similar to the below ice point case. The governing equations still applied, however, no ice phase was present. There was only water and hydrate present in the system. This case was much easier to model. The water temperature was still determined using Equation (7.20).

The boundary conditions changed slightly to become the following:

\[
U = 1 \quad R = 0 \quad (7.52)
\]

\[
\frac{\partial U}{\partial R} = -(1 - \epsilon) \rho^* \lambda^* \frac{dR_{fi}}{dt} \quad R = R_{fi} \quad (7.53)
\]

\[
U = 0 \quad R = R_{fi} \quad (7.54)
\]

where the dimensionless variables are defined as:

\[
\rho^* = \frac{\rho_H}{\rho_w} \quad (7.55)
\]

\[
\lambda^* = \frac{\lambda_H}{C_H \left( T_0 - T_D \right)} \quad (7.56)
\]
The computational algorithm remained virtually the same. Now there was only one moving boundary to keep track of and only one temperature profile. All situations that arise during this solution were discussed in the case where all three phases were present. The code to the computer program is included on disk. The thesis by Roberts (1982) presented the solution to water freezing in a pipeline. This analysis was very similar to the dissociation of hydrate without ice. The solution strategy and coding for this case was modified from the work done by Roberts (1982).

7.6 Results of the Computer Models

This section will present some of the most important results from the two models, the below ice point and the above ice point models. Qualitatively, the models behave as expected. The dissociation time approaches infinity as the difference between the hydrate temperature and the ambient temperature approach zero (Figure 7.16). This is expected since the dissociation of hydrate requires the input of heat to the system and if the temperatures are the same, there will be no driving force for heat input to the system. The second thing expected from the two models is that the solutions should match at the ice point, which they do (Figure 7.16).

All modeling results were generated using a pipe wall temperature of 277 K, the deep ocean ambient temperature. The results for different temperatures were qualitatively the same as the following results, only the absolute magnitude of the numbers changed.
Figure 7.16: Comparison of Times to Remove Hydrate and Ice from Pipeline for Different Values of Porosity
The results of this model (see Figure 7.16) do not indicate any minimum in
dissociation time as the model in rectangular coordinates did. The time in Figure 7.16
refers to the time necessary to remove all solids, both hydrates and ice from the system.
This will be the important time since ice can create the same type of blockage problems
as a hydrate plug. This model indicates that as the temperature is decreased, the
dissociation time also decreases, and never reaches any minimum value. The dissociation
time does stop dropping noticeably at about 260 K. This trend was also observed in the
experiments. The model comparison to the experimental data will be presented in the
next chapter.

It should be noted on Figure 7.16 that there is a dashed line just below the ice
point. The below ice point model has a discontinuity at the ice point and the solution
diverges. The dashed lines are interpolations between the below ice point model at 271 K
and the above ice point model at 0.1 K above the ice point. This feature is common to all
plots that include results from both models. The results of the below ice point model are
acceptable for dissociation temperatures below 272 K. Dissociation temperatures
between 272 K and 273 K require an interpolation between the two models.

The model also predicts that dissociation time is a strong function of porosity.
The dissociation time increases dramatically from a porosity of 0.8 to 0.5. There is a
56% decrease in dissociation time between these porosities. By comparison, the time
only decreased by 37% going from 0.2 to 0.5 porosity.
Figure 7.17 shows the difference in times to remove only the hydrate plug and the
time necessary to remove all the solids, hydrate and ice, in the pipeline. It is expected
that the two solutions should meet at the ice point. This is not shown in this graph since
there is a discontinuity at the ice point and both solutions diverge to infinity at this point.
On this graph, it is evident that the hydrate dissociation line begins to curve upward to
meet the total solid removed line, before they both diverge.

The model predicts that the structure II hydrate will take longer to dissociate than
the structure I hydrate (Figure 7.18). The above ice point model predicts that the
structure II hydrate will take approximately 18% longer to dissociate than the structure I
hydrate. The difference between the structure II and the structure I hydrate in the below
ice point model varies depending on the dissociation temperature. The below ice point
model predicts structure II will take about 10% longer at 270 K and then the percent
difference decreases to about 1% at 255 K.

These are the important results from the FORTRAN model. The model is also
able to track the movement of the water/hydrate and water/ice or water/hydrate moving
interfaces as a function of dissociation time. This model predicts that the interfaces move
as approximately the square root of time. This further implies that dissociation time will
be proportional to the radius squared. The results by themselves are not interesting.
These plots will be more interesting and meaningful when compared with data in the next
chapter.
Figure 7.17: Comparison of Times to Remove Hydrate or Ice
Figure 7.18: Comparison of Times to Remove Both Hydrate and Ice from Pipeline for Different Hydrate Structures
CHAPTER 8
COMPARISON OF MODEL WITH DATA

8.1 Comparison with Data from this Work

The true test to any model prediction is how well it fits experimental data. Figure 8.1 is a plot with all dissociation data taken during this research. The data were plotted as the natural log of the time, in hours, to dissociate only the hydrate versus the dimensionless temperature $T_D^*$. This dimensionless temperature was used because it was the most convenient way to account for different bath temperatures and dissociation temperatures. These two temperatures were not constant in all experiments. The values for the dissociation temperature were taken to be an average of the first hour of dissociation.

The model predictions in Figure 8.1 are for a structure I hydrate. The model predictions are for values of porosity of 0.2 and 0.6. These values were chosen because they were within the range of experimental porosities. The porosity in all experiments varied between 0.3 and 0.5. It is important to note that Figure 8.1 is for an ambient or pipe wall temperature of 277 K. It is expected that the experiments at different ambient temperatures should not fit the model as well.
$T_D^* = k_i(T_M - T_D)/k_B(T_0 - T_B)$

**Figure 8.1: Fit of Model to Experimental Data**
A positive value of $T_D^*$ indicates a dissociation temperature below the ice point and a negative value is above the ice point. There was a very limited range of temperatures below the ice point due the buffering effect of ice described earlier. The dissociation temperature below the ice point in all experiments was on average about 272 K. This made comparison with the model difficult below the ice point.

All of the below ice point data were clustered in a small group. The model fit this cluster very well. Almost all of the data points lie within the values the model predicts. There were only a few data points that the model did not fit. The data points that do not fit the model are either at a bath temperature different than 277 K or they are for a gas mixture other than methane.

The model predicted the one experiment that did achieve a lower dissociation temperature rather well. However, this is a difficult experiment to compare to the model, since it was anomalous and the only experiment to achieve these low temperatures.

Above the ice point, the model seems to underpredict the dissociation times. However, it is important to note that the model does predict the correct trend as shown by the data.

The data taken with the pseudo-Qatar gas mixture are also included on Figure 8.1. As mentioned in the previous chapter, the model predicts that the structure II hydrate should take slightly longer to dissociate than the structure I. However, in all experiments, the structure II hydrates took less time to dissociate than the structure I hydrate. There may be phenomena with the structure II hydrate that are not accounted for in the model.
In previous work by Kim (1985) and Jamaluddin et al. (1989) suggest that kinetics play a role in the dissociation of hydrate. They were able to relate the fugacity of the methane in the gas phase to the hydrate phase. The difference in fugacities for the structure II hydrate would be greater than the structure I hydrate because the equilibrium condition for the Qatar gas mixture is at higher temperatures for a given pressure. This would mean that the structure II hydrate would be less stable at lower temperatures. Thus the Qatar gas hydrate, limited by kinetics, would be expected to dissociate faster. This model only considered heat transfer effect. The incorporation of kinetics into hydrate dissociation is reserved for future modeling efforts.

Figure 8.2 shows the dissociation curve for one of the dissociation experiments. This figure shows a graph of total moles evolved versus time. The model was able to keep track of the moving boundary (equated to moles of gas evolved) as a function of time. This curve shows that the model and the experiment match well. Again, the model predicts the correct dissociation trend.

Figure 8.3 is similar to the graph in Figure 8.2 except that it is for the pseudo-Qatar gas mixture. As noted earlier, the model predicts a longer dissociation time for this gas mixture. Figure 8.4 was a hydrate plug that was dissociated above the ice point. In this case, the model slightly underpredicts the experimental dissociation time.

Table 8.1 shows the results of the dissociation experiments along with the model predictions. The percent error between the model and the experiment, for the hydrate dissociation time, differs significantly between individual experiments. In general,
Figure 8.2: Comparison of Gas Evolved between Experiment and Model

Figure 8.3: Comparison of Gas Evolved between Experiment and Model with the Pseudo-Qatar Gas Mixture
the percent error was the greatest for experiments in which the bath temperature was different than 277 K or the porosity lower than about 0.35. For the case of ice melting, the model does a better job of predicting that time than the hydrate dissociation time. Some possible reasons are included in Table 8.1 when the error is greater than 50%.

Figure 8.4: Comparison of Gas Evolved between Experiment and Model When the Dissociation Temperature Was Above the Ice Point
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<td>3.9</td>
<td>4.02</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>HY0311988.sh</td>
<td>0.4</td>
<td>4.3</td>
<td>-2.9</td>
<td>34.4</td>
<td>28.34</td>
<td>0.99%</td>
<td>3.9</td>
<td>4.02</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>HY0312988.sh</td>
<td>0.51</td>
<td>4.1</td>
<td>-0.4</td>
<td>3.2</td>
<td>2.9</td>
<td>0.98%</td>
<td>3.9</td>
<td>4.02</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>HY0403988.sh</td>
<td>0.34</td>
<td>4.1</td>
<td>3.0</td>
<td>26.1</td>
<td>26.01</td>
<td>0%</td>
<td>3.9</td>
<td>4.02</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>HY0412988.sh</td>
<td>0.56</td>
<td>4.1</td>
<td>3.0</td>
<td>19.5</td>
<td>94.16</td>
<td>3%</td>
<td>3.9</td>
<td>4.02</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>HY0501998.sh</td>
<td>0.52</td>
<td>4.1</td>
<td>-0.6</td>
<td>3.2</td>
<td>4.77</td>
<td>0.99%</td>
<td>3.9</td>
<td>4.02</td>
<td>0.98</td>
<td></td>
</tr>
</tbody>
</table>
For the case when the dissociation temperature was above the ice point, the model prediction was close to the experimental results. The only experiment that was not close was for the case when the bath temperature and the hydrate temperature only differed by 0.3 K. The error in the temperature measurements was greater than 0.3 K and so the determination of the final dissociation time was difficult, but the correct order of magnitude is predicted.

Qualitatively, the same trends are observed in the data as in the model. The fastest dissociation time is at the lower hydrate temperatures. Above the ice point a range of dissociation temperatures was possible. This allowed trends to be observed in the data and a better correlation of the data with model predictions. Contrary to previous ideas about hydrate dissociation, it is best to have ice in the system when trying to remove a hydrate plug. As discussed before, this is due to (1) a higher $\Delta T$ for heat transfer and (2) an order of magnitude higher thermal diffusivity of ice relative to water.

### 8.2 Comparison with Data from other Laboratories and Field Data

The number of documented cases of hydrate plugs that have been dissociated by pressure reduction on both sides is very limited. Table 8.2 represents a collection of all available data found in the literature. These results were compared to the current computer model. In the cases listed in Table 8.2, except the work by Lysne, not all included the data necessary to run the model, so some parameters had to be assumed.
### Table 8.2: Field Data Comparison with Model

<table>
<thead>
<tr>
<th>source of data</th>
<th>hydrate porosity</th>
<th>dissociation temperature (K)</th>
<th>dissociation pressure (MPa)</th>
<th>dissociation time (hrs)</th>
<th>predicted dissociation time (hrs)</th>
<th>error</th>
<th>porosity needed to fit data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lysne (1995)</td>
<td>0.763</td>
<td>273.6</td>
<td>0.5</td>
<td>33.6</td>
<td>8.3</td>
<td>75%</td>
<td>*</td>
</tr>
<tr>
<td>Lysne (1995)</td>
<td>0.544</td>
<td>274.5</td>
<td>0.5</td>
<td>36.7</td>
<td>18.18</td>
<td>50%</td>
<td>0.1</td>
</tr>
<tr>
<td>Lysne (1995)</td>
<td>0.844</td>
<td>274.5</td>
<td>0.5</td>
<td>21.7</td>
<td>6.42</td>
<td>70%</td>
<td>0.4</td>
</tr>
<tr>
<td>Lysne (1995)</td>
<td>0.331</td>
<td>274.5</td>
<td>0.5</td>
<td>48.1</td>
<td>25.91</td>
<td>46%</td>
<td>*</td>
</tr>
</tbody>
</table>

Temperatures and pressures fluctuated during dissociation, averages.

<table>
<thead>
<tr>
<th>ARCO-North Sea Sloan 1998b p 78</th>
<th>0.5</th>
<th>273.2</th>
<th>1.3</th>
<th>552</th>
<th>419.0</th>
<th>24%</th>
<th>0.35</th>
</tr>
</thead>
<tbody>
<tr>
<td>18&quot; buried pipeline, decreased heat transfer to plug, no porosity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Austvik et al. 1995</th>
<th>0.5</th>
<th>273</th>
<th>8-1.5</th>
<th>16</th>
<th>58.92</th>
<th>-268%</th>
<th>0.85</th>
</tr>
</thead>
<tbody>
<tr>
<td>6&quot; pipeline, no porosity, 2 different plugs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DeepStar Report A208-2</th>
<th>0.5</th>
<th>273</th>
<th>*</th>
<th>36</th>
<th>86.27</th>
<th>-140%</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>12&quot; pipeline, ambient 50F, no porosity, pressure, or temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* cannot fit data with model

The model underpredicts all the data by Lysne (1995). This data represents the only other available laboratory data. This is consistent with the experimental results obtained in this thesis. All data for experiments when there was no ice in the system, the model underpredicted the data. In these experiments by Lysne (1995), the dissociation pressure, and consequently the temperature, were not constant during the dissociation experiment so an average value had to be used. This could account for the large difference between the data and predictions.
There were also several field experiments reported where a hydrate plug was dissociated in a pipeline by two-sided depressurization. In all three cases, porosity was not reported so a default value of 0.5 was used. There is no real justification for this number other than it was the approximate average of the porosity obtained by Lysne (1995) in his research. This may not be a good approximation since every hydrate plug forms differently and consequently, should be expected to have different porosities.

There were values of porosity that could be used to fit the dissociation time exactly. In the plug reported by ARCO (Sloan 1998b) the porosity predicted by the model was 0.35, while the porosity for the other two plugs was higher at 0.8 and 0.85. There was not enough information about the formation of these plugs to determine if there is any justification for using values of porosity other than 0.5.

This model could prove a valuable tool for the determination of hydrate dissociation times in a pipeline. The most sensitive parameter in the model is the hydrate porosity. A value of the porosity is needed to obtain a reasonable estimate of the dissociation time. Unfortunately, the porosity of a hydrate plug is difficult to determine. In order for this model to be useful, a means of determining the hydrate porosity of a plug is necessary.

As can be see by the field results, porosity is one of the most important variables. It was possible to match all field data by varying the porosity. If the reader wishes to use the model developed in this thesis, a porosity sensitivity study is recommended, by varying porosity for 0.1 to 0.9 and recording the time for each.
CHAPTER 9
EXCEL-VISUAL BASIC MODEL

9.1 Introduction

The FORTRAN computer model presented in the previous chapters is capable of simulating the dissociation of hydrates in a pipeline. However, the FORTRAN computer interface is difficult to use and running the program is time consuming. The program can take up to several minutes to run on a PC. The purpose of the EXCEL-Visual Basic program is to make the hydrate dissociation model easier and faster to use by engineers and field personnel.

9.2 Generation of Excel-Visual Basic Model

Fitting the results from the FORTRAN model to a simpler equation generated the Excel model. The FORTRAN model was run for many different conditions and a table was generated with the results. The main variables of interest were different ambient temperatures (or pipe wall temperature), different hydrate dissociation temperatures, and different porosities. An equation was needed that could account for changes in any of these variables.
The FORTRAN models consist of both an above ice point and a below ice point model. Both of these models needed to be fit to a simpler equation. In the above ice point model the only important variable, besides porosity, was the temperature difference between the hydrate and the ambient temperature. Irrespective of the absolute values of these temperatures, the difference in temperatures determined the dissociation time.

The below ice point model was more difficult to fit to an equation because the temperatures appeared in several dimensionless groups. There was not any single variable that the dissociation time could be plotted against to mimic the FORTRAN model results. Additionally, the dissociation time for both hydrates and ice had to be fit to different equations.

9.3 Generation of the Below Ice Point Excel Model

The FORTRAN model was run many times so that the dimensionless dissociation time could be determined for a wide range of the variables of interest. Figure 9.1 shows a typical plot of dimensionless dissociation time versus $1/T_D^*$, a dimensionless dissociation temperature. When these values were plotted on a log-log scale, they were close to a straight line. This figure is only for a single ambient temperature. The trends observed in Figure 9.1 are applicable to any other ambient temperature used, but the magnitude of the numbers are changed.

The specific details of how the FORTRAN model was fit to a simpler equation is not important or useful to the understanding of the results. Only the final equation and
Figure 9.1: FORTRAN Model Predictions
the general solution method will be presented so the reader does not get lost in the details. The values of the natural log of the dissociation time versus the natural log of \(1/T_D\) were used in all attempts to fit the model to simpler equation. A fifth order polynomial was used to fit the results and assumed the following form:

\[
\ln(\tau) = a + b \times \ln\left(\frac{1}{T_D}\right) + c \times \ln\left(\frac{1}{T_D^2}\right) + d \times \ln\left(\frac{1}{T_D^3}\right) + e \times \ln\left(\frac{1}{T_D^4}\right) + f \times \ln\left(\frac{1}{T_D^5}\right)
\]  

(9.1)

Where 'a' is a function of porosity and ambient temperature, 'b' and 'c' are functions of porosity only, 'd', 'e', and 'f' are constants, \(T_D\) is a dimensionless temperature and \(\tau\) is the dimensionless dissociation time. A fifth order polynomial was needed to best fit all the data. A simpler polynomial was used in earlier attempts, but the Excel model was not able to fit the FORTRAN results very well for different ambient conditions.

In order to make the analysis easier, some assumptions were made. The parameters 'd', 'e', and 'f' were assumed constant for all porosities and ambient temperatures. The parameters 'b' and 'c' were assumed functions of porosity only and could be fit to the following equations:

\[
b = b1 + b2 \times \varepsilon + b3 \times \varepsilon^2
\]  

(9.2)

\[
c = c1 + c2 \times \varepsilon + c3 \times \varepsilon^2
\]  

(9.3)

where 'b1', 'b2', 'b3', 'c1', 'c2', and 'c3' are all constants. The parameter 'a' was a little more difficult to fit and required a higher order polynomial

\[
a = a1 + a2 \times \varepsilon + a3 \times \varepsilon^2 + a4 \times \varepsilon^3 + a5 \times \varepsilon^4
\]  

(9.4)
The parameters 'a1', 'a2', 'a3', 'a4', and 'a5' are all functions of the ambient temperature. These parameters were all fit to polynomial functions of the ambient temperature, $T_o$. All parameters could be fit with a second order polynomial, only 'a1' required a higher order polynomial.

\[
\begin{align*}
a1 &= a_{11} + a_{12}T_o + a_{13}T_o^2 + a_{14}T_o^3 \\
a2 &= a_{21} + a_{22}T_o + a_{23}T_o^2 \\
a3 &= a_{31} + a_{32}T_o + a_{33}T_o^2 \\
a4 &= a_{41} + a_{42}T_o + a_{43}T_o^2 \\
a5 &= a_{51} + a_{52}T_o + a_{53}T_o^2
\end{align*}
\]

Using Excel's solver function, the values of all parameters were used in fitting the FORTRAN model. The solver function was used to find the minimum average percent error between the FORTRAN model and the Excel model. By minimizing the average error, the maximum percent error between the Excel predictions and the FORTRAN results was 11\% and the average error was about 1.5\%. Figure 9.2 shows the same graph as Figure 9.1 but with the model predictions. This figure is representative of how the Excel model matches with the FORTRAN model. Considering the variety of conditions this simpler equation had to fit, this error is acceptable.

The analysis used to find the simpler equation to model the time to melt the ice in the system was identical to the procedure used to find the parameters in the hydrate dissociation. The maximum percent error for these predictions was also 11\% and the
Figure 9.2: Comparison of Excel Model with FORTRAN Model
Hydrate Dissociation Times
average error was also about 1.5%. Figure 9.3 is a plot of the dimensionless times to melt the ice versus $1/T_D^*$ and shows that these results are very similar to the hydrate regression.

Table 9.1 includes all the final values of the regressed parameters used in the Excel equation for the below ice point model.

9.4 Generation of the Above Point Excel Model

The generation of the above ice point model was considerably easier. There was no dependence on the ambient temperature. In this case, the temperature difference, the difference between the ambient temperature and the hydrate temperature, was used in the predictions instead of $T_D^*$. The equation used to fit the FORTRAN results was a fourth order polynomial of the following form:

$$\ln(\tau) = a + b \times \ln(\Delta T) + c \times \ln(\Delta T)^2 + d \times \ln(\Delta T)^3 + e \times \ln(\Delta T)^4$$  (9.10)

In Equation (9.10), the $\Delta T$ represents the difference between the ambient temperature and the hydrate dissociation temperature.

The parameters 'a', 'b', 'c', 'd', and 'e' are all functions of porosity. The parameter 'a' was fit to a fourth order polynomial, 'b' and 'c' could both be fit with a second order polynomial and 'd' and 'e' could be fit using a simple linear equation.

The maximum percent error in this Excel model was about 10% and the average error was about 1%. Figure 9.4 shows a plot of the dimensionless dissociation time versus $\Delta T$. The points represent the FORTRAN model and the lines are the Excel model
Figure 9.3: Comparison of Excel Model with FORTRAN Model
Ice Melting Times
Table 9.1 Regression Parameters for Excel Models

### Below Ice Point Model

<table>
<thead>
<tr>
<th>Hydrate Dissociation Time</th>
<th>Ice Melting Time</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a1</strong></td>
<td><strong>a1</strong></td>
</tr>
<tr>
<td>2.68</td>
<td>3.78</td>
</tr>
<tr>
<td>-0.37</td>
<td>-0.55</td>
</tr>
<tr>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>-3.6E-04</td>
<td>-8.1E-04</td>
</tr>
<tr>
<td><strong>a2</strong></td>
<td><strong>a2</strong></td>
</tr>
<tr>
<td>0.18</td>
<td>-0.29</td>
</tr>
<tr>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>-3.6E-03</td>
<td>-2.4E-04</td>
</tr>
<tr>
<td><strong>a3</strong></td>
<td><strong>a3</strong></td>
</tr>
<tr>
<td>-6.36</td>
<td>-3.86</td>
</tr>
<tr>
<td>-0.08</td>
<td>-0.01</td>
</tr>
<tr>
<td>5.8E-03</td>
<td>2.3E-04</td>
</tr>
<tr>
<td><strong>a4</strong></td>
<td><strong>a4</strong></td>
</tr>
<tr>
<td>10.65</td>
<td>6.14</td>
</tr>
<tr>
<td>-0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>-8.3E-04</td>
<td>-2.7E-04</td>
</tr>
<tr>
<td><strong>a5</strong></td>
<td><strong>a5</strong></td>
</tr>
<tr>
<td>-7.89</td>
<td>-5.47</td>
</tr>
<tr>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>-3.5E-03</td>
<td>-2.1E-03</td>
</tr>
</tbody>
</table>

### Above Ice Point Model

<table>
<thead>
<tr>
<th>Hydrate Dissociation Time</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a</strong></td>
<td><strong>b</strong></td>
</tr>
<tr>
<td>3.57</td>
<td>-0.26</td>
</tr>
<tr>
<td>-0.26</td>
<td>-4.50</td>
</tr>
<tr>
<td>8.11</td>
<td>-6.43</td>
</tr>
<tr>
<td><strong>b</strong></td>
<td><strong>c</strong></td>
</tr>
<tr>
<td>-0.99</td>
<td>3.2E-03</td>
</tr>
<tr>
<td>-0.03</td>
<td>-0.01</td>
</tr>
<tr>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>c</strong></td>
<td><strong>d</strong></td>
</tr>
<tr>
<td>3.2E-03</td>
<td>7.2E-04</td>
</tr>
<tr>
<td>-0.01</td>
<td>2.4E-03</td>
</tr>
<tr>
<td>0.02</td>
<td>1.6E-04</td>
</tr>
<tr>
<td><strong>d</strong></td>
<td><strong>e</strong></td>
</tr>
<tr>
<td>1.6E-04</td>
<td>4.0E-04</td>
</tr>
</tbody>
</table>
Figure 9.4: Comparison of Excel Model with FORTRAN Model-Above Ice Point
predictions. The results of this plot are independent of the ambient temperature. Table 9.1 includes all of the constants used in the Excel model for the above ice point case.

9.5 Final Excel Model

The final product that came from generating this simpler equation to fit the FORTRAN model was a single worksheet in Excel that could calculate a dissociation time given values for the ambient temperature, hydrate dissociation temperature, and porosity. The Excel model can give results in a matter of seconds whereas the FORTRAN model took several minutes. Another benefit to the Excel model is the capability of instantly giving a representative dissociation curve, a plot of the moving boundary position as a function of time.

The reason that the term Visual Basic has also been associated with this Excel model is that some computer code was written along with the model that simulates the moving boundary motion. Instead of the graphical representation of the moving boundaries as a function of time, a schematic depiction of the boundary motion was simulated.

Figure 9.5 shows the front screen to the Excel model. The darkened boxes, ambient temperature, hydrate dissociation temperature, hydrate porosity, and pipe radius are the input parameters. These values may be changed at any time. As soon as any of these values are changed, the dissociation time will change accordingly. The graph will also change to represent the new dissociation times. The graph shows two different lines;
HYDRATE DISSOCIATION PREDICTION PROGRAM

Ambient Temperature  4°C
Hydrate Temperature  -1°C
Hydrate Porosity  0.1
radius  4 cm

Hydrate Dissociation Time (hrs)  18.26
Ice Melting Time (hrs)  22.48

Figure 9.5: Front End of the Excel-Visual Basic Model
one line is the water/ice moving boundary and the other is the ice/hydrate moving boundary. If the hydrate dissociation temperature is above the ice point, then these two curves collapse to a single curve.

The figure on the right side of the spreadsheet (Figure 9.5) shows a cross-sectional view of a pipeline. When the button below (Press Here to View Hydrate Dissociation) is pressed, a representation of the dissociating hydrate is simulated. This figure shows a water layer surrounding a shrinking ice layer, which surrounds a shrinking hydrate core. The movement of the interfaces, as determined from the graph, is translated into this picture of hydrate dissociation. If the hydrate dissociation temperature is above the ice point, the picture then only shows a water layer surrounding a shrinking hydrate core.

9.6 Further Comments about the Excel Model

The Excel model is very easy to use relative to the FORTRAN model. However, it does not have as much functionality. The Excel model uses, for all simulations, the structure I hydrate physical properties. There is no way to change them within the Excel program. The FORTRAN model is needed to change any of these values.

The Excel model was fit for an ambient temperature range from 273.5 K to 303 K. The dissociation temperature in the Excel model has a temperature range of 252 K to 0.1 K below the ambient temperature. The porosity was fit for the range 0.1 to 0.9.
To use the Excel model, the pipe radius, hydrate porosity, hydrate dissociation temperature, and the ambient temperature are required. Values for both the pipe radius and ambient temperature should be known. The values of porosity and dissociation temperature are more difficult to determine.

The hydrate temperature is assumed to be in equilibrium with the prevailing pressure. If some hydrate equilibrium prediction program is available, such as CSM Hydrate, then the temperature can be calculated, since the pressure in the pipeline should be known. If the predicted hydrate temperature is below the ice point, the temperature will not be in equilibrium with the temperature. Due to the temperature buffering capacity of ice, the hydrate temperature will not drop much below the ice point. A recommended default value to use would be 272 K. This number is based on the average dissociation temperature observed in this work.

The porosity is the most difficult parameter to determine. A value of 0.5 represents an average of experimental work done by Lysne (1995) and is recommended in absence of any other data. If some knowledge of the plug is known, such as how it formed or permeability, this porosity value may either increase or decrease. Much work needs to be done in this area before an accurate value of porosity can be predicted.

Using these default values, the model can predict an order of magnitude estimate of the dissociation time. Since the Excel model is simple to use, a variety of input parameters can be easily input to determine their effect on dissociation time.
CHAPTER 10

CONCLUSIONS

In summarizing the results from the experimental and modeling portions of this work, several conclusions can be drawn.

The experimental portion of the work indicated that the hydrate plug would dissociate radially in a pipeline. This has important consequences for anyone removing a hydrate plug in a pipeline. When a hydrate plug begins to dissociate, it will release from the pipe wall first. If any pressure gradient exists along the plug, the plug will begin to move. Depending on the size of the plug and the pressure gradient along the plug, the plug may have sufficient momentum once it begins to move to cause serious damage to the equipment and the people operating the pipeline.

When a pipeline is depressurized, the hydrate temperature will remain in equilibrium with the pressure. However, if the equilibrium temperature is below the ice point, the formation of ice will buffer the temperature and prevent the hydrate from decreasing much below the ice point. Both the experiment and the modeling indicated that the formation of ice in the system aided in the dissociation of hydrates.

The model indicated that there is no optimal dissociation temperature. The dissociation time continues to decrease as the temperature of the dissociating hydrate was
decreased. Since temperature is related to pressure by hydrate equilibrium, this indicates that the dissociation time decreases as the pressure is decreased. This would mean that the ideal scenario for dissociating a plug would be when the pressure is as low as possible, most likely, this is at atmospheric pressure. Both the model and experiment indicate that ice helps in the removal of hydrate in a pipeline. This would indicate that it is best to depressurize the pipeline as quickly as possible to form as much ice as possible.

When the pressure is slowly decreased, the temperature buffering capacity of ice is enhanced because the ice is given sufficient time to regulate temperature. When cooled quickly, the hydrate plug will initially decrease below the ice point before it increases back up to the ice point. This lower temperature will help aid slightly in the dissociation process.

The results of the model comparison with the data indicate the model is reasonably able to simulate methane hydrate dissociation with no fitted parameters. The model does best to fit the data when the hydrate temperature is below the ice point. Fortunately, this is the best criterion for hydrate dissociation. Above the ice point, the model underpredicts the dissociation time. The trends in dissociation, as evidenced by Figures 8.2 indicate that the fundamental basis for the model is sound. It qualitatively predicts the hydrate dissociation. With the addition of fitting parameters, the model could easily fit the data.
CHAPTER 11
RECOMMENDATIONS

The results of this work indicate that the model and experiment provide a satisfactory description of hydrate dissociation in pipelines. This is a highly idealized system and the results are difficult to extend to situations that are more realistic.

Typically, when a hydrate plug is formed in industry, two-sided depressurization is not an option. The model should be extended to account for situations in which only one side of the pipeline can be depressurized.

To provide the basis for such a model, the experiment should also be modified to simulate the one-sided depressurization case. In this case, a pressure reservoir would be required on the upstream side of the plug. The upstream side of the plug should be in the hydrate-forming region so that hydrate does not dissociate on the upstream side of the plug. Only the downstream end of the plug should be able to dissociate. The effect of gas cooling due to flow through the plug should be monitored in these experiments to determine how significant this effect is.

The structure II gas did not fit with the modeling predictions. The model predicted that it would take longer for the structure II to dissociate, but the experiment showed that it took less time. This phenomenon should be studied in more detail. It is
possible that kinetics plays a role in the dissociation of hydrate. That may be the cause of the discrepancy between the experiment and the model. Since, most industrial situations deal with structure II hydrate plugs, the cause of this discrepancy would be good to determine.

The models developed by Lysne (1992) and the current model both note the effect that porosity of the hydrate has on total dissociation time. Future experiments should be designed to determine the role that porosity plays in dissociation.
**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Latin Letters</th>
<th>Units/Dimension</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{p,i}$</td>
<td>[J/g/K]</td>
<td>specific heat of ice</td>
</tr>
<tr>
<td>$C_{p,w}$</td>
<td>[J/g/K]</td>
<td>specific heat of water</td>
</tr>
<tr>
<td>$k_i$</td>
<td>[W/cm/s/K]</td>
<td>thermal conductivity of ice</td>
</tr>
<tr>
<td>$k_w$</td>
<td>[W/cm/s/K]</td>
<td>thermal conductivity of water</td>
</tr>
<tr>
<td>mb1point</td>
<td>[-]</td>
<td>grid point to left of water/ice interface</td>
</tr>
<tr>
<td>mb2point</td>
<td>[-]</td>
<td>grid point to left of ice/hydrate interface</td>
</tr>
<tr>
<td>npoints</td>
<td>[-]</td>
<td>number of grid points</td>
</tr>
<tr>
<td>$r$</td>
<td>[m]</td>
<td>radius</td>
</tr>
<tr>
<td>$r_0$</td>
<td>[m]</td>
<td>pipe radius</td>
</tr>
<tr>
<td>$r_{P1}$</td>
<td>[m]</td>
<td>water/ice interface</td>
</tr>
<tr>
<td>$r_{P2}$</td>
<td>[m]</td>
<td>ice/hydrate interface</td>
</tr>
<tr>
<td>$T_0$</td>
<td>[K]</td>
<td>temperature of the pipe wall</td>
</tr>
<tr>
<td>$T_{D}$</td>
<td>[K]</td>
<td>hydrate dissociation temperature</td>
</tr>
<tr>
<td>$T_I$</td>
<td>[K]</td>
<td>temperature of the ice</td>
</tr>
<tr>
<td>$T_M$</td>
<td>[K]</td>
<td>melting temperature of ice</td>
</tr>
<tr>
<td>$T_w$</td>
<td>[K]</td>
<td>temperature of the water</td>
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**Dimensionless Groups**

<table>
<thead>
<tr>
<th>Dimensionless Groups</th>
<th>Dimensionless Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>[-]</td>
</tr>
<tr>
<td>$\Delta R$</td>
<td>[-]</td>
</tr>
<tr>
<td>$R_{P1, mb}$</td>
<td>[-]</td>
</tr>
<tr>
<td>$R_{P2, mb}$</td>
<td>[-]</td>
</tr>
<tr>
<td>$T_{D*}$</td>
<td>[-]</td>
</tr>
<tr>
<td>$U$</td>
<td>[-]</td>
</tr>
<tr>
<td>$V$</td>
<td>[-]</td>
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**Greek Letters**

<table>
<thead>
<tr>
<th>Greek Letters</th>
<th>Units/Dimension</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\alpha_i$</td>
<td>[m^2/s]</td>
<td>thermal diffusivity of ice, $k_i/\rho_i C_{p,i}$</td>
</tr>
<tr>
<td>$\alpha_w$</td>
<td>[m^2/s]</td>
<td>thermal diffusivity of water, $k_w/\rho_w C_{p,w}$</td>
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<tr>
<td>$\Delta \tau$</td>
<td>[-]</td>
<td>time increment</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>[-]</td>
<td>porosity of hydrate and ice</td>
</tr>
<tr>
<td>$\lambda_H$</td>
<td>[J/g hydrate]</td>
<td>latent heat of hydrate</td>
</tr>
<tr>
<td>Symbol</td>
<td>Units</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td>-------------</td>
</tr>
<tr>
<td>(\lambda_i)</td>
<td>([J/g\text{ ice}])</td>
<td>latent heat of ice</td>
</tr>
<tr>
<td>(\rho_h)</td>
<td>([g \text{ hydrate} /m^3])</td>
<td>density of hydrate</td>
</tr>
<tr>
<td>(\rho_i)</td>
<td>([g \text{ ice} /m^3])</td>
<td>density of ice</td>
</tr>
<tr>
<td>(\rho_w)</td>
<td>([g \text{ water} /m^3])</td>
<td>density of water</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>([s/m^2])</td>
<td>stability criterion of SE method, (\Delta \tau/\Delta R^2)</td>
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**Dimensionless Groups**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
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<tbody>
<tr>
<td>(\alpha^*)</td>
<td>[-]</td>
<td>(\alpha_w/\alpha_i)</td>
</tr>
<tr>
<td>(\lambda^*)</td>
<td>[-]</td>
<td>(\lambda_{iy}/C_{pv}/(T_p-T_{id}))</td>
</tr>
<tr>
<td>(\lambda_{yi^*})</td>
<td>[-]</td>
<td>(\lambda_{iy}/C_{pg}/(T_{yi}-T_{D}))</td>
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<tr>
<td>(\lambda_i^*)</td>
<td>[-]</td>
<td>(\lambda_i/C_{pw}/(T_p-T_{M}))</td>
</tr>
<tr>
<td>(\rho^*)</td>
<td>[-]</td>
<td>(\rho_i/\rho_w)</td>
</tr>
<tr>
<td>(\rho_{hi^*})</td>
<td>[-]</td>
<td>(\rho_h/\rho_i)</td>
</tr>
<tr>
<td>(\rho_{t^*})</td>
<td>[-]</td>
<td>(\rho_t/\rho_w)</td>
</tr>
<tr>
<td>(\tau)</td>
<td>[-]</td>
<td>dimensionless time (\alpha_w\mu D_0^2)</td>
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APPENDIX A

CALCULATION OF ICE CONVERSION TO HYDRATE

The calculation of the conversion hydrate formation from ice is a relatively straightforward procedure. The variables required to calculate conversion are the system volume, reactor volume, ice volume, system temperature, and system pressure. The system volume includes both the reactor volume and the volume of the piping. The volume of piping includes any volume that is occupied by the gas during the formation portion of the experiment.

The mass of ice loaded into the reactor is known during the formation portion of the experiment. The volume of ice is then calculated using the density of ice.

\[ V_I = \frac{m_I}{\rho_I} \quad (A.1) \]

Where \( V_I \) is the volume of ice, \( m_I \) is the mass of ice, and \( \rho_I \) is the density of ice. The following relation then gives the volume occupied by the gas

\[ V_g = V_P + [ V_R - (V_H + V_I) ] \quad (A.2) \]

Where \( V_g \) is the volume of gas, \( V_P \) is the volume of piping, \( V_R \) is the volume of the reactor, and \( V_H \) is the volume of hydrate.

After the system is pressurized with gas, the initial number of moles can be calculated using the Peng-Robinson equation of state (Peng and Robinson 1976).
\[ P = \frac{RT}{v-b} - \frac{a(\omega, T)}{v(v+b)+b(v-b)} \]  \hspace{1cm} (A.3)

Where \( v \) is the molar volume of gas, \( R \) is the gas constant, \( P \) is the system pressure, \( T \) is the system temperature, and \( a, b, \text{ and } \omega \) are defined in the following equations.

\[ a(\omega, T) = a_e \left[ 1 + \kappa \left( 1 - \sqrt[3]{T} \right) \right] \]  \hspace{1cm} (A.4)

\[ a_e = \frac{0.45724 R^2 T_c^2}{P_c} \]  \hspace{1cm} (A.5)

\[ \kappa = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \]  \hspace{1cm} (A.6)

\[ b = \frac{0.0778RT_c}{P_c} \]  \hspace{1cm} (A.7)

Where \( T_c \) and \( P_c \) are the critical temperature and pressure of the gas, \( \omega \) is the eccentricity factor of the gas, and \( T_r \) is the reduced temperature.

\[ T_r = \frac{T}{T_c} \]  \hspace{1cm} (A.8)

Once Equation (A.3) is solved for \( v \), the number of moles can be found using the equation

\[ N_g = \frac{V_f}{v} \]  \hspace{1cm} (A.9)

As hydrates begin to form, the pressure decreases in the system, indicating hydrate formation. The example discussed will be for the case when the system pressure is increased twice during the experiment, as discussed in chapter 4 in the recommended
formation procedure. The pressure just before the pressure is increased again is used in
the first part of the calculation.

To calculate the amount of hydrate that forms in this first part of the formation
experiment requires an iterative process, since the volume of gas is dependent upon the
amount of hydrate formed. As gas is incorporated into the hydrate, the hydrate volume
increases, relative to the ice volume. The hydrate volume increases faster than the ice
volume decreases. The volume occupied by the gas will change according to Equation
(A.2).

To find the amount of hydrate formed, a value of the overall cage occupancy, \( \theta \),
was assumed. For these calculations the value was obtained from CSM Hydrate, a
hydrate equilibrium prediction program. Once the amount of gas that is consumed is
known, the amount of hydrate formed will also be known.

\[
m_H = N_g MW_g + 6N_g MW_{H_2O}
\]  
(A.10)

Where \( MW_g \) is the molecular weight of the gas, \( MW_{H_2O} \) is the molecular weight of water.
The value of \( \theta \) is defined to have units of mole \( H_2O / \) mole gas. If a gas mixture is used,
then the mole fraction average \( MW \) is used. The value of cage occupancy will also
change depending on the type of gas used.

To solve for the amount of gas incorporated into the hydrate, a final amount of
hydrate is assumed. A new gas volume is calculated using Equation (A.2). The molar
volume is calculated using Equation (A.3) and then the final amount of gas is found using
equation (A.9). The difference between the initial amount and this final amount can be
used to calculate the amount of hydrate in the system. This amount of hydrate is compared to the amount assumed in the first step and the process is repeated until the two values are the same.

The same procedure is followed for the second pressure increase in the system. The final values from the initial pressuring are used as the initial conditions for this calculation. The solution procedure must be repeated for each time the system pressure is increased.

This same procedure is followed irrespective of the gas used in the experiment. If a gas mixture is used, only the values of the critical pressure and temperature and the eccentricity factor that were used in Equations (A.4)-(A.8) will change. The values of these parameters for the gas mixture can be determined using the following mixing rules:

$$ T_{C,m} = \sum_{i=1}^{n} \phi_i T_{C,i} \tag{A.11} $$

$$ \phi_i = \frac{y_i V_{C,i}}{\sum_{i=1}^{n} y_i V_{C,i}} \tag{A.12} $$

$$ T_{m,ij} = \sum_{i=1}^{n} y_i T_{C,i} \tag{A.13} $$

$$ P_{m,ij} = \sum_{i=1}^{n} y_i P_{C,i} \tag{A.14} $$

$$ \omega_m = \sum_{i=1}^{n} y_i \omega_i \tag{A.15} $$
\[ P_{C,n} = P_{m,lg} + P_{m,lg} \left[ (8.6 - 11\omega_m) \frac{(T_{C,m} - T_{m,lg})}{T_{m,lg}} \right] \]  \hspace{1cm} (A.16)

Where \( n \) is the number of components in the gas mixture, \( y_i \) is the mole fraction of component \( i \) in the mixture, \( P_{C,i} \) is the critical pressure of component \( i \), \( T_{C,i} \) is the critical temperature of component \( i \), \( V_{C,i} \) is the critical molar volume of component \( i \), and \( \omega_i \) is the eccentricity factor of component \( i \). The values of \( T_{C,m}, P_{C,m}, \) and \( \omega_m \) are the mixture critical values used in Equations (A.4)-(A.8).