Hydrate dissociation during drilling through in-situ hydrate formations

Erdem Catak
Louisiana State University and Agricultural and Mechanical College

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HYDRATE DISSOCIATION DURING DRILLING THROUGH
IN-SITU HYDRATE FORMATIONS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
Requirements for the degree of
Master of Science in Petroleum Engineering

in

The Department of Petroleum Engineering

by

Erdem Catak
B.S. Petroleum and Natural Gas Engineering, Technical University of Istanbul, 2001
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ABSTRACT

Natural gas hydrates are thought to be the future hydrocarbon source of the energy hungry world. Tremendous amount of research has been done to investigate the feasibility of gas production from the hydrate formations. In this direction, three basic production methods, thermal stimulation, depressurization and thermodynamic inhibitor injection have been proposed to produce hydrocarbons off the hydrates. On the other hand, they present high potential risk of drilling hazards, such as severe gasification of drilling fluid, casing collapse due to increase in pressure after dissociation of hydrate zone, and instability of ocean floor, which may cause a platform failure.

Scientists and engineers have done very valuable research to understand the phase behavior of hydrates and to prevent hydrate formation throughout the well system during drilling. Reliable hydrate inhibitors have been developed for drilling and production activities. Common practice for the drilling industry has been avoidance of hydrate formations by either abandoning the project or drilling expensive directional wells to reach the target zones for many years.

The goal of this project was to quantify the significance of potential problems to allow operational methods and well design to be adopted to minimize the impact of hydrate zone on drilling operations for Eastern Black Sea Offshore Exploration Project. Investigating the existing hydrate dissociation models and adopting a model to predict the amount of dissociated gas was the first step. Further steps were investigation of temperature distribution throughout the well using a thermal simulator and prediction of heat influx from the drilling fluid into the hydrate zone.

In this study, hydrate dissociation mechanisms are described. Drilling and production hazards associated with dissociation are stated. For the investigation of hydrate stability/
instability, well bore temperature distribution in the near well bore is determined. Hydrate
dissociation rate is calculated, and results are evaluated for further changes in drilling program
and well design parameters.

Results obtained from the dissociation calculations were applied to a set of data from two
wells drilled by ARCO/Turkish Petroleum Corporation Joint Venture in Western Black Sea, and
were used to design the prospective Eastern Black Sea Offshore Exploration wells.
1. INTRODUCTION

Hydrates are crystalline compounds, which are a mixture of water and low molecular weight gases. Hydrates are formed by the inclusion of guest molecules inside the cavities of a crystal framework composed of host molecules. Their formation depends on temperature and pressure conditions of the environment, composition or type of gas molecules, and the salinity of the water, which traps the gas molecules in a cage-like structure. Hydrates can form anywhere and anytime when the necessary combination of low temperatures and high pressures are present. One volume of hydrate could release as much as 150 to 180 volumes of natural gas at standard conditions.

Methane hydrates represent a potential new source of energy, especially for countries that lack conventional hydrocarbon reserves. It is estimated that the amount of natural gas trapped in hydrates around the world is approximately two orders of magnitude larger than the recoverable gas in conventional reservoirs\(^1\). Unfortunately, geographical obstacles, difficult technical problems and economics prevent the possible production of hydrates with current technology. While the value of gas hydrates as a future energy source remains uncertain, the hazards they pose to exploration and production of conventional energy are better understood. Evaluation of and mitigation plans for handling those hazards in deepwater drilling is the focus of this study.

1.1 Gas Hydrate Challenges

Enhanced technology in deep water drilling enables operators to explore, develop and produce deepwater offshore hydrocarbon fields. With the increasing water depth, operating conditions, such as high pressure and low temperature started falling into the hydrate stability boundaries, where formation of hydrates is expected. During routine drilling operations, pressure and temperature conditions are mostly unfavorable for hydrate formation. However, during long shut-in periods and special field operations, the system must be protected against
hydrate formation, and this is often done by adding salt (NaCl, NaBr, CaCl$_2$) into the drilling fluid.

Hydrates are often a concern in deep water drilling well control. The high hydrostatic pressure due to the water column and low temperature at or below the seabed create a favorable environment for hydrate formation if both are present. Therefore if a gas kick is taken and circulated to surface, the combination of high hydrostatic pressure, low seabed temperature, gas and water can lead to hydrate formation.

When hydrates start to form, they can create blockages in the BOP and associated equipment. This could be in the annular gap between the BOP and the drill string, the choke and kill lines or both. During a well kill operation, hydrates can form in the choke line and prevent further circulation of the kick. If hydrates form in the annular gap, they can prevent the well from flowing. This could lead the rig crew to believe that the well is dead when it is not. They can also prevent the operation of the BOP’s.

1.2 In-situ Hydrate Dissociation Concerns

Gas hydrates are known to be stable at low temperatures and high pressures, mainly restricting them to areas of polar and permafrost regions, and deep-water seas. Running out of onshore reserves is forcing the operators to explore in areas where they may drill through hydrate formations. As mentioned before, while the value of gas hydrates as a future energy source remains uncertain, the hazards they pose to exploration and production of conventional energy are more clear. In-situ hydrate dissociation concerns are addressed from two perspectives, open hole challenges and cased hole challenges.

Gas hydrate stability conditions usually extend from the seafloor to 500 to 1,700 feet below sea floor$^1$. However, hydrates have been recovered from the ocean floor in some cases$^1$. Therefore, in-situ hydrate formations are expected at shallow depths, typically above the surface
casing setting depth. The main concern with no BOP installed is hydrate dissociation. If the solid hydrate in the sediments is dissociated while drilling, a gas kick will occur and the wellbore may become unstable. “If you are drilling into the gas hydrate, you have to worry that the hydrate could suddenly dissociate, leading to collapse of the sediment supporting the drill stem,” Carolyn Ruppel, associate professor of geophysics in Georgia Tech’s School of Earth and Atmospheric Sciences, and coordinator of the gas hydrate program, says.

In the past, drilling companies have experienced unusual problems when they drilled through hydrate zones. Events of well control due to severe mud gasification, fizzing drilled cuttings, and near blowout situations were reported by the researchers. Large amount of cuttings generated from the hydrate zone may release large volumes of gas at the surface, threatening the safety of the personnel and the surface equipment.

After completing the surface hole drilling, surface casing is set and cemented in place. Roadifer concluded that the hydrate zone should be cased off immediately with high-collapse-strength casing, before drilling continues to deeper formations. After cement reaches a predetermined compressive strength, operations start for the intermediate hole drilling. While drilling the deeper sections of the well the drilling fluid carries heat up from high temperature formations. Heat transfer to the hydrate layers can cause dissociation behind the cemented casing. Makogon has reported casing collapse due to increased pressure of dissociated gas.

Another concern is the risk of hydrate dissociation during setting of cement. The setting process of cement is an exothermic reaction, in other words, cement releases heat to the surrounding formations during its setting. Hydrate formations absorbing the heat released from cement may become unstable, and gas dissociated from hydrates may find its way to the surface, or to the other formations. If dissociation takes place just after cementing, gas bubbles flowing into fresh cement may reduce the quality of cement job.
1.3 General Project Description

Given the problems they pose to the oil industry, hydrates are considered to be drilling hazards. Avoidance has been common practice within the industry for many years. Drilling expensive, extended reach, directional wells is one approach for hydrate avoidance. On the other hand, understanding the phase behavior of hydrates and studying the worst-case scenarios helps operators to redesign the proposed wells to avoid problems. Potential hydrate zones should be determined by detailed geological, and geophysical surveys prior to drilling so that precautions can be taken to minimize the impact of hydrate associated problems.

The focus of this project is to answer the question whether the naturally occurring hydrate zones in Eastern Black Sea, Turkey, can be drilled and cased off safely. The project addresses two major well design concerns: effects of hydrate dissociation in the open hole on operational safety, and effects of potential dissociation on casing design. These are presented and analyzed in a sequential order. The results presented for each question are based on simulations with the GTEMP\textsuperscript{8}, wellbore temperature simulator, and a mathematical thermal hydrate dissociation model. Most of the previous hydrate dissociation models\textsuperscript{9,10,11,12,13,14} are based on thermal method. On the other hand, some researchers\textsuperscript{15,16,17} studied hydrate dissociation based on a depressurization technique. These studies concentrated on feasibility of gas production from naturally occurring hydrate layers. However, neither hydrate dissociation as a drilling hazard, nor the effects of dissociation on well design were addressed. Therefore, this project is a valuable work for drilling and well design when hydrate dissociation while drilling through in-situ formations are expected.

1.4 Objectives of the Study

The Turkish National Oil Company, TPAO, established a joint venture with BP to explore for oil and gas within the deep waters of Eastern Black Sea. There are presently no
offshore exploration wells in the Eastern Black Sea. The immediate overall objective of this study is to avoid hydrate related problems in HOPA-1, the first deepwater exploration well to be drilled in the region. Naturally occurring hydrates below the sea floor are expected to be encountered in Hopa-1. Determining whether and how the naturally occurring hydrate zones in this well can be drilled and cased off safely is the primary focus of this project.

1.5 Summary of Work Planned

A detailed literature review about hydrates indicated that hydrates are drilling hazards to the oil industry rather than being a near-future energy source. Understanding hydrates require a good understanding of hydrate structures, properties, and hydrate stability conditions. This study gives a brief enlightenment of hydrates structures, basic properties, phase diagrams of hydrocarbon-water systems and prediction of hydrate formation and dissociation.

Temperature distribution at the near wellbore was used to calculate the heat flux from the drilling fluid into the hydrate, which causes dissociation of hydrate due to thermal effects. Dissociation front calculations were done to investigate the hydrate instability, and amount of gas to be dissociated from hydrate zone. Dissociation volume calculations were used to calculate gas influx rate and hydrostatics reduction due to dissociation gas. In addition, maximum pressures behind the surface casing associated with the dissociation process were predicted so that the risk of surface casing failure can be investigated.

Data obtained from two wells drilled in 1999 in Western Black Sea, Limankoy-1 and Limankoy-2, were used to evaluate and optimize the well design parameters where in-situ natural gas hydrate formations are expected. Finally, the knowledge that we gained in this study was applied to Hopa-1, a deepwater exploratory well in Turkey, which is being drilled as a part of the Eastern Black Sea Offshore Exploration Project. The drilling operations have started in early August 2005, and are still in progress.
1.6 Overview of Report

This report documents the work performed to address the question whether the naturally occurring hydrate zones can be drilled and cased off safely. A brief overview of the report is given below.

Chapter 1 describes gas hydrate challenges in general and concerns regarding dissociation of naturally occurring hydrates in particular. A general overview of the project and objectives of the research are also presented in this chapter.

Chapter 2 reviews the existing technical literature concerning hydrates and hydrate dissociation. Quantitative models for predicting hydrate dissociation are highlighted.

Chapter 3 describes the research method used in this study. Project description and work plan are presented in this chapter.

Chapter 4 provides information about the background for this research, principally the experience from previous drilling in the Black Sea and plans for future exploratory drilling that establish the need for this study. A brief summary of data and experience from two exploratory wells drilled in the Western Black Sea, Limankoy-1, and Limankoy-2 is provided. Hopa-1 well, which is a part of the Eastern Black Sea Offshore Exploration Project is introduced, and associated challenges are described.

Chapter 5 presents an analytical hydrate dissociation model that is used to predict the behavior of dissociation for the Eastern Black Sea Project. Example calculations for dissociation front location, gas volume associated with hydrate dissociation and mud density reduction due to gas influx are available in this chapter.

Chapter 6 concentrates on the wellbore temperature distribution. Effects of different parameters on temperature profiles are investigated by using GTEMP, a wellbore temperature simulator. Heat transferred by the drilling fluid and heat flux into the formations is presented.
Chapter 7 shows the application of proposed method on the two offshore wells in the Western Black Sea. Actual drilling parameters are used to investigate the predicted temperature distribution and hydrate dissociation for these two wells. Results are compared to the facts given in the daily reports section of the end of project report.

Chapter 8 provides recommended practices for drilling the prospective Eastern Offshore Black Sea wells to mitigate hydrate formation and dissociation problems.

Chapter 9 summarizes this study with the overall conclusions and recommendations for the future research.
2. LITERATURE REVIEW

A literature search was undertaken to identify and review published information regarding hydrate structures, stability conditions, dissociation mechanisms and related proposed models. The goal was to find and review information on hydrates as drilling hazards, and check whether researchers previously proposed a model that can be used as a dissociation model during drilling. Hydrate dissociation models previously proposed by Holder\textsuperscript{9}, McGuire\textsuperscript{10}, Bayles\textsuperscript{11}, Selim\textsuperscript{12}, Moridis\textsuperscript{13} and Swinkels\textsuperscript{14} are based on thermal effects. On the other hand, Burshears\textsuperscript{15}, Yousif\textsuperscript{16} and Ahmadi\textsuperscript{17} studied hydrate dissociation based on depressurization. An overall summary of the hydrate modeling findings is included in this chapter. All of these researchers concentrated on feasibility of gas production from naturally occurring hydrate layers. Nevertheless, neither hydrate dissociation as a drilling hazard, nor the effects of dissociation on well design were addressed. However, drilling companies have experienced unusual problems in the past when they drilled through hydrate zones. Imperial Oil Ltd\textsuperscript{3} and Panarctic Oils Ltd\textsuperscript{4} faced problems of well control due to severe mud gasification. Other hydrate related drilling experiences include fizzing drill cuttings, and near blowout situations\textsuperscript{5}.

2.1 History of Hydrate Research

The history of hydrate research is extensive; the first report on hydrate research by Sir Humphrey Davy\textsuperscript{18} is nearly two hundred years old. In 1934, Hammerschmidt\textsuperscript{19} realized that the freezing in high-pressure pipelines was due to hydrate formation, not ice formation. In 1940's, Soviet investigators hypothesized the existence of natural methane hydrates in cold northern climates. Later, Katz\textsuperscript{20,21,22} and co-workers summarized an impressive amount of work. By 1950 there was a large database available concerning hydrates but knowledge of hydrate structures was still limited. Von Stackelberg\textsuperscript{23} studied hydrates using x-ray diffraction and identified the
hydrates as clathrates. Claussen\textsuperscript{24} proposed structure I and II in 1951. Müller\textsuperscript{25} soon verified these structures by x-ray analysis of several gas hydrates in 1951.

In 1959, van der Waals and Platteeuw\textsuperscript{26} were the first scientists to calculate the conditions of hydrate formation. Later on in the early 1960’s, Soviets recognized methane hydrate as a possible energy source. They discovered and produced the first major hydrate deposit in permafrost\textsuperscript{27}. In the 1970’s, a bottom simulating reflector was drilled and was found to be associated with the base of hydrate stability\textsuperscript{27}. Research has increased in the 1980’s, and new instrumental methods were introduced in the research, such as Nuclear Magnetic Resonance spectroscopy, vibrational spectroscopy and Raman spectroscopy. With the help of Nuclear Magnetic Resonance techniques, Ripmeester\textsuperscript{28} et al identified a new hydrate structure, structure H, in 1987.

Currently, more intense research is being done, which mainly focuses on kinetics of hydrate formation, gas production from hydrate reservoirs and transport and storage properties of hydrates. One example is a Joint Industry Program\textsuperscript{29} in Gulf of Mexico involving U.S. Department of Energy, U.S. Department of Interior, Chevron-Texaco, Schlumberger, Halliburton, ConocoPhillips, TotalFinaElf, and Japan National Oil Corporation. Their goals are to characterize natural gas hydrates in the GOM and to understand the hazards of drilling through the hydrate stability zone. The National Methane Hydrate R&D Program\textsuperscript{30} executed by the U.S. Department of Energy expresses their goal as “developing the tools and knowledge that will ensure the safety of drilling and producing deep-water oil and gas resources located below marine hydrate deposits.”

2.2 Hydrate Structures

Gas hydrates are formed under certain conditions of temperature and pressure. Through hydrogen bonding, water molecules form a framework containing relatively large cavities that
can be occupied by certain gas molecules that get linked to the framework by van der Waals forces. Water's readiness to make these bonds is responsible for the stability of gas hydrates. The gas molecules held within the lattice can be a range of hydrocarbons and other gases, including ethane, propane, iso-butane, butane, nitrogen, carbon dioxide, and hydrogen sulfide. The most common occurrence in natural reservoirs is methane.

Several different structures of hydrates are known; with the three most common being structure I, structure II, and structure H. Claussen\textsuperscript{24} proposed structure I and II in 1951. Müller\textsuperscript{25} soon verified these structures by x-ray analysis of several gas hydrates in 1951. Ripmeester\textsuperscript{28} et al. discovered structure H in 1987.

The crystal structures of hydrates are given with reference to the water skeleton\textsuperscript{31}. The water molecules form pentagonal dodecahedron which is the basic building block cavity, known by notation \(5^{12}\) i.e. 12 faces with five sides per face. Other cavity types\textsuperscript{31} are \(5^{12}6^2\) (tetrakaidecahedron), \(5^{12}6^4\) (hexakaidecahedron), \(4^35^66^3\), and \(5^{12}6^8\). The cavity types are illustrated in Figure 2.1.

![Figure 2.1 Basic cavity types of the hydrate structures\textsuperscript{31}](image-url)
The number of cavities per unit cell determines the type of hydrate structure. For example, structure I hydrate has two small and six large cavities. On the other hand, structure II hydrate has sixteen small and eight large cavities. Cavities smaller than the average cavity radius are filled with guest gas molecules. The coordination number\(^{32}\) is the sum of the total number of neighbors of a central atom in a chemical compound and the number of lone pairs on it. In methane the coordination number for the carbon atom is 4. Several properties of different hydrate structures are given in Table 2.1 followed by brief descriptions of basic hydrate structures.

Table 2.1 – Properties of Different Hydrate Structures\(^{31}\)

<table>
<thead>
<tr>
<th>Hydrate Crystal Structure</th>
<th>I</th>
<th>II</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cavity</td>
<td>Small</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>Cavity description</td>
<td>5(^{12})</td>
<td>5(^{12})(^2)</td>
<td>5(^{12})</td>
</tr>
<tr>
<td>Number of cavities per unit cell</td>
<td>2</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>Average cavity radius, Å</td>
<td>3.95</td>
<td>4.33</td>
<td>3.91</td>
</tr>
<tr>
<td>Coordination number*</td>
<td>20</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>Number of water molecules per unit cell</td>
<td>46</td>
<td>136</td>
<td>20</td>
</tr>
<tr>
<td>Crystal type</td>
<td>Cubic</td>
<td>Diamond</td>
<td>Hexagonal</td>
</tr>
</tbody>
</table>

* number of oxygen atoms at the border of each cavity
** estimated from geometric models

The density of gas hydrates is easily found if it is known which structure they possess, since the lattice constants are always close to the same values, 12.0 or 17.4 Å. The average distance between gas molecules in a hydrate of structure I is only 6.0 Å, and 3.1 Å between molecules in water\(^{33}\). Therefore, when the hydrate is formed, the gas is condensed to a density nearly that of a liquid. One mol of methane hydrate weighs 988 grams. The unit cell of structure I has a volume of 12.0\(^3\) Å\(^3\), so one mole occupies 6.022 \(\times 10^{23}\) times as much, or 1040 cm\(^3\). The density of the hydrate is then easily found to be about 0.95 g/cm\(^3\), between ice and water.
2.2.1 Structure I

Structure I gas hydrate is a body centered cubic structure. It is obtained by linking the vertices of $5^{12}$ cavities. Structure I is a usually smaller molecule including the hydrate formers of methane, ethane, carbon dioxide, and hydrogen sulfide. Structure I hydrate is made up of 8 polyhedral cages – 6 large ones and 2 small. This structure is made up of 46 water molecules, and thus has a theoretical composition of $8X \cdot 46 \text{ H}_2\text{O}$ where $X$ is the guest molecule. Structure I hydrates are usually found in-situ in deeper oceans with biogenic gases. A typical Structure I hydrate is presented in Figure 2.2.

![Figure 2.2 Structure I type hydrate](image)

2.2.2 Structure II

Structure II type hydrate is a diamond lattice formed by connecting the faces of $5^{12}$ cavities within a cubic framework. This type forms when natural gases or oils contain molecules larger than ethane. Structure II hydrate formers include propane, iso-butane and butane; however, nitrogen, a relatively small molecule, also forms a structure II hydrate. Structure II hydrates are made up of 24 polyhedral cages – 8 large ones and 16 small. They are made up of
136 water molecules and thus have a theoretical composition of $24 \times 136 \text{H}_2\text{O}$. If only the large cages are occupied, which is typical, then the theoretical composition is $8 \times 136 \text{H}_2\text{O}$. A typical structure II hydrate is presented in Figure 2.3

![Figure 2.3 Structure II type hydrate](image)

**2.2.3 Structure H**

Structure H crystals have the largest volume capacity, and contain iso-pentane hydrocarbons, which are relatively large, branched-chain hydrocarbons. Structure H was discovered by Ripmeester et al who proved that structure H was a double hydrate i.e. this type requires two types of molecules to be stabilized. In structure H, a layer of $5^{12}$ cavities connects a layer of other cavity types. Structure H is composed of three different types of cavities. It contains 34 water molecules associated with three $5^{12}$ cavity guest molecules, two $4^35^66^3$ cavity guest molecules and one $5^{12}6^8$ cavity guest molecules. Smaller guest molecules, such as CH$_4$, N$_2$ and CO$_2$ occupy $5^{12}$ cavities, and large guest molecules such as 2-methylbutane, methylcyclopentane, methylcyclohexane, ethylcyclohexane and cyclooctane occupy $4^35^66^3$
cavities. It bears repeating, Type H hydrates only form if another, small molecule is present. Figure 2.4 shows the constituent cages and an orthogonal view of structure H hydrate.

![Figure 2.4 Structure H type hydrate](image)

2.3 Hydrate Stability

Hydrates are solid mixtures of natural gas and water, which looks like dirty ice. Each mixture of natural gas forms at a range of pressure and temperature combinations. Different natural gas mixtures have their different ranges of hydrate. The maximum temperature for a given pressure or minimum pressure for a given temperature is the equilibrium condition for hydrate formation for a fixed composition mixture. Holder et al published a detailed study of the effects of gas composition and geothermal properties of the environment on hydrate stability. Figure 2.5 shows the three-phase hydrate equilibrium for 80 mol % methane and 20 mol % ethane mixture and identifies the area above the curve as the hydrate stability zone. If pressure and temperature conditions fall into this region, existence of hydrates is expected. Low pressure and high temperature conditions fall below the line indicating the existence of gas, water and/or ice, but no hydrate.
The hydrate phase is a main part of hydrocarbon-water phase diagrams for hydrocarbons whose molecular weight is lower than n-butane. The simplest form of phase relations in hydrocarbon-water systems is a binary system of water and one pure hydrocarbon. Figure 2.6 illustrates the hydrate-forming conditions for paraffin hydrocarbons.

Figure 2.5 Phase behavior diagram of a structure I hydrate\textsuperscript{14}

Figure 2.6 Hydrate-forming conditions for paraffin hydrocarbons\textsuperscript{20}
Low temperatures and/or high pressures are required for the stability of the hydrate structure. In natural environments, these conditions could occur in deep water at shallow depths below the ocean floor. The geothermal gradient of the earth increases the pressure requirement for the stability of the hydrate at a much greater rate than that provided by the available increased pressure from the hydrostatic gradient. Therefore, there is a depth interval where hydrates may be stable. Figure 2.7 demonstrates hydrate stability with depth in a representative marine environment.

![Figure 2.7: Hydrate stability with depth in marine environment](image)

**2.4 Importance of Hydrates in Petroleum Industry**

Hydrates are important as a potential energy source, and as a potential product or phase state for making natural gas easier to transport or store. On the other hand, gas hydrates have been a source of serious problems to the oil and gas industry. Low seabed temperatures
combined with high fluid pressures promote formation of clathrates. These clathrates can block subsea pipelines, and, in the event of a gas kick during drilling, form in the well, and within blowout preventers and choke lines. With ongoing development of offshore oil and gas fields into progressively deeper waters, the potential hazard gas hydrates pose to operations is gaining recognition.

2.4.1 Production

It has been estimated that world reserves of natural gas from hydrates are several times the proven reserves of natural gas\textsuperscript{36}. Thus, methods for production of natural gas from hydrates are getting considerable interest. Kvenvolden\textsuperscript{37} estimates that, the amount of methane trapped in gas hydrates at shallow sediment depths within 6,000 feet of the surface of the earth is approximately between $3.5 \times 10^{16} \text{ ft}^3$ and $1.7 \times 10^{18} \text{ ft}^3$ at standard temperature and pressure. Also, as seen in Figure 2.8, the widespread distribution of hydrate deposits has generated attention as a potential energy resource.

![Figure 2.8 – Worldwide Distribution of Hydrate Deposits\textsuperscript{37}](image)
There are three proposed production methods for commercial production of natural gas from hydrates. These are depressurization, thermal stimulation and inhibitor injection. Depressurization, decreasing the pressure under the hydrate stability zone causes the hydrate to decompose. As a result, dissociated gas moves toward the wellbore. The production scheme is shown in Figure 2.9. The second method is basically to heat reservoir beyond hydrate dissociation temperature, and the last method is to inject an inhibitor such as methanol into the reservoir to decrease the hydrate stability conditions.

![Figure 2.9 – Producing a gas zone by depressurization](image)

2.4.2 Hydrate Prevention and Inhibition

Since hydrates cause major problems in oil and natural gas production operations; the petroleum industry has developed techniques to avoid hydrate formation. The most common technique is thermodynamic inhibition, which can be summarized as: removing one of the components, either the hydrocarbon or water; injecting an inhibitor (particularly methanol); and changing the pressure or temperature of the system. Once hydrate forms in the flow line it is hard to break it down. The difficulty of removing hydrates after they form makes the hydrate prevention measures even more important.
A hydrate requires the presence of natural gas and water under certain conditions of pressure and temperature. In drilling operations, good primary control of the well will prevent kicks and keep the wellbore free of gas. The most practical way to stop hydrates forming during deepwater production operations is to prevent reaction of gas with water by use of chemical inhibitors. If a hydrate forms, inhibitors, heat, and pressure reduction may break it down, but at all times prevention is better than cure.

2.4.3 Transportation and Gas Storage

It is known that 1 ft$^3$ of hydrates contain as much as 150 – 180 ft$^3$ of natural gas$^1$. Also, if gas production from natural gas hydrates is possible then the usage of hydrates in the gas storage can be suggested. Research has been done$^{39,40}$, and it is reported that gas storage can be possible.

In addition to gas storage, converting the gas into hydrate and using it as a transportation mode is being researched. Some researchers$^{41}$ pointed out that use of natural gas hydrates for transportation was a serious alternative to gas liquefaction. But it is also agreed that still more work has to be done.

2.4.4 Problems Encountered During Drilling

Natural gas hydrates present high potential risk of drilling hazards, such as severe gasification of drilling fluid, casing collapse and instability of the open hole or the ocean floor. During offshore drilling, the introduction of external heat source, such as drilling fluid, in the hydrate stability zone causes dissociation of hydrates near the borehole potentially causing severe gasification of drilling fluid, overpressure resulting in blow out, and collapse of casing due to increase in pressure after dissociation. In addition, hydrates can form in the drill string, BOP stack, and choke and kill lines resulting in flow blockage, possibly even requiring abandonment of the well.
In-situ hydrate formations are expected at shallow depths, typically above the surface casing setting depth. The main concern with no BOP installed is hydrate dissociation. If the solid hydrate in the sediments is dissociated while drilling, a gas kick will occur, and the wellbore may become unstable. “If you are drilling into the gas hydrate, you have to worry that the hydrate could suddenly dissociate, leading to collapse of the sediment supporting the drill stem,” Carolyn Ruppel, associate professor of geophysics in Georgia Tech's School of Earth and Atmospheric Sciences, and coordinator of the gas hydrate program, says

In the past, drilling companies have experienced unusual problems when they drilled through hydrate zones. Imperial Oil Ltd and Panarctic Oils Ltd faced problems of well control due to severe mud gasification. Other hydrate related drilling experiences include fizzing drill cuttings, and near blowout situations. Large amount of cuttings generated from the hydrate zone may release large volumes of gas at the surface, threatening the safety of the personnel and the surface equipment. “To prevent hydrate dissociation in the hydrate layers, the mud temperature at depth must be kept below 60°F. Mud temperatures usually were below 37°F. However, it is difficult to prevent hydrate dissociation in cuttings as they come to the surface. While drilling the hydrate layers, return mud was often bubbling with methane gas, and mud gas was more than 70%. To reduce mud gas, the drilling rate was reduced,” reported Takahashi et al.

Conoco UK Ltd experienced a hydrate plug in a deepwater well testing operation in 2,750 feet of water in September 1998. Reyna et al reported that a hydrate plug developed in the landing tubing string between the seafloor and the surface while bringing the well in after perforating the well located in deep water on the UK Atlantic Margin.

2.5 Hydrate Dissociation

Dissociation is defined as breaking down of a compound into its components. When hydrates dissociate, the products are the forming molecules, gas and water. Methane hydrate,
which makes up most of the naturally occurring hydrates, is composed of eight molecules of methane and 46 molecules of water. Therefore, the decomposition reaction can be represented by

$$(8\text{CH}_4 \cdot 46\text{H}_2\text{O})_{\text{solid}} \rightarrow 8(\text{CH}_4)_{\text{gas}} + 46(\text{H}_2\text{O})_{\text{liquid}}$$  \hspace{1cm} (2.1)

One mol of 8CH$_4$·46H$_2$O, methane hydrate, weighs 2.1762 lbs, and occupies 0.03673 ft$^3$. The density of the hydrate is then easily found to be about 59.25 lb/ft$^3$. When the hydrate decomposes in-situ in a sedimentary formation, 46 moles of water, which occupy about 0.0292 ft$^3$, only 0.00749 ft$^3$ in-situ volume remains for the methane. At STP, 8 moles of methane occupy 6.3283 ft$^3$. If methane were unable to flow out of the sediments and was an ideal gas at all pressures, 12,425 psi would be necessary to confine it to the volume available. Obviously, dissociation would be halted by the increasing pressure long before pressures this high were reached. However, this indicates the expansion hazard of increasing the temperature of gas hydrates confined in subsurface formations. Figure 2.10 is a schematic representation of the three-phase equilibrium curve and methods of hydrate decomposition.

Figure 2.10 Schematic representation of the hydrate dissociation methods
The hydrate dissociation reaction is an endothermic reaction. Therefore, it requires an external heat source. Dissociation occurs when the pressure and temperature conditions around the hydrate particles are brought outside the hydrate stability zone. Conceptually, this may happen by reducing the pressure (depressurization), increasing the temperature (thermal stimulation), or changing the hydrate stability conditions (inhibitor injection). The following sections describe previous research by others, primarily focused on production of hydrates, into each dissociation method.

2.5.1 Thermal Stimulation

In these methods, heat is introduced into the hydrate-bearing formation or reservoir, causing destabilization of the hydrate particles. Kamath suggests that the introduction of thermal energy may be achieved from the surface by the injection of hot fluids, including water, brine, or steam, or may involve a downhole process, such as in-situ combustion or electric and electromagnetic heating. However, thermal methods for production are adversely affected by heat loss to nonproductive formations and heat left in the reservoir. Therefore, the economic cost associated with such a gas-recovery technique calls for careful planning and engineering.

2.5.2 Depressurization

In this technique, the pressure of the fluids in contact with hydrate is lowered, pushing the hydrate out of its stability region and leading to its decomposition. Because no extra heat is introduced into the reservoir, the heat of decomposition must be supplied from the surrounding formation. Many studies have indicated that this could be the rate-controlling step in the overall decomposition process. Therefore, this technique could be attractive for production primarily when a large surface area exists for heat transfer and decomposition. The presence of a free-gas zone beneath the hydrate may be essential to the success of the depressurization method for production.
The most common depressurization technique envisions drilling through the hydrate layer and completing the well in the free-gas zone. Gas production from this layer leads to pressure reduction and decomposition of the overlying hydrate. Gas production from the Messoyakha field was based primarily on this depressurization technique\(^\text{36}\).

### 2.5.3 Inhibitor Injection

Injecting inhibitors causes decomposition of a gas hydrate by shifting its thermodynamic-equilibrium curve. However, their application is limited to small volumes because of the high cost associated with inhibitors. It is reported that methanol and a calcium chloride solution were successfully injected for remediation to reopen flow paths in Messoyakha Field\(^\text{36}\).

### 2.5.4 Summary

Initial economic evaluations\(^\text{44}\) show that, for an equal volume of gas produced, thermal stimulation is significantly more expensive than the depressurization method, while gas recovery based on inhibitor injection is probably the most expensive method. Thermal methods may, however, be preferred over the depressurization technique if the latter technique does not lead to practical rates of gas production from low heat-transfer rates.

Most of these production techniques are conceptual and have not been tested in a large scale. With the exception of the reported history of the Messoyakha field, reservoir tests for the production of gas from hydrates are in their infancy. One method of understanding the reservoir behavior during hydrate decomposition is the use of mathematical models validated against production-test results.

### 2.6 Hydrate Dissociation Models

There are several existing models proposed for gas production from hydrate layers. Hydrate dissociation models previously proposed by Holder\(^\text{9}\), McGuire\(^\text{10}\), Bayles\(^\text{11}\), Selim\(^\text{12}\),
Moridis\textsuperscript{13} and Swinkels\textsuperscript{14} are based on thermal method. On the other hand, Burshears\textsuperscript{15}, Yousif\textsuperscript{16} and Ahmadi\textsuperscript{17} studied hydrate dissociation based on depressurization.

Holder\textsuperscript{9} developed a thermal dissociation model in 1982 to simulate the production of gas from a hydrate zone adjacent to a conventional gas reservoir. He did not consider the water production from hydrate dissociation. McGuire\textsuperscript{10} developed two analytical thermal models the same year (1982), which represented the upper and lower bounds on gas hydrate production. Importance of porosity, bed thickness, and injection temperature were determined. An analytical thermal model was developed by Bayles\textsuperscript{11} in 1986 to predict the effects of various reservoir parameters on the energy efficiency ratio. Wellbore heat losses and heat losses to strata above and below the hydrate zone were considered. Selim\textsuperscript{12} studied hydrate dissociation in a semi-infinite, hydrate-filled porous medium. He developed an analytical thermal model using a continuity equation, Darcy’s Law, and energy balance equations for the dissociated and undissociated phases. Moridis\textsuperscript{13} added a CH\textsubscript{4} hydrate module to the existing code of the TOUGH2, which is a thermal, fluid-flow heat transfer simulator. The TOUGH2 model can simulate hydrate dissociation by either thermal stimulation or depressurization via the EOSHYDR module. Swinkels\textsuperscript{14} used a 3D, thermal finite-difference simulator in which the reservoir fluids were represented by three phases: gaseous, hydrate, and aqueous. The heat required for dissociation of hydrate was accounted for in the model.

Burshears\textsuperscript{15} used a 3D, two-phase simulator to address the questions regarding the feasibility of producing gas from hydrates when a conventional gas reservoir is in contact with a hydrate cap. He assumed that the dissociation of hydrates is affected by depressurization. The temperature at any point on the hydrate-gas interface was assumed to be the equilibrium dissociation temperature at the local pressure. Yousif\textsuperscript{16} developed a 1D, three-phase numerical finite difference simulator to simulate gas production from hydrate in a Berea sandstone sample.
in the laboratory. Several experiments were conducted in the laboratory to validate the model. Ahmadi\textsuperscript{17} used a 1D, analytical model to describe gas production from dissociation of methane hydrate in a confined reservoir by depressurization. The release of water during dissociation was not considered. In addition to these, Ullerich\textsuperscript{45} et al studied thermal hydrate dissociation by conducting dissociation experiments on fabricated hydrate samples. They also proposed a mathematical model for predicting the position of the dissociation interface for long time period.

Each of the models reviewed has made a significant contribution toward the development of a practical, realistic, hydrate gas production simulation model. Each model focused on specific characteristics of dissociation, migration, and production of methane from hydrates. Table 2.2 compares the models based on their primary production mechanisms and features, such as porous flow of fluids, dissociation heat, 3D Cartesian reservoir geometry, and field scale capability.

Table 2.2 Comparison of the models based on their features

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<tr>
<th>Model</th>
<th>Primary Production Mechanism</th>
<th>Features</th>
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<tbody>
<tr>
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<td>Dissociation Heat</td>
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<td></td>
</tr>
<tr>
<td>Ahmadi</td>
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<td></td>
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</tbody>
</table>
3. RESEARCH METHOD

3.1 Introduction

High pressure and low temperature underneath the deep sea waters of the Black Sea present a favorable environment for hydrate formation. TPAO/BP considers hydrates a potential safety hazard to drilling operations. Protecting the drilling fluid against hydrate formation is necessary to reduce the risk of flow blockages. Also the Black Sea basin has naturally occurring gas hydrates in the sediments. Structures related to gas plumes, gas saturated sediments and pockmarks can be observed all around the Eastern Black Sea region\textsuperscript{46}. Hence, the Eastern Black Sea has extensive methane accumulations. Moreover, Ivanov\textsuperscript{47} et al reported presence of naturally occurring gas hydrates in the Black Sea. The focus of this project is to answer the question whether the naturally occurring hydrate zones in Eastern Black Sea, Turkey, can be drilled and cased off safely.

Gas hydrate stability conditions usually extend from the seafloor to 500 to 1,700 feet below the sea floor\textsuperscript{1}. In general, gas hydrates are found to be in shallow sediments above the surface casing point and therefore are encountered before the BOP equipment is installed. This means that when gas from hydrates enters the wellbore it rises to the seafloor with the drilling fluid. Under these conditions, the presence of gas can provide the potential for fires and explosions if it surfaces through the water near the rig.

The need for this study lays in the potential risk of destabilization of the in-situ hydrate layers while drilling the surface hole or later when hydrates are behind the casing. Destabilization of in-situ hydrates is different from the problem of hydrate in sub-sea pipelines or drilling riser. Although there has been valuable research done to combat hydrate formation, destabilization of in-situ hydrates while drilling is still an open ended research area.
3.2 Project Description

During drilling through an in-situ hydrate zone, hydrates are exposed to an increased temperature due to heat transferred by the drilling fluid. This causes dissociation of hydrates providing gas influx into the wellbore. If the dissociation is rapid and significant, it can introduce a large influx from the dissociated hydrate zone into the wellbore causing a gas kick.

In order to minimize the problems, potential hydrate zones should be identified by detailed geological and geophysical surveys prior to drilling. Once the presence of hydrates is detected, then precautions can be taken to avoid the problems associated with drilling through hydrates. This typically begins with construction of pressure/depth – temperature diagrams. These diagrams can provide intuitive solutions to control the dissociation of hydrates during drilling.

One solution is to increase the pressure at the hydrate layer by increasing the mud density. The second solution is to use cooler mud, so that the mud column does not become the heat source for the dissociation. However, cooling the mud cannot stop the heat transfer from the deeper formations. A third approach regarding hydrate dissociation control was suggested by Franklin. Instead of inhibiting the dissociation of in-situ hydrates, he suggested drilling with lower mud weight allowing the hydrate to decompose and controlling dissociation rate. The penetration rate would be decreased to keep gas volumes at a rate that surface equipment can handle. Gasified mud would be degassed after returning to the rig, cooled to lower temperatures and re-circulated.

Gas from hydrate dissociation while drilling will enter the wellbore. This gas reduces the hydrostatic pressure of the mud column and further accelerates the hydrate dissociation. If the dissociation is rapid, the risk of gas unloading the well is significant. Gas unloading the well can lead to a blowout.
3.3 Work Plan

The goal of this project is to quantify the significance of potential problems to allow operational methods and well design to be adopted to minimize the impact of hydrates on drilling operations for Eastern Black Sea Offshore Exploration Project. A literature search was undertaken to identify and review published information regarding hydrate structures, stability conditions, dissociation mechanisms and related proposed models. The goal was to find and review information on hydrates as drilling hazards and to determine whether researchers previously proposed a model that can be used as a dissociation model during drilling.

This study presents a thermal model to compute the degree of dissociation during drilling. The model is used to determine the dissociation rates, gas influx rates for given mud weight, mud temperature and specific reservoir conditions. The dissociation model was coupled with a thermal wellbore temperature simulator for the investigation of temperature distribution throughout the well and prediction of heat influx from the drilling fluid into the hydrate zone. Furthermore, the model results are utilized to determine the optimum values of mud weight, temperature and circulating rate to control dissociation.

Evaluation of the hydrate dissociation model validity was made by comparing the dissociation predictions to the results of laboratory experiments by Ullerich et al. The mathematical model used in this study is based on thermal dissociation of hydrates. The assumptions of the mathematical model and Ullerich’s experimental work are similar. Therefore, results of the dissociation model are compared to these laboratory experiments data. Comparisons showed that the agreement between the model predictions and the experimental data is within 15%.

TPAO management provided the End of Project Report for the Western Black Sea Joint Venture Exploration Project. Report includes well design, mud design and casing design details,
formation and seawater properties, and daily drilling report summaries. Drilling report summaries indicated that there was gas shows detected by the remote operate vehicle camera during drilling the shallow portions of the well. Data from Limankoy-1 well was used for temperature simulations and validation of dissociation predictions.
4. BLACK SEA DRILLING HISTORY AND PLANS

This chapter provides information about the background for this research, principally the experience from previous drilling in the Black Sea, and plans for future exploratory drilling that establish the need for this study. A brief summary of data and experience from two exploratory wells drilled in the Western Black Sea, Limankoy-1, and Limankoy-2 is provided. Hopa-1 well, which is a part of the Eastern Black Sea Offshore Exploration Project is introduced, and associated challenges are described.

4.1 Overview of Drilling in Black Sea

The Black Sea lies northeast of the Mediterranean Sea in waters belonging to Bulgaria, Romania, Ukraine, Russia, Georgia, and Turkey. Bounded by areas affected mainly by Tertiary compressive deformation, the sea is composed of two extensional basins, the western and eastern Black Seas, which are separated by the Mid Black Sea High. Figure 4.1 shows the location of Black Sea in the region.

Figure 4.1 Location of Black Sea

Figure 4.1 Location of Black Sea\(^{49}\)
The Black Sea has been poorly explored to date, and success in the region has been limited. Only nine wells have been drilled in the Turkish sector of the Black Sea. Madison Oil Turkey Inc., a subsidiary of Toreador Resources, spudded a tenth well in early May 2005. Madison operates 14 coastal blocks labeled as “TPAO/Madison Blocks” in Figure 4.1. Its work focuses around its Ayazli-1 gas discovery and the surrounding South Akcakoca sub-basin, where 13 potential drilling locations and six prospects have been identified. The six prospects have a reserve potential-per-prospect ranging from 100 bcf to 1 tcf.

The Turkish National Oil Company, TPAO, has a joint venture with BP, a major international oil company, to explore for oil and gas within the deep waters of the Black Sea. TPAO/BP expect to spud their first exploration well, Hopa-1, in late 2005. Hopa-1 lies in water depths between 5,000 feet and 6,000 feet, and was to reach an approximate total depth (TD) of 15,000 feet. The well is in block 3534, and marks the first well drilled in deepwater since ARCO’s two Limankoy wells, which were plugged and abandoned after encountering gas shows in 1999.

4.2 Western Black Sea Offshore Exploration Project

The most relevant deepwater drilling experience in the Black Sea is in the Western Black Sea Concession. TPAO and ARCO entered into a Joint Operating Agreement upon ARCO farming into the Western Black Sea Concession in September of 1995. The farmout agreement gave TPAO a working interest of 51% and ARCO the remaining interest of 49%. The concession was approximately 3,000,000 acres and covers 50% of Turkey’s Black Sea acres. As per the agreement, ARCO shot 6,000,000 acres of 2D seismic in 1996. TPAO and ARCO shot 170,000 acres of 3D seismic over the Limankoy Prospect in 1997. Following the 2D and 3D seismic programs, the partners agreed to drill two deepwater exploration wells on the Limankoy Prospect. The location of Limankoy Prospect is presented in Figure 4.2.
TPAO was the operator and ARCO supervised the drilling. A Joint Drilling Team was formed in January 1998. The Sedco rig contract was signed in April 1999. Sedco 700 arrived in Istanbul on June 12th 1999, spudded Limankoy-1 on July 4th and the rig was released from Limankoy-2 on October 11th. The objective of the Limankoy was to determine the presence of hydrocarbons and their probable volumes.

Limankoy-1 was drilled to a TD of 9,039 feet RKB in a water depth of 2,802 feet. A 9-7/8” pilot hole was drilled riserless to the planned 13-3/8” casing setting depth of 4,701 feet RKB. The main purpose of the pilot hole was to determine whether shallow gas, or shallow water flows would be a problem and the ability to jet the 30” conductor casing. A wellbore
Daily drilling report summaries\textsuperscript{48} indicated that strong gas shows were observed by the remote operated vehicle (ROV) camera between 584 feet and 663 feet below seafloor. Although there was continuous small gas shows below this depth, a short trip at 1,043 feet below seafloor was made without any problems. After the pilot hole was completed, a flow check was made. The well did not flow, and the pilot hole was abandoned with 10.5 ppg mud.

The surface hole was drilled riserless with sea water to a total depth of 4,701 feet with a 16” bit. Similar to the pilot hole, small gas shows were observed by the ROV camera between 351 feet (3117 ft RKB) and 1,512 feet (4314 ft RKB) below seafloor. 13-3/8” casing was run with a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Planned vs. actual casing diagram of Limankoy-1 well\textsuperscript{48}}
\end{figure}
18-3/4” well head housing. Mud was circulated and conditioned for cementing. Casing was landed and cemented at a total depth of 4,682 feet RKB.

The 9 5/8” casing string was set prematurely due to a kick taken at 5,853 feet. The original planned depth to set the 9 5/8” casing was at 6,890 feet. During the course of drilling the 12 ¼” hole with a mud weight of 9.4 ppg at a depth of 5,853 feet, it was noticed that a loss of 80 psi had occurred on the equivalent circulating density (ECD) read out from the Anadrill pressure-while-drilling (PWD) tool. The drill string was picked up and the well shut in. An influx of 8 barrels was recorded. The well was successfully killed in three circulations with 10.3 ppg mud. Due to the 10.5 ppg leak-off test (LOT) at the 13 3/8” shoe set at 4,682 feet it was decided to set 9 5/8” casing here. The well was plugged and abandoned after reaching a total depth of 9,039 feet without further incidents.

Limankoy-2 was drilled to a total depth of 10,912 feet RKB in 2,247 feet water depth. A 9-7/8” pilot hole was drilled riserless to the 20” casing setting depth of 3,694 feet RKB. As in the Limankoy-1, the purpose of the pilot hole was to check the firmness of the near surface formations before jetting the 30” casing and to determine if any shallow gas or water flow hazards were present. A wellbore diagram showing the planned and actual casing programs for the Limankoy-2 well is presented in Figure 4.4.

The pilot hole was drilled without any indication of gas. While drilling the 24” surface hole, small gas shows were observed by the ROV camera between 358 feet (2,602 ft RKB) and 1,220 feet (3,464 ft RKB) below seafloor. The gas shows in this hole interval were potentially the result of hydrate dissociation, but no related complications were encountered. 20” casing was landed and cemented at a total depth of 3,766 feet below RKB. Blow out preventers (BOP) were run and tested. The cement shoe was drilled out with a 17-1/2” bit, and a leak off test was conducted. Leak off occurred at 10.9 ppg equivalent.
Figure 4.4 Planned vs. actual casing diagram of Limankoy-2 well

The next section of the well was drilled to a total depth of 5,614 feet with a 12-1/4” bit, and was opened with a 16” bit. While drilling with a 12-1/4” bit, mud weight had to be increased from 10 to 10.3 ppg at a total depth of 5,577 feet due to a considerable increase in connection gas. Mud weight was increased from 10.3 to 10.5 at 5,610 feet. This section of the well was drilled with a salt/glycol/polymer mud to avoid hydrate formation in the wellbore. Salt concentration was maintained at 20% with sodium chloride and potassium chloride to ensure a completely hydrate inhibitive mud. The well was drilled to a total depth of 10,913 feet, and plugged and abandoned. No hydrate related problems were encountered.

4.3 Eastern Black Sea Offshore Exploration Project

The Eastern Black Sea Offshore Exploration Project is described on the TPAO website.

The concession comprises the area east of 37°07’30”E and west of 38°52’30”E between the outer limit of the 12 mile territorial water boundary of the Republic of Turkey and the Black Sea.
Median Line boundary with the Former Soviet Union. The license covers an area of 5,639,792 acres. Water depth within the license is in the range of 4,000 feet to 7,500 feet.

There are no exploration wells in the Eastern Black Sea Offshore except for a shallow (2,049 ft) deep-sea drilling program (DSDP) well. However, onshore near the Central Black Sea, 15 exploration wells have been drilled by TPAO to the south of the license area. Figure 4.5 shows the borders of eastern Black Sea offshore exploration concession.

![Figure 4.5. Eastern Black Sea Offshore Exploration Concession Borders]

TPAO and BP entered into a Joint Operating Agreement upon BP farming into the Eastern Black Sea Concession in December 20, 2001. The joint operating agreement is being described on the TPAO website as follows: “TPAO/BP Joint Exploration Project has since continued within the scope of Joint Venture (JV) Agreement in the east of Black Sea where BP is operator. In 2004, the evaluation of 725 miles of 2D and 3D seismic data was begun. As a result
of the intensive studies realized by BP and TPAO, a drilling location, the Hopa prospect, was selected in November 2004 for drilling to obtain information about the potential of the Eastern Black Sea.” In 2004, the drill ship Explorer of the Global SantaFe company, coming from the Mexican Gulf to the Black Sea, was selected for drilling the Hopa-1 well. The Global SantaFe Explorer arrived at the Black Sea in late July 2005, and has been drilling the Hopa-1 well since August 2005. Figure 4.6 shows the Global SantaFe Explorer under the bridge passing through the Bosporus.

4.3.1 Eastern Black Sea Challenges

The Black Sea is one of the largest inland seas in the world. Off the shelf, the water depth quickly plunges to an average depth of 6000 feet. The Black Sea sediments are rich in calcite and organic carbon, the latter showing a high degree of preservation due to anoxia in the waters below 400 feet. The potential for slope failure and sediment instability related to immense gas and gas hydrate accumulations have been identified as a serious problem that could lead to the failure of offshore installations.
Recently, sonar and high-resolution seismic surveys were carried out to obtain information about the effects of gas and gas-filled sediments throughout the Turkish margin of the Eastern Black Sea, and shallow gas was detected on the sub-bottom profiler records. It typically continues to about 80-200 feet below the sea floor. Large amounts of gas hydrates were also discovered on the lower section of the Turkish shelf\textsuperscript{51}. Figure 4.7 is a sub-bottom profiler record from the Turkish shelf area showing two pockmarks and strongly reflective gas hydrate layers.

![Sub-bottom Profiler Record from the Turkish Shelf Area Showing Two Pockmarks and Strongly Reflective Gas Hydrate Layers](image)

Figure 4.7 Sub-bottom Profiler Record from the Turkish Shelf Area Showing Two Pockmarks and Strongly Reflective Gas Hydrate Layers\textsuperscript{51}

Alkan\textsuperscript{52} investigated the physical parameters of the water column such as temperature, salinity and density in Eastern Black Sea very close to the Hopa-1 well location. According to this study, seawater temperature at the surface was recorded to be the highest at 84°F in August, and the lowest at 50°F in March. The seawater temperature at 650 feet was 41°F, and found to be
independent of the seasonal changes. Below 3,500 feet the water temperature was constant at 36°F.

4.3.2. Eastern Black Sea Offshore Exploration Project Challenges

The first exploration well within the project, Hopa-1, is being drilled in a water depth between 5,000 feet and 6,000 feet, and will reach an approximate 15,000 feet TD. The well was spud in August 2005, and drilling has been continuing. The well marks the first well drilled in deepwater in the Turkish Black Sea since 1999. The well has all the typical challenges of a deepwater well.

Eastern Black Sea sediments have naturally occurring gas hydrates in addition to the challenges listed above. These in-situ hydrates in the Eastern Black Sea are shallow. Ciftci et al reported that hydrate accumulations start 50-150 feet below the seafloor. Hydrate stability conditions at the Eastern Black Sea Concession area extend to a depth of 1,500 feet below the seafloor so that the hydrate layer thickness is potentially as much as 1,350-1,450 feet. Dissociation of hydrates while drilling is a possibility because of the changes in pressure and temperature during drilling, and the effects of drilling fluid composition. Prevention of hydrate dissociation is necessary to maintain well control and safety of both the well and well-site personnel. Therefore, the purpose of this study is to determine how to avoid or mitigate these concerns relating to in-situ hydrates during drilling operations on the Hopa-1 well.
5. HYDRATE DISSOCIATION MODEL FOR DRILLING OPERATIONS

Solid hydrates under the naturally occurring pressure and temperature conditions may dissociate if pressure and temperature conditions are changed. On this basis, several recovery processes have been suggested that can be divided broadly into three categories: depressurization, thermal stimulation, and inhibitor injection. There are numerous hydrate dissociation models available to predict the amount of gas production from hydrate layers. Most of the previous hydrate dissociation models\textsuperscript{9,10,11,12,13,14} are based on thermal methods. On the other hand, some researchers\textsuperscript{15,16,17} studied hydrate dissociation based on a depressurization technique. These studies concentrated on feasibility of gas production from naturally occurring hydrate layers. However, neither hydrate dissociation as a drilling hazard, nor the effects of dissociation on well design were addressed. Therefore, a simple 1D linear analytical thermal model is proposed for hydrate dissociation calculations that can be used in conjunction with a radial temperature distribution model to investigate the behavior of dissociation during drilling. Moreover, this model can also be used to predict the amount of dissociation behind the casing.

5.1 Evaluation of Wellbore Conditions During Drilling

In order to ensure the safety of drilling and producing deepwater oil and gas resources located below marine hydrate deposits we need to investigate the hydrate behavior with changing pressure and temperature conditions. During conventional drilling operations, drilling fluid is circulated down the drill string and up the annulus. Returns are taken to the shale shakers through the bell nipple. Usually drilling fluid density is kept slightly greater than the formation pore pressure to avoid any well kick situations. However, most of the surface holes in deepwater wells are drilled riserless with returns back to sea floor.

While drilling the surface hole with returns back to sea floor, wellbore pressures are primarily controlled by the drilling fluid density. In order to prevent the dissociation of in-situ
hydrates due to depressurization, the wellbore pressure at hydrate layers must be kept greater than the hydrate stability pressure. This can be achieved by maintaining the drilling fluid density such that wellbore pressure is always slightly greater than the hydrate stability pressure. If the pressure requirement to keep hydrate layers in solid state is met, then hydrate dissociation due to depressurization is not likely to occur.

Salt is added to drilling fluids to prevent hydrate formation during drilling. Ebeltorf\textsuperscript{53} et al studied the effect of salt concentration in drilling fluids on hydrate equilibrium conditions. They reported that increased salt concentrations significantly reduce the hydrate equilibrium temperature for a constant pressure. According to their experiments under a pressure of 5,580 psi the hydrate equilibrium temperature reduced by 16.7°F with a 20\% by weight potassium chloride (KCl) addition to the drilling fluid. At 1,683 psi, a 15.7°F reduction was observed. Similarly, addition of 20\% by weight sodium chloride salt to the drilling fluid changes hydrate equilibrium by 24°F. However, most surface holes are drilled with seawater. Compared to fresh water, seawater, under constant pressure, reduces hydrate equilibrium temperature by 2–3°F. Therefore, the risk of dissociation due to changing thermodynamic equilibrium conditions is low and may be eliminated if the drilling fluid is not protected against hydrate formation.

The third dissociation mechanism is thermal stimulation. Under constant pressure, hydrates may dissociate if an external heat source is introduced. During drilling operations the drilling fluid is being circulated down the drillstring and up the annulus. The temperature of the drilling fluid will increase if the geothermal temperatures of the formations are greater than the mud temperature. While the warm mud is being circulated up the annulus, it interacts with the hydrates. The in-situ temperature of the hydrate is typically less than the drilling fluid temperature. Therefore, during drilling operations, drilling fluid may serve as an external heat source. Changing the thermal properties of the drilling fluid, optimizing the circulation rates and
cooling the mud at surface may slow the dissociation process. However, heat transfer between the drilling fluid and the deeper, hotter formations cannot be completely eliminated. Hence, the warm fluid being circulated up the annulus can give a wellbore temperature at the hydrate layers that may exceed the equilibrium temperature during drilling.

5.2 Proposed Analytical Hydrate Dissociation Model

A mathematical model for hydrate dissociation has been developed. The model calculates dissociation of pure hydrate in one dimension of a semi-infinite medium with constant physical properties due to a constant heat flux incident on a plane perpendicular to the direction of flux. The dissociation is driven by a constant heat flux from the drilling fluid. However, the diameter of the wellbore increases due to dissociation, and this causes a decrease in effective heat flux at hydrate boundary. The governing differential equations describing the rate of dissociation are presented. Results from the solution are presented in graphs, which can be used to estimate the amount of hydrate dissociated as a function time. Drilling fluid is assumed to be a heat source for thermally dissociating the hydrate. Results of a laboratory experiment conducted by Ullerich are used to validate the predictions from the proposed model. Model assumptions and limitations are given below.

5.2.1 Model Assumptions

The thermal hydrate dissociation model presented here was built on basic assumptions. These assumptions can be listed as follows:

- The hydrate is assumed to be a pure structure I methane hydrate.
- There is no sediment in the dissociating hydrate layer.
- Dissociation is due to thermal effects only; that is depressurization is negligible.
- A one-dimensional, semi-infinite geometry is considered.
- There is no other heat source other than circulating drilling fluid.
• Wellbore temperature is greater than the dissociation temperature.
• Heat flux from the drilling fluid is constant.
• The water formed in the dissociation process is removed as the dissociation proceeds.
• There is a small time period to increase the hydrate face temperature to dissociation temperature, and this time is negligible.

5.2.2 Model Limitations

This model cannot handle dissociation with depressurization. When hydrate associated gases enter the wellbore, they mix with the drilling fluid, and density of the drilling fluid decreases. This may trigger dissociation due to pressure reduction. Given that the goal of this project is to avoid dissociation, this possibility has not been considered. For the sake of simplicity, this model does not account for sediments; however, hydrates fill only the pores in the rock body. Heat loss into the adjacent formations was not considered. Heat from the drilling fluid is spent to increase the hydrate layer’s temperature to its dissociation temperature, and thereafter for dissociation. The model does not consider the heat spent to increase water and gas temperatures after dissociation.

5.2.3 Mathematical Formulation of the Hydrate Dissociation Model

Consider a hydrate body initially at a uniform temperature, \( T_i \), and occupying a semi-infinite region \( 0 < x < \infty \). At \( t = 0 \), a constant heat flux, \( Q \), is applied to the hydrate body. Body temperature starts increasing from \( T_i \) to \( T_d \), which is the dissociation temperature of the hydrate. There exists a thermally disturbed zone initially with a thickness of \( \delta \) starting from the wellbore. Dissociation starts and the boundary surface, \( X_D \), moves in the positive x-direction. Thickness of the thermally disturbed zone is \( (X_D - \delta) \) after dissociation starts. At the same time, the temperature of the boundary rises from \( T_i \) to \( T_d \). Thereafter; the temperature of the moving
boundary remains constant at $T_d$. Figure 5.1 shows the physical situation around a wellbore in a hydrate zone when the wellbore temperature is greater than the dissociation temperature of hydrates. The dissociated zone, $Z_D$, and solid hydrate zone, $Z_S$, are separated by a moving boundary $X_D$. The boundary moves away from the wellbore as heat is supplied to the system.

![Figure 5.1 Physical conditions around a wellbore in a hydrate zone](image)

There is a heat flow from the wellbore to the hydrate. The heat flow from the wellbore to the hydrate increases the temperature of the hydrate. There is a thermally disturbed zone with a thickness of $\delta$ where the temperature has increased before dissociation starts. Figure 5.2 shows the movement of the dissociation front in the hydrate zone for a radial geometry.

![Figure 5.2 Movement of the boundary in the hydrate zone for a radial geometry](image)
Figure 5.2 (a) illustrates the initial conditions, before any heat flux is applied to the hydrate. (b) shows the thermally disturbed zone before dissociation starts. (c) shows the position of the dissociation interface and the thermally disturbed zone after dissociation starts.

However, the model is a one-dimensional, linear model. The dissociation interface is assumed to be a slab that has the same length as its circumference. Movement of the dissociation front in the hydrate body for the slab assumption is given in Figure 5.3. As given in Figure 5.2, Figure 5.3 (a) illustrates the initial conditions, (b) shows the thermally disturbed zone, and (c) shows the location of dissociation and the thermally disturbed zone for a 1D system.

![Figure 5.3 Movement of the dissociation front in the hydrate body for a slab](image)

Once the dissociation front location is calculated from the model, radial geometry can be used for hole enlargement, effective heat flux, and gas influx calculations.

### 5.2.3.1 Initiating Dissociation

Let $t_d$ be the time required for the boundary surface to reach the equilibrium temperature. When the wellbore temperature is considerably higher than the hydrate dissociation temperature, $t_d$ is fairly small. Thus, for $t < t_d$ the problem may be considered as a fixed boundary problem. The fixed boundary problem may be then regarded as a heating problem preceding hydrate dissociation.
The appropriate differential equation for the fixed-boundary problem is basically the linear form of the heat equation. Differential equations for associated boundary conditions and initial conditions are given by

\[ \frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad 0 < x < \infty, \quad t > 0 \]  

................................. (5.1)

Inner boundary condition:

\[ -k \frac{\partial T}{\partial x} = Q \quad x = 0, \quad t > 0 \]  

................................. (5.2)

Outer boundary condition:

\[ T = T_i \quad x = \infty, \quad t > 0 \]  

................................. (5.3)

Initial Condition:

\[ T = T_i \quad 0 < x < \infty, \quad t = 0 \]  

................................. (5.4)

The variables used in derivations are defined in Appendix C – Nomenclature.

Integrating (5.1) with respect to x over the interval \([0, \delta(t)]\) we get

\[ \frac{d}{dt} \left( \int_{x=0}^{x=\delta(t)} Tdx - T_i \delta \right) = -\alpha \frac{\partial T}{\partial x}(0, t) \]  

................................. (5.5)

Mr. Suat Namli, a PhD candidate at Louisiana State University Mathematics Department, proposed that this problem could be solved with an \(n^{th}\) degree polynomial approximation. For the sake of simplicity, we assumed that the temperature can be expressed as a forth degree polynomial function.

Let \( T = c_4 x^4 + c_3 x^3 + c_2 x^2 + c_1 x + c_0 \)  

................................. (5.6)

The five necessary conditions to determine the coefficients, \(c_i\)

\[ \frac{\partial T}{\partial x}(0, t) = -\frac{Q}{k} \]  

................................. (5.7)
\[ T(\delta, t) = T_i \] ................................................................. (5.8)

\[ \frac{\partial T}{\partial x}(\delta, t) = 0 \] ................................................................. (5.9)

\[ \frac{\partial^2 T}{\partial x^2}(\delta, t) = 0 \] ................................................................. (5.10)

\[ \frac{\partial^3 T}{\partial x^3}(\delta, t) = 0 \] ................................................................. (5.11)

Using conditions (5.7) through (5.11) we get coefficients \(c_1\) through \(c_4\). Writing these coefficients into the fourth degree polynomial (5.6) becomes

\[ T(x, t) = \frac{Q}{k} \delta \left[ \frac{1}{4} \left( \frac{x}{\delta} \right)^4 - \left( \frac{x}{\delta} \right)^3 + \frac{3}{2} \left( \frac{x}{\delta} \right)^2 - \left( \frac{x}{\delta} \right) + \frac{1}{4} \right] + T_i \] ........................................... (5.12)

Writing (5.12) into (5.5)

\[ \frac{d}{dt} \int_0^{\delta(1)} \left( \frac{Q}{k} \delta \left[ \frac{1}{4} \left( \frac{x}{\delta} \right)^4 - \left( \frac{x}{\delta} \right)^3 + \frac{3}{2} \left( \frac{x}{\delta} \right)^2 - \left( \frac{x}{\delta} \right) + \frac{1}{4} \right] + T_i \right) dx - T_i \delta \right) = -\alpha \frac{\partial T}{\partial x}(0, t) \ldots (5.13) \]

Solving the LHS of (5.13) we get

\[ \frac{d}{dt} \left( \frac{1}{20} \frac{Q}{k} \delta^2 \right) = -\alpha \frac{\partial T}{\partial x}(0, t) \] ................................................................. (5.14)

Applying the power rule to the LHS of (5.14), combining with (5.7) and doing the substitutions

\[ \delta d\delta = 10\alpha dt \] ................................................................. (5.15)

Integrating (5.15) we get

\[ \frac{\delta^2}{2} = 10\alpha t \Rightarrow \delta^2 = 20\alpha t \Rightarrow \delta = \sqrt{20\alpha t} \] ................................................................. (5.16)

Writing \( x = 0 \) into (5.12) and writing (5.16) in place we get

\[ T(0, t) = \frac{Q}{k} \sqrt{\frac{5}{4}} \alpha t + T_i \] ................................................................. (5.17)
Hydrate dissociation starts when $T(0, t) = T_d$ at $t = t_d$, then

$$T(0, t_d) = T_d = \frac{Q}{k} \sqrt{\frac{5}{4}} \alpha t_d + T_i \quad \text{.......................... (5.18)}$$

Solving (5.31) for $t_d$

$$t_d = 4 \frac{k^2}{5 \alpha Q^2} (T_d - T_i)^2 \quad \text{.......................... (5.19)}$$

**Example Calculation:**

Circulating seawater with a rate of 1000 gal/min, mass rate is:

$$m = (1000 \text{gpm})(3.785 \text{lt/gal})(60 \text{min/hr}) \times (8.8 \text{ppg/8.33kg/ltr}) = 239,914 \text{kg/hr}$$

We assume that the temperature drop in the annulus at steady state is due to the heat loss into the surrounding formations. For this particular example temperature drop through the annulus is 0.015K/m. This temperature gradient was obtained from a thermal wellbore simulator discussed in Chapter 6. Then, the total heat flow into the formation can be easily calculated.

$$Q_t = (239,914 \text{kg/hr})(1.0 \text{cal/K})(0.015 \text{K/m})(1.163 \text{watt.hr/kcal}) = 4185 \text{watt}$$

Then, the effective heat flow to the hydrate face is

$$Q = \frac{Q_t}{\pi d} = \frac{4,185 \text{watt/m}}{\pi(17.5 \text{in})(0.0254 \text{m/in})} = 2,997 \text{watt/m}^2$$

The effective heat flux is 2,997 watt/m$^2$ and is constant unless the face area changes. Before the start of dissociation, the hydrate face area is constant. Assuming an initial temperature of 41°F (278K) at hydrate layer and a dissociation temperature of 50°F (283K), and using the thermal conductivity and thermal diffusivity in table 5.1, we can calculate the position of thermally disturbed zone, $\delta(t)$, and time at start of dissociation, $t_d$.

$$t_d = 4 \frac{k^2}{5 \alpha Q^2} (T_d - T_i)^2 \Rightarrow t_d = \frac{4}{5} \left( \frac{(0.5^2)}{(3.02 \times 10^{-7})(2,997^2)} \right) (283 - 278)^2 = 1.84 \text{sec}$$
\[ \delta = \sqrt{20 \alpha t_d} \Rightarrow \delta = \sqrt{20 \times (3.02 \times 10^{-7})(1.84)} = 0.00333 \text{ m} = 0.33 \text{ cm} \approx 0.13 \text{ in} \]

<table>
<thead>
<tr>
<th>Table 5.1 Parameters used for example calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity of hydrate, k, W/m-K</td>
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<tr>
<td>Thermal diffusivity ( \alpha ) of hydrate, m(^2)/s</td>
</tr>
<tr>
<td>Initial temperature of hydrate, ( T_i ), K</td>
</tr>
<tr>
<td>Hydrate dissociation temperature, ( T_d ), K</td>
</tr>
<tr>
<td>Heat Flux at the boundary, ( Q ), W/m(^2)</td>
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</tbody>
</table>

It is obvious from the example calculation that time spent heating the hydrate zone before the start of dissociation is small, and thickness of thermally disturbed zone is also negligible.

### 5.2.3.2 Progressing Dissociation Front

When \( t > t_d \) the problem becomes a moving boundary problem. The appropriate differential equations for the moving-boundary problem, and associated boundary conditions and initial conditions are given by:

\[
\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad X_D(t) < x < \infty, \quad t > 0 \quad \ldots \quad (5.20)
\]

Moving boundary conditions:

\[
T = T_d \quad \quad x = X_D(t), \quad t > 0 \quad \ldots \quad (5.21)
\]

\[
-k \frac{\partial T}{\partial x} + \rho L \frac{dX_D}{dt} = Q \quad x = X_D(t), \quad t > 0 \quad \ldots \quad (5.22)
\]

Outer boundary condition:

\[
T = T_i \quad \quad x = \infty, \quad t > 0 \quad \ldots \quad (5.23)
\]

Initial Condition:

\[
T = f(x) \quad \quad 0 < x < \infty, \quad t = t_d \quad \ldots \quad (5.24)
\]

Where, the function \( f(x) \) is obtained from the solution of the fixed-boundary problem.
Integrating (5.20) with respect to x over the interval $[X_D(t), \delta(t)]$

\[
\int_{x=X_b(t)}^{x=\delta(t)} \frac{\partial T}{\partial t} \, dx = \int_{x=X_b(t)}^{x=\delta(t)} \alpha \frac{\partial^2 T}{\partial x^2} \, dx 
\]

(5.25)

Solving the LHS we get

\[
\int_{X_b(t)}^{\delta(t)} \frac{\partial T}{\partial t} \, dx = \frac{d}{dt} \left[ \int_{x=X_b(t)}^{x=\delta(t)} T \, dx - T_d \delta + \left( T_d + \rho L \frac{\alpha}{k} \right) X_D(t) \right] 
\]

(5.26)

Solving the RHS with the help of the moving boundary described in (5.22) we get

\[
\int_{X(t)}^{\delta(t)} \alpha \frac{\partial^2 T}{\partial x^2} \, dx = \frac{Q}{k} 
\]

(5.27)

Combining the LHS and the RHS equations, (5.20) becomes:

\[
\frac{d}{dt} \left[ \int_{x=X(t)}^{x=\delta(t)} T \, dx - T_d \delta + \left( T_d + \rho L \frac{\alpha}{k} \right) X_D(t) \right] = \alpha \frac{Q}{k} 
\]

(5.28)

As before, let the temperature $T$ at any point be a fourth order polynomial represented by the equation below.

\[
T = c_4 x^4 + c_3 x^3 + c_2 x^2 + c_1 x + c_0 
\]

(5.29)

The five necessary conditions to determine the coefficients, $c_i$

\[
T(X_D, t) = T_d 
\]

(5.30)

\[
T(\delta, t) = T_1 
\]

(5.31)

\[
\frac{\partial T}{\partial x}(\delta, t) = 0 
\]

(5.32)

\[
\frac{\partial^2 T}{\partial x^2}(\delta, t) = 0 
\]

(5.33)

\[
\frac{\partial^3 T}{\partial x^3}(\delta, t) = 0 
\]

(5.34)

With the help of (5.30)
\[ T = c_4X_D^4 + c_3X_D^3 + c_2X_D^2 + c_1X_D + c_0 = T_d \] ............................................. (5.35)

With the help of (5.31)
\[ T = c_4\delta^4 + c_3\delta^3 + c_2\delta^2 + c_1\delta + c_0 = T_i \] ............................................. (5.36)

Using conditions (5.32) through (5.34) we get \( c_1, c_2 \) and \( c_3 \) in terms of \( c_4 \)

\[ c_3 = -4c_4\delta \] ................................................................. (5.37)

\[ c_2 = 6c_4\delta^2 \] ................................................................. (5.38)

\[ c_1 = -4c_4\delta^3 \] ................................................................. (5.39)

Writing \( c_1, c_2, c_3 \) and \( c_4 \) into (5.35) and (5.36), and eliminating \( c_0 \) we get

\[ c_4 = -\frac{T_i - T_d}{(\delta - X_D)^4} \] ................................................................. (5.40)

So, the rest of the coefficients can easily be calculated

\[ c_3 = -4c_4\delta \Rightarrow c_3 = 4\delta \frac{T_i - T_d}{(\delta - X_D)^4} \] ................................................................. (5.41)

\[ c_2 = 6c_4\delta^2 \Rightarrow c_2 = -6\delta^2 \frac{T_i - T_d}{(\delta - X_D)^4} \] ................................................................. (5.42)

\[ c_1 = -4c_4\delta^3 \Rightarrow c_1 = 4\delta^3 \frac{T_i - T_s}{(\delta - X_D)^4} \] ................................................................. (5.43)

\[ c_0 = -\delta^4 \frac{T_i - T_d}{(\delta - X_D)^4} + T_i \] ................................................................. (5.44)

Writing all coefficients in (5.29) and rearranging the expression we get

\[ T = \frac{T_i - T_d}{(\delta - X_D)^4} \left[ -x^4 + 4\delta x^3 - 6\delta^2 x^2 - 4\delta^3 x - \delta^4 \right] + T_i \] ................................................................. (5.45)

Integrating (5.45) with respect to \( x \) over the interval \([X(t), \delta(t)]\) and rearranging
\[
\int_{x=X}^{x=\delta} T\,dx = \frac{T_i - T_d}{(\delta - X_D)^4} \left(\frac{\delta - x}{5}\right)^5 + T_i x \bigg|_{x=X(1)}^{x=\delta(t)} = -\frac{T_i - T_d}{5} (\delta - X_D)^5 + T_i \delta - T_i X_D \quad \cdots (5.46)
\]

Then (5.28) becomes
\[
\frac{d}{dt} \left[ -\frac{T_i - T_d}{5} (\delta - X_D) - T_i X + \left( T_d + \rho L \frac{\alpha}{k} \right) X_D(t) \right] = \frac{\alpha}{k} Q \quad \cdots \cdots \cdots (5.47)
\]

Rearranging (5.47) we get
\[
\frac{d}{dt} (\delta - X_D) + 5 \left( 1 + \frac{\rho L \alpha}{k(T_d - T_i)} \right) \frac{dX_D}{dt} = \frac{5\alpha Q}{k(T_d - T_i)} \quad \cdots \cdots \cdots (5.48)
\]

Stefan number is known as the ratio of latent to sensible heat, and is defined as:
\[
\nu = \frac{L}{C_p \Delta T} = \frac{L}{C_p(T_d - T_i)} = \frac{\rho L \alpha}{k(T_d - T_i)} \quad \cdots \cdots \cdots (5.49)
\]

Writing Stefan number in (5.48) we get
\[
\frac{d}{dt} (\delta - X_D) + 5(1 + \nu) \frac{dX_D}{dt} = \frac{5\alpha Q}{k(T_d - T_i)} \quad \cdots \cdots \cdots (5.50)
\]

Rearranging (5.22)
\[
\rho L \frac{dX_D}{dt} = Q + k \frac{\partial T}{\partial x} \bigg|_{x=X_\nu(t)} \quad \cdots \cdots \cdots (5.51)
\]

If we write (5.45) into (5.51) we get
\[
\rho L \frac{dX_D}{dt} = Q + k \left( \frac{T_i - T_d}{(\delta - X_D)^4} \left( x^4 + 4\delta x^3 - 6\delta^2 x^2 - 4\delta^3 x - \delta^4 \right) + T_i \right) \bigg|_{x=X_\nu(t)}
\]
\[
\rho L \frac{dX_D}{dt} = Q + k \left( \frac{T_i - T_d}{(\delta - X_D)^4} (\delta - x)^3 \right) \bigg|_{x=X_\nu(t)}
\]
\[
\frac{dX}{dt} = Q - \frac{4k}{\rho L} \left( \frac{T_d - T_i}{\delta - X_D} \right) \quad \cdots \cdots \cdots (5.52)
\]
Equations (5.50) and (5.52) are two simultaneous differential equations for \((\delta - X_D)\) and \(X_D\). The initial conditions are

\[
X_D = 0 \quad \text{at} \quad t = t_d \quad \text{.................................} \quad (5.53)
\]

\[
\delta = \frac{4k(T_d - T_i)}{Q} \quad \text{at} \quad t = t_d \quad \text{.................................} \quad (5.54)
\]

Writing (5.54) in (5.51) and rearranging the expression we get

\[
\frac{d}{dt}(\delta - X_D) - 5(1 + \nu)\frac{4k(T_d - T_i)}{\rho L (\delta - X_D)} + 5 \left(1 + \frac{\rho L \alpha}{k(T_d - T_i)}\right) \frac{Q}{\rho L} - \frac{5\alpha Q}{k(T_d - T_i)} = 0 \quad \ldots \quad (5.55)
\]

Writing Stefan number into (5.55) and multiplying both sides of the equation by \(\frac{\rho L}{5Q}\) we get

\[
\frac{\rho L}{5Q} \frac{d}{dt}(\delta - X_D) - (1 + \nu)\frac{4k(T_d - T_i)}{Q(\delta - X_D)} + 1 = 0 \quad \text{.................................} \quad (5.56)
\]

Dimensionless thickness of the thermally disturbed zone, \(\varepsilon\), can be defined as:

\[
\varepsilon = \frac{Q(\delta - X_D)}{4k(T_d - T_i)} \quad \text{.................................} \quad (5.57)
\]

Then \(d\varepsilon = \frac{Q}{4k(T_d - T_i)}d(\delta - X_D)\) and

\[
d(\delta - X_D) = \frac{4k(T_d - T_i)}{Q} d\varepsilon \quad \text{.................................} \quad (5.58)
\]

Writing (5.58) in (5.56) we get

\[
\frac{4k(T_d - T_i)\rho L}{5Q^2} \frac{d\varepsilon}{dt} - (1 + \nu)\left(\frac{1}{\varepsilon}\right) + 1 = 0 \quad \text{.................................} \quad (5.59)
\]

A dimensionless time, \(\tau\), can be defined as:

\[
\tau = \frac{5Q^2}{4k(T_d - T_i)\rho L} t \quad \text{.................................} \quad (5.60)
\]
Then \[ d\tau = \frac{5Q^2}{4k(T_d - T_i)\rho L} \] \[ dt = \frac{4k(T_d - T_i)\rho L}{5Q^2} d\tau \] \[ \] \[ \] \[ (5.61) \]

Writing (5.61) in (5.59) we get

\[ \frac{d\varepsilon}{d\tau} - (1 + \nu)\frac{1}{\varepsilon} + 1 = 0 \] \[ \] \[ \] \[ (5.62) \]

Writing the initial conditions, (5.53) and (5.54), in (5.57) we get

\[ \varepsilon = \frac{Q(\frac{4k(T_d - T_i)}{Q} - 0)}{\frac{Q}{4k(T_d - T_i)}} = 1 \] \[ \] \[ \] \[ (5.63) \]

Writing (5.60) at \( t = t_d \) we can find the dimensionless time, \( \tau_d \), at start of dissociation.

\[ \tau_d = \frac{5Q^2}{4k(T_d - T_i)\rho L} t_d = \frac{5Q^2}{4k(T_d - T_i)\rho L} \frac{4k^2(T_d - T_i)^2}{5\alpha Q^2} \]

\[ \tau_d = \frac{k(T_d - T_i)}{\rho \alpha L} = \frac{1}{\nu} \] \[ \] \[ \] \[ (5.64) \]

Rearranging (5.62) we get

\[ \frac{d\varepsilon}{d\tau} = (1 + \nu)\frac{1}{\varepsilon} - 1 \] \[ \] \[ \] \[ (5.65) \]

This function is hard to integrate so,

\[ \frac{d\tau}{d\varepsilon} = \frac{\varepsilon}{(1 + \nu)\varepsilon - \varepsilon} \]

\[ d\tau = \frac{\varepsilon d\varepsilon}{(1 + \nu)\varepsilon - \varepsilon} \] \[ \] \[ \] \[ (5.66) \]

Integrating (5.66) we get\[ \int_{\tau_d}^{\tau} d\tau = \int_{\varepsilon}^{\varepsilon} \frac{\varepsilon}{(1 + \nu)\varepsilon - \varepsilon} d\varepsilon . \]

Solution of this integral is
\[ \tau - \tau_d = 1 - \epsilon + (1 + \nu) \ln \left( \frac{\nu}{1 + \nu - \epsilon} \right) \] ........................................ (5.67)

If we write (5.55) and (5.61) in (5.52) we get
\[ \frac{\rho L}{Q} \frac{dX_D}{4k(T_d - T_i)\rho L d\tau} = 1 - \frac{1}{\epsilon} \] ........................................ (5.68)

Dimensionless position of the dissociation interface, \( X^* \), can be defined as:
\[ X^* = \frac{5QX_D}{4k(T_d - T_i)} \] ........................................ (5.69)

Writing (5.69) in (5.68) and rearranging the equation we get
\[ \frac{dX^*}{d\tau} = \frac{\epsilon - 1}{\epsilon} \] ........................................ (5.70)

With the initial condition
\[ X^* = 0 \quad \text{at} \quad \tau = 0 \] ........................................ (5.71)

It is hard to solve (5.70) in this form. If we multiply and divide the LHS of (5.70) by \( d\epsilon \) we get
\[ \frac{dX^*}{d\epsilon} \frac{d\epsilon}{d\tau} = \frac{\epsilon - 1}{\epsilon} \] ........................................ (5.72)

Rearranging and taking the reciprocal of (5.62)
\[ \frac{d\tau}{d\epsilon} = \frac{1}{(1 + \nu) \frac{1}{\epsilon} - 1} = \frac{\epsilon}{1 + \nu - \epsilon} \] ........................................ (5.73)

Writing (5.73) in (5.72) and after doing substitutions, and rearranging the equation we get
\[ \frac{dX^*}{d\epsilon} = \frac{\epsilon - 1}{1 + \nu - \epsilon} \] ........................................ (5.74)

With \( X^* = 0 \) at \( \epsilon = 1 \) ........................................ (5.75)

In (5.74)
\[ \frac{\epsilon - 1}{1 + \nu - \epsilon} = \frac{\epsilon - 1 + \nu - \nu}{1 + \nu - \epsilon} = \frac{\nu}{1 + \nu - \epsilon} = \frac{\nu}{1 + \nu - \epsilon} - 1 \]
Substituting this expression in place and integrating (5.74) we get

\[ \int_0^{X^*} dX^* = \int_{1}^{\epsilon} \left( \frac{\nu}{1 + \nu - \epsilon} - 1 \right) d\epsilon \]

Solution of this integral is

\[ X^* = 1 - \epsilon + \nu \ln \left( \frac{\nu}{1 + \nu - \epsilon} \right) \]

\[ \text{..........................} \]

(5.76)

Mr. Namli\textsuperscript{54} indicated (5.76) could not be solved analytically. He added that this problem could be solved with the help of inverse functions, and work is under its way in this direction.

Progression of the dimensionless thermally disturbed zone thickness versus dimensionless time can be calculated from (5.67). Figure 5.4 illustrates the development of the dimensionless disturbed zone thickness versus dimensionless time for different Stefan numbers.

![Figure 5.4 Development of the dimensionless thermally disturbed zone thickness versus dimensionless time](image)

From the figure, it is seen that the disturbed zone thickness becomes constant after a certain time. Equation (5.48) may be used to give a long-time solution:
\[
\frac{d}{dt}(\delta - X_D) + 5 \left(1 + \frac{\rho L \alpha}{k(T_d - T_i)}\right) \frac{dX_D}{dt} = \frac{5\alpha Q}{k(T_d - T_i)}, \quad \text{and} \quad \nu = \frac{\rho L \alpha}{k(T_d - T_i)}
\]

\[
\frac{dX_D}{dt} = \frac{\alpha Q}{k(T_d - T_i)(1 + \nu)}
\]

Integrating (5.77) over the interval \([0, \infty]\) we get

\[
X_D = \frac{\alpha Q}{k(T_d - T_i)(1 + \nu)} t \quad \text{.................................................. (5.78)}
\]

Substituting dimensionless time and dimensionless position of the dissociation front into (5.78) we get

\[
\frac{4k(T_d - T_i)}{5Q} X^* = \frac{\alpha Q}{k(T_d - T_i)(1 + \nu)} \frac{4\rho L k(T_d - T_i)}{5Q^2} \tau
\]

\[
X^* = \frac{\nu}{1 + \nu} \tau \quad \text{.................................................. (5.79)}
\]

Integrating (5.79) over the interval \([0, \infty]\) we get

\[
X^* = \frac{\nu}{1 + \nu} (\tau - \tau_d) \quad \text{.................................................. (5.80)}
\]

It is known from (5.64) that \(\tau_d\) is equal to \(1/\nu\). Substituting (5.64) into (5.80), and with necessary substitutions, we get \(X^* = (\tau - 1)/(\nu + 1)\). Therefore, the position of the dimensionless dissociation interface, \(X^*\), can be calculated as a function of dimensionless time, \(\tau\). Figure 5.5 shows the relationship between \(\tau\) and \(X^*\).

As seen from figure 5.5, the speed of the dissociation interface slows down with increasing time, eventually attaining a constant value. After \(\tau = 1\), \(\tau\) and \(X^*\) are directly proportional regardless of the Stefan number. Setting \(\tau = 1\), in (5.60) we can solve for time, \(t\).

\[
t = \frac{5Q^2}{4k(T_d - T_i)\rho L} \Rightarrow t = \frac{0.8k\rho L(T_d - T_i)}{Q^2}
\]
Using the properties given in Table 5.1 and Table 5.2, time, t, is found to be 69.24 seconds. We can then easily calculate the position of the dissociation front for times larger than 69.24 seconds. Below is an example calculation of dissociation for one hour.

\[ \nu = \frac{L}{C_p(T_d - T_i)} = \frac{338,000}{1,800(283 - 278)} = 37.55 \]

\[ X_D = \frac{1}{1 + \nu} \frac{\alpha Q}{k(T_d - T_i)} t = \frac{1}{(1 + 37.55) \left( \frac{3.02 \times 10^{-7}}{(0.5)(283 - 278)} \right)} (2,997) = 0.034 \text{ m} = 3.4 \text{ cm} \]

Using the long time solution for one hour, it is seen that the hydrates will have dissociated a distance of 3.4 cm.

Table 5.2 Properties used in example dissociation calculation

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of dissociation, L, Ws/kg</td>
<td>338,000</td>
</tr>
<tr>
<td>Specific heat of hydrate, C_p, Ws/kg-K</td>
<td>1800</td>
</tr>
<tr>
<td>Density of hydrate, ( \rho ), kg/m^3</td>
<td>920</td>
</tr>
</tbody>
</table>
5.2.4 Application of 1-D Dissociation Model to Radial System

The dissociation model presented in this study is a 1-D, linear analytical model that can be used to calculate the location of the dissociation interface for given parameters. However, the model can be applied to a radial geometry assuming x = 0 at the wellbore, and calculating the location of the dissociation as a function of distance from the wellbore. After dissociation starts, the wellbore size increases to larger diameters as the dissociation front progresses. Setting x = 0 at the new wellbore location of the dissociation front at a given point in time, \( X_D(t_n) \), becomes the distance from the new wellbore. Thus, \( X_D \) becomes an increment rather than the actual position as shown in Figure 5.1. To improve accuracy of the calculations, small time increments must be selected.

The radial solution is based on the following approach. Assume a wellbore with an initial diameter of \( d_i \). The drilling fluid is providing a constant heat flux at the wellbore while being circulated up the annulus. When the hydrate is heated to a temperature at or above its dissociation temperature, dissociation starts. After the dissociation front starts moving in the positive x-direction, a hole size progression begins. Therefore, the hydrate face area increases, causing a decrease in effective heat flux at the wellbore radius.

A spreadsheet computer program can be used to calculate the location of the dissociation front with changing heat flux, which is a function of the wellbore diameter. The dissociation interface can be calculated for initial heat flux. After dissociation, the wellbore diameter is increased to \( d_{i+1} \). The new wellbore diameter is used to calculate the interface area, and the effective heat flux at the new wellbore.

Hole diameter, as a function of time, can be calculated from

\[
d(t_{n+1}) = d(t_n) + 2X_D(t_n) \quad \text{..........................................................} \quad (5.81)
\]
Where \( X_D(t_n) = \frac{\alpha Q(t_n)}{k(T_d - T_i)(1 + \nu)} \Delta t_n \)

Effective heat flux at the interface is basically a function of the wellbore diameter and can be expressed as:

\[
Q(t_{n+1}) = Q(t_n) \frac{d(t_n)}{d(t_{n+1})} \quad \text{.............................................................. (5.82)}
\]

Hole diameters presented in Figure 5.6 are calculated from (5.81) using \( X_D(t_n) \) from the dissociation model. An example calculation, for an initial wellbore diameter of 17.5 in and using the same parameters used in the previous example, is given below.

\[
d(t = 1 \text{ hr}) = d(t = 0) + 2X_D(t = 1 \text{ hr})
\]

\[
d(t = 1 \text{ hr}) = 17.5 \text{ in} + 2 \times 3.4 \text{ cm} \times \frac{1 \text{ in}}{2.54 \text{ cm}} = 20.18 \text{ in}
\]

Figure 5.6 Hole size vs. time

Figure 5.6 shows the hole size as a function of time. This enlargement affects the effective heat influx into the hydrate. Effective heat influx can be calculated by replacing
wellbore size with new wellbore diameter after dissociation begins, as given in (5.82). An example calculation, for an initial heat flux of 2,997 watt/m² and using the same parameters as given in the previous example, is given below.

\[ Q(t = 1 \text{ hr}) = Q(t = 0) \frac{d(t = 0)}{d(t = 1 \text{ hr})} \]

\[ Q(t = 1 \text{ hr}) = 2,997 \frac{17.5}{20.18} = 2,599 \text{ watt/m}^2 \]

Similarly, heat flux is found to be 2,371 W/m² after two hours, and 2,202 W/m² after three hours. The decrease in predicted effective heat flux over time is presented in Figure 5.7.

![Figure 5.7 Effective heat flux vs. time](image)

The dissociation front location can be calculated from (5.78). Figure 5.8 presents the location of the dissociation front as a function of time from the beginning to 48 hours. It is obvious from the figure that the dissociation front velocity decreases with time. When the same wellbore and formation parameters are used for a shorter time (60 min) period, the model
predicts that dissociation is faster and more significant within the first 10-15 minutes. Figure 5.9 is a graphical illustration of the location of the dissociation front for the first hour. The movement of the dissociation front for longer time can also be predicted with the model.

Figure 5.8 Location of dissociation front as a function of time

Figure 5.9 Location of dissociation front as a function of time for first hour
5.3 Validation of the Model

The dissociation model presented in this study can be validated by a comparison to a previous experimental study by Ullerich et al. In addition, the facts (gas shows while drilling Limankoy-1) presented in Chapter 4 can be used to evaluate the model.

Ullerich et al conducted a series of experiments to investigate the dissociation of methane hydrates. Hydrates were formed first by pressurizing fine grained compacted snow to 600 psi using 99.97% methane while the sample temperature was kept constant at -45°F, then increasing the cell temperature to 34°F. A constant heat flux was introduced to the system to measure the degree of dissociation based on thermal stimulation. The model used in this study is based on thermal dissociation. Therefore, results of the dissociation model are compared with the experiment data. Figure 5.10 compares the model predictions to Ullerich’s experiment.

![Figure 5.10 Comparison of the model predictions with laboratory experiment results](image)

The agreement between the model predictions, assuming a thermal conductivity of 0.49 W/m-K, and the experimental data is within 15%. In fact, the agreement for the short time (0.1 hr) is within a range of 5%.
Limankoy-1 and Limankoy-2, the wells drilled in the Black Sea, had gas shows detected by the remote operated vehicle camera while drilling the upper sections of the wells. Daily drilling report summaries indicated that strong gas shows were observed by the remote operated vehicle camera while drilling the Limankoy-1 pilot hole between 584 feet and 663 feet below seafloor. Similarly, small gas shows were observed by the remote operated vehicle camera while drilling between 351 feet (3117 ft RKB) and 1,512 feet (4314 ft RKB) below the seafloor in the surface hole.

The Limankoy-2 pilot hole was drilled without any indication of gas. While drilling the 24” surface hole, small gas shows were observed by the ROV camera while drilling between 358 feet (2,602 ft RKB) and 1,220 feet (3,464 ft RKB) below seafloor.

Since the upper sections of the wells were drilled riserless, there is no quantitative record indicating the volume of gas, or rate of influx from these formations. However, the intervals where the gas was observed fall within and below the hydrate stability boundaries. The gas observed may have been the result of dissociation of in-situ hydrates even though this cannot be proven with the existing data.

5.4 Gas Influx Calculations

Once the location of the dissociation front is determined, cumulative gas production from the hydrate formation can easily be calculated. Figure 5.11 illustrates the dissociated zone for unit thickness at time t.

![Figure 5.11 Graphical illustration of the dissociated zone at time t](image-url)
Assuming that one unit volume of hydrate gives 160 unit volumes of gas at standard conditions, the cumulative volume of the gas associated with hydrates can be estimated. The cumulative volume of gas produced from one foot of pure hydrate at surface conditions is:

\[ N = 160 \times \frac{[d + 2X_D(t)]^2 - d^2}{1029.4} \times 5.615 \]

\[ N = 3.49 \times [(X_D(t))^2 + dX_D(t)] \]

The same parameters, as given in Table 5.1 and 5.2, were used to calculate the cumulative gas volume and results are presented in Figure 5.12. The figure shows the cumulative gas production (in scf) per foot of hydrate drilled as a function of time. If the hydrate thickness, \( h_d \), is known, cumulative gas influx can be calculated by multiplying (5.81) by the thickness. For example, 200 feet of hydrates will produce 271.4 MSF of gas at surface after 24 hours.

Figure 5.12 Cumulative gas influx per ft of pure hydrate layer as a function of time
The gas influx rate at standard conditions can be estimated from the movement of the dissociation front. The dissociation front at time $t_1$, $X_D(t_1)$, will move to $X_D(t_2)$ at time $t_2$. Dividing the dissociated volume by differential time, $(t_2 - t_1)$ gives the gas influx rate at reservoir conditions. Thus, multiplying the dissociated volume by 160 gives the rate of influx at standard conditions. The gas influx rate equation is given in (5.84). Figure 5.13 graphically illustrates the physical meaning of the parameters used in (5.84).

$$n = 160 \times \frac{[d + 2X_D(t_2)]^2 - [d + 2X_D(t_1)]^2}{1029.4 \times (t_2 - t_1)} \times 5.615$$

$$n = 3.49 \times \frac{[X_D(t_2)]^2 - [X_D(t_1)]^2 + d[X_D(t_2) - X_D(t_1)]}{t_2 - t_1} \quad \cdots \quad (5.84)$$

Figure 5.13 Physical meaning of the parameters used in (5.84).

Figure 5.14 shows the gas influx rate (in scf/min) per ft of pure hydrate as a function of time. It is evident from Figure 5.14 that the gas influx rate decreases with time. As the hydrate face area becomes larger, the effective heat influx at the hydrate face decreases. After a rapid decrease at early times, gas influx rate is almost halved at 24 hours, and stays essentially constant thereafter. For a fixed hydrate thickness of 200 ft the initial gas influx is 86 scf/min. This is reduced down to 60 scf/min at 6 hours, and 50 scf/min after 24 hours.
5.5 Mud Density Reduction due to Influx

Drilling fluids are primarily a mixture of water and finely divided solids. The drilling mud in the annulus also contains the drilled solids from the rock broken by the bit and the formation fluids that were contained in the rock.

The average density of a mixture of several components is given by

\[ \rho = \frac{\sum_{i=1}^{n} \rho_i f_i}{\sum_{i=1}^{n} f_i} \]  \hspace{1cm} (5.85)

As long as the components are liquids and solids, the component density is essentially constant throughout the entire length of the column. Thus, the average density of the mixture also will be essentially constant. If one component is a finely divided gas, the density of the gas component decreases with decreasing pressure. The determination of hydrostatic pressure at a given depth in a gas cut mud can be made through use of the real gas equations. If \( n \) moles of gas
are associated with 1 gallon of drilling fluid, the volume fraction of gas at a given point in the column is given by

\[
 f_g = \frac{\frac{\text{znRT}}{P}}{1 + \frac{\text{znRT}}{P}} \quad \text{………………………………………………………} (5.86)
\]

Then, the effective density of the mixture is given by

\[
 \bar{\rho} = \rho_f (1 - f_g) + \rho_g f_g = \frac{(\rho_f + \text{Mn})P}{P + \text{znRT}} \quad \text{………………………………………………………} (5.87)
\]

For common field units, substitution of this expression for mean density into the equation for hydrostatic pressure yields

\[
 \int_{D_1}^{D_2} \text{d}D = \int_{P_1}^{P_2} \frac{\text{P + znRT}}{0.052(\rho_f + \text{Mn})} \text{d}P \quad \text{………………………………………………………} (5.88)
\]

If the variation of z and T is not too great over the column length of interest, they can be treated as constants of mean values $\bar{z}$ and $\bar{T}$. Integrating the equation above

\[
 D_2 - D_1 = \frac{P_2 - P_1}{0.052(\rho_f + \text{Mn})} + \frac{\bar{z} \text{R} \bar{T}}{0.052(\rho_f + \text{Mn})} \ln \frac{P_2}{P_1} \quad \text{………………………………………………………} (5.89)
\]

After calculating $P_1$ the average fluid density can easily be calculated by

\[
 \bar{\rho} = \frac{P_1}{0.052D} \quad \text{…………………………………………………………………..} (5.90)
\]

5.6 Cuttings Generation

The volumetric rate of cutting generated is directly proportional to the rate of penetration (ROP). Thus, the volumetric rate of cuttings generated during drilling can be calculated as given below.

\[
 q_c \text{[bbl/hr]} = \frac{\left(\text{d(in)}\right)^2}{1029.4(\text{in}^2\text{ft}/\text{bbl})} \times \text{ROP[ft/hr]} \quad \text{……………………………………} (5.91)
\]
5.7 Dissociation of Hydrate Cuttings

Using the dissociation model for constant heat flux and constant bottom hole area, the dissociation of cuttings can be predicted. Figure 5.15 shows the constant heat flux, \( Q \), to the bottom of the well.

![Figure 5.15 Constant heat flux to the bottom of the well](image)

Drilling fluid temperature could be greater than the hydrate dissociation temperature at the bottom of the well. In this case, depending on the surface fluid temperature and the cooling from the seawater column, the heat flux to the bottom of the well was assumed to be same as the heat flux applied to the walls of the wellbore. However, this is a rough estimate, and cannot be used as a rule of thumb. The bottomhole area is constant, therefore the effective heat flux into the bottom of the well can be estimated by dividing the heat flux into the bottom hole area. An example of the dissociation calculation for constant heat flux is given below.

\[
Q = \frac{4.185 \text{ watt}}{\frac{\pi}{4} \left( (17.5\text{ in})(0.0254\text{ m/in}) \right)^2} = 26,969\text{ watt/m}^2
\]

Using the same parameters from the previous example rate of dissociation per hour at the bottom of the well can be calculated as follows.

\[
X_D = \frac{1}{1 + \nu} \frac{\alpha Q}{k(T_d - T_i)} t = \frac{1}{(1 + 37.55)} \frac{(3.02 \times 10^{-7})(26,969)}{(0.5)(283 - 278)} \times 3,600 = 0.304 \text{ m/hr} = 0.998 \text{ ft/hr}
\]
It is seen from the example that approximately 1 ft of hydrate dissociates as the cuttings are generated. Assuming a ROP of 100 ft/hr, it is obvious that only 1% of the cuttings dissociate as the hydrate layer is being drilled. The remaining portion of the cuttings will be carried to the surface or seafloor by the drilling fluid.

The density of the hydrate cuttings is less than the density of the sea water. Therefore the hydrate cuttings will float in the water, and will be carried to the surface by the bouyant forces. For the sake of simplicity, it may be assumed that dissociation while drilling can be ignored. Also, it may be assumed that the hydrate cuttings will dissociate immediately at a depth where pressure and temperature conditions are out of the hydrate stability.

The volume of gas at the surface associated with dissociation of cuttings while drilling through pure hydrates can be estimated from the rate of penetration as follows.

\[
q_g [\text{bbl/hr}] = 160 \times (\text{ROP})[\text{ft/hr}] \frac{[d(\text{in})]^2}{1029.4[\text{in}^2/\text{ft}]/\text{bbl}}
\]

\text{...............} \quad (5.92)

Using the same parameters as in the previous examples, the volumetric rate of gas at standard conditions associated with cuttings dissociation is

\[
q_g = 160 \times 100[\text{ft/hr}] \frac{[17.5(\text{in})]^2}{1029.4[\text{in}^2/\text{ft}]/\text{bbl}} = 4760 \text{ bbl/hr}, \text{ which is equivalent to a gas rate of } 641.5 \text{ MScf/day at surface conditions. If the rate of penetration was reduced by half, then the volume of gas at surface would be } 320.7 \text{ MScf/day. In the likely case of hydrates residing in the porosity of the mineral sediments, the gas rate would be this rate multiplied by the porosity.}

5.8 Hydrate Dissociation Behind Casing

When drilling below casing set across hydrates, circulating temperatures will typically exceed the hydrate stability temperature. The solid line in Figure 5.16 is the hydrate stability curve. Hydrate behind the casing may dissociate due to the increase in temperature during
circulation. The top dashed line is the expected dissociation behavior of the hydrate formation behind the casing. As mentioned before, dissociation products are water and gas. When hydrate dissociates, approximately 80% of the volume is occupied by water. Gas has to fit in only 20% of the volume. Because of the limited volume, the pressure in the free gas will be greater than the original formation pressure. In addition, the pressure of the free gas in the hydrate layer tends to increase if the temperature increases. Dissociation behind the casing continues until the pressure in the free gas becomes greater than the hydrate stability pressure at that particular temperature. If the pressure reaches the hydrate stability pressure, no further dissociation will occur.

As formation pressure increases above the initial in-situ pressure, the collapse differential pressure on the casing increases. The bottom dashed line in Figure 5.16 illustrates the development of the collapse differential pressure. Increased pressure behind the casing may cause collapse of the casing if the collapse rating of the casing is insufficient. Figure 5.16 was created using actual data from Limankoy-1 well provided by TPAO, the Turkish National Oil Company. The collapse rating of the 13-3/8” surface casing landed in Limankoy-1 was 2,260 psi.
In the case shown, a wellbore temperature greater than 72°F would potentially cause casing collapse. Makogon⁵ has reported a casing collapse incident due to hydrate dissociation. However in most cases, casing collapse rating is greater than the overburden pressure. If gas pressure is greater than the overburden pressure, the gas will escape before the pressure is high enough to cause casing collapse. However, it may propagate a fracture toward the surface with the resulting risk of initiating a crater or a seafloor blowout.

Hydrates in sediments are generally not pure hydrates but are located in porosity. Hydrates in a porous media keep the grains consolidated. After the dissociation of the hydrates, grain to grain loading of the formation may increase causing formation compaction. Point loading effects on the casing may occur if the unconsolidated formation cannot support the weight of the overburden. Also, if the well is located on a steeply sloping seafloor, then there is an additional risk that a mudslide could be initiated that might damage, or even shear, the casing.
6. TEMPERATURE DISTRIBUTION IN THE WELLBORE

Throughout drilling operations, temperatures of fluids in the wellbore vary and the temperature distribution in the formation changes. Solid hydrates under the naturally occurring pressure and temperature conditions may dissociate if pressure and temperature conditions change during drilling operations. Knowledge of these temperatures is necessary in order to predict the heat flow and behavior of the hydrate layers exposed in the wellbore. In this section, static and circulating mud temperatures, and factors affecting the temperature distribution in the well will be explained. GTEMP, a wellbore temperature simulator, was used to determine the effects of various parameters that influence the temperature distribution in the wellbore. In addition, the simulator was used for calculating the heat temperature distributions in and near wellbore. Furthermore, the temperature distribution in the annulus was used to calculate the heat flux from the drilling fluid to the hydrate formations. Validity of GTEMP\textsuperscript{8} temperature simulator used in this study will be assessed by comparisons with an analytical model proposed by Holmes and Swift\textsuperscript{57}.

6.1 GTEMP Wellbore Temperature Simulation Model

GTEMP\textsuperscript{8}, Maurer Technology’s (MTI) Wellbore Temperature Simulation Model, is a tool for analyzing temperature profiles in drilling/completion/production applications. This model was jointly developed by MTI and the Department of Modern Mechanics of the University of Science and Technology of China, USTC.

GTEMP\textsuperscript{8} is a downhole thermal simulation model developed for improving the prediction of down-hole temperatures. The program models natural and forced convection, conduction within the wellbore, as well as heat conduction within the surrounding rock formation. A wide variety of well operations can be modeled including liquid or steam injection, liquid or steam production, and forward and reverse circulation with liquid or gas.
Important technical features of GTEMP$^8$ include the following: It handles boreholes of any inclination from vertical to horizontal. It graphically shows temperatures in tubing, annulus, and other selected locations. It can calculate temperature gradients in multi-layer rock formations. It handles mixing and cooling in the surface fluid tanks. It calculates fully transient heat conduction for wellbore flow stream and rock formations.

Wellbore fluid-flow options include injection and production, forward and reverse circulation, inlet temperature, flow rate, and fluid property changes, multiple fluids in wellbore, and two-phase steam injection and production. Well completion options include casing size, weight, and setting depth, variable tubing area, length of cement columns, and annulus packer fluids. GTEMP$^8$ supports English, metric and customized systems of units. Customized units allow you to select any combination of English and/or metric units. The output window provides a wide variety of informative graphs and reports, such as wellbore schematic, undisturbed geothermal temperature plot, measured depth temperature profile table and graph, radial temperature profile table and graph, pressure and temperature at fixed time and pressure and temperature at a fixed depth that may be printed or stored to disk.

6.2 Static Wellbore Temperature

The geothermal gradient is the rate of change of temperature with depth, in the earth. Units of measurement are °F/100 ft or °C/km. Temperatures at the surface of the earth are controlled by the Sun and the atmosphere, except for areas such as hot springs and lava flows. From shallow depths to about 200 feet below the surface, the temperature is generally constant at about 55°F. In a zone between the near surface and about 400 feet, the gradient is variable because it is affected by atmospheric changes and circulating ground water. Below that zone, temperature almost always increases with depth. However, the rate of increase with depth varies considerably with both tectonic setting and the thermal properties of the rock$^{58}$.
The vertical temperature distribution in the well follows the geothermal gradient, which is a measure of how rapidly the temperature increases as a function of depth. On the other hand, seawater temperatures often decrease with the increasing water column. The rate of change in the water temperature with respect to depth is known as hydrothermal gradient. The temperatures in the wellbore are equal to the geothermal and/or hydrothermal temperatures after long shut in periods or suspended operations. Figure 6.1 shows a typical hydrothermal and geothermal temperature distribution in an offshore environment.

![Figure 6.1 Geothermal and Hydrothermal Temperatures](Image)

### 6.3 Dynamic Wellbore Temperature

A through knowledge of the mud temperature profiles developed during drilling is helpful. Complete temperature profiles for the fluid in both pipe and the annulus may aid in revealing information about downhole conditions. In addition, accurate prediction of maximum temperatures to be encountered during drilling allows for hydrate dissociation calculations.

#### 6.3.1 Calculation of Circulating Mud Temperatures

Holmes and Swift\(^5\)\(^7\) proposed a model for calculation of circulating mud temperatures, which is a solution of steady-state equation for the heat transfer between the fluids in the annulus
and the fluids in the drill pipe. This is then combined with an approximate equation for the transient heat transfer between the fluids in the annulus and in the formation. Using the proposed model, temperatures can be calculated as a function of well depth, circulation flow rate, mud properties, formation properties, wellbore size and the drill pipe size. The Holmes and Swift\textsuperscript{57} model will be used to evaluate the validity of GTEMP\textsuperscript{8}, thermal wellbore simulator. A description of the Holmes and Swift model is provided in Appendix B. Using the properties given in Table 6.1 for a gulf coast well, the temperature distribution can be calculated. Figure 6.2 shows the temperature distribution throughout the well calculated with the analytical model.

The same data was used as input data for temperature simulation with GTEMP\textsuperscript{8} to verify the validity of the temperature simulator. Figure 6.3 shows the temperature distribution calculated with the GTEMP\textsuperscript{8} simulator. The results from analytical temperature model and GTEMP\textsuperscript{8} wellbore temperature simulator match very well. Consequently, GTEMP will be used for determining wellbore temperatures for this study.

![Figure 6.2 Temperature distribution with analytical model](image-url)
Figure 6.3 Temperature distribution with GTEMP simulator

Table 6.1 Well and Drilling Fluid Circulating Properties for a Gulf Coast Well\(^5^7\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well depth, ft</td>
<td>15,000</td>
</tr>
<tr>
<td>Drill pipe OD, in</td>
<td>6.625</td>
</tr>
<tr>
<td>Bit size, in</td>
<td>8.375</td>
</tr>
<tr>
<td>Circulation rate, bbl/hr</td>
<td>300</td>
</tr>
<tr>
<td>Inlet mud temperature, °F</td>
<td>75</td>
</tr>
<tr>
<td>Mud thermal conductivity, Btu/(ft-°F-hr)</td>
<td>1.0</td>
</tr>
<tr>
<td>Mud specific heat, Btu/(lb-°F)</td>
<td>0.4</td>
</tr>
<tr>
<td>Mud density, lb/gal</td>
<td>10.0</td>
</tr>
<tr>
<td>Formation thermal conductivity, Btu/(ft-°F-hr)</td>
<td>1.3</td>
</tr>
<tr>
<td>Formation specific heat, Btu/(lb-°F)</td>
<td>0.2</td>
</tr>
<tr>
<td>Formation density, lb/cuft</td>
<td>165</td>
</tr>
<tr>
<td>Surface earth temperature, °F</td>
<td>59.5</td>
</tr>
<tr>
<td>Geothermal gradient, °F/ft</td>
<td>0.0127</td>
</tr>
</tbody>
</table>

6.3.2 Factors Influencing Circulating Mud Temperature

Naturally occurring hydrates dissociate if wellbore temperatures become higher than the hydrate dissociation temperature. In general, wellbore temperatures greater than the formation
temperatures cause a heat flux into the formation. The heat flux is the leading parameter in
dissociation process. Therefore, the dissociation of hydrates is directly related to the temperature
distribution in the wellbore. In order to avoid hydrate dissociation during drilling in the open
hole or behind the casing, the wellbore temperature at hydrate layers must be kept less than
hydrate dissociation temperature. This parametric study was done to investigate the effects of
different factors on the wellbore temperature distribution so that insight would be gained as to
what parameters might be most efficiently adjusted to minimize hydrate dissociation.

There are numerous factors affecting the circulating mud temperature, such as properties of
the drilling fluid, drilling fluid circulation rate, wellbore geometry, properties of the drill string,
formation properties, static geothermal temperatures, geothermal temperature gradient, surface
temperature and stand pipe temperature. In this section, the effects of the different factors above
on the temperature distribution will be investigated. Results will be presented in graphs.
Wellbore and drilling fluid circulation properties for the base case are given in Table 6.2 below.

<table>
<thead>
<tr>
<th>Table 6.2 Well and drilling fluid circulating properties for the base case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well depth, ft</td>
</tr>
<tr>
<td>Drill pipe OD, in</td>
</tr>
<tr>
<td>Pipe thermal conductivity, Btu/(ft-°F-hr)</td>
</tr>
<tr>
<td>Bit size, in</td>
</tr>
<tr>
<td>Circulation rate, gpm</td>
</tr>
<tr>
<td>Inlet mud temperature, °F</td>
</tr>
<tr>
<td>Mud thermal conductivity, Btu/(ft-°F-hr)</td>
</tr>
<tr>
<td>Mud specific heat, Btu/(lb-°F)</td>
</tr>
<tr>
<td>Mud density, lb/gal</td>
</tr>
<tr>
<td>Formation thermal conductivity, Btu/(ft-°F-hr)</td>
</tr>
<tr>
<td>Formation specific heat, Btu/(lb-°F)</td>
</tr>
<tr>
<td>Formation density, lb/cuft</td>
</tr>
<tr>
<td>Surface earth temperature, °F</td>
</tr>
<tr>
<td>Geothermal gradient, °F/ft</td>
</tr>
</tbody>
</table>
6.3.2.1 Flow Rate

As flow rate is decreased, the resulting decrease in energy input to the wellbore causes the temperature profile initially to become cooler. However, a point is reached where further flow rate reductions produce less heat loss to the cooler overburden and therefore lead to warmer overall wellbore temperatures. Temperature distribution for a 5000 feet well was calculated for three different circulation rates, 100 gpm, 300 gpm, and 500 gpm. Results of the simulations are given below in Figure 6.4.

![Figure 6.4 Effect of circulation rate on temperature distribution](image)

6.3.2.2 Mud Properties

Mud properties; such as density and specific heat capacity have significant effect on the temperature distribution in the well. For example, temperatures of oil-based fluids increase about two times more than water-based fluids with the same amount of heat\(^5\).

Increase in mud density requires more solids in the mud, and concentration of solids affect the specific heat capacity of the drilling fluid. Specific heat is the ratio of the quantity of
heat required to raise the temperature of a body one degree to that required to raise an equal mass of water one degree. Specific heat of water is 1.0 Btu/(lb-°F), on the other hand, 10.0 ppg mud has a specific heat of 0.4 Btu/(lb-°F).\(^{57}\)

A simulation was done to investigate the effect of mud properties on the wellbore temperature distribution. Figure 6.5 illustrates the comparison between circulating the well with a 10.0 ppg water based mud, and with 8.33 ppg water.

![Figure 6.5 Effect of type of drilling fluid on temperature distribution](image)

### 6.3.2.3 Thermal Conductivity and Heat Transfer Coefficient

Thermal conductivity can be defined as the rate of heat transfer through a unit thickness of a material per unit area and per unit temperature difference. The thermal conductivity is expressed in the units of (energy rate/(length.temperature)). The heat transfer coefficient is used as a calibration factor in calculating heat transfer in thermodynamics. Often it can be estimated by dividing the thermal conductivity by a length scale. Heat transfer coefficients add inversely, like resistances. It can be thought of as a thermal resistance.
Thermal conductivity of the drill pipe affects the temperature distribution in the well. Thermal conductivities of the material that are used to produce drill pipe are given in Table 6.3. Conventional steel pipes and low carbon steel pipes have thermal conductivities that are very close, 26.1 and 30.0 Btu/(ft-°F-hr) respectively. Wellbore temperature profiles for these two pipes overlap. Figure 6.6 shows the effect of thermal conductivity of the drillpipe on temperature distribution in the well.

<table>
<thead>
<tr>
<th>Drill Pipe Material</th>
<th>Conductivity Btu/(ft-°F-hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>26.1</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>9.4</td>
</tr>
<tr>
<td>Low Carbon Steel</td>
<td>30.0</td>
</tr>
<tr>
<td>Beryllium</td>
<td>80.3</td>
</tr>
<tr>
<td>Aluminum</td>
<td>131.0</td>
</tr>
</tbody>
</table>

Table 6.3 Thermal conductivities of different types of drill pipe.

Figure 6.6 Effect of thermal conductivity of the drillpipe on temperature distribution in the well.
6.3.2.4 Wellbore Diameter

Increasing the wellbore diameter increases the surface area of contact between the drilling fluid and the formations. All other parameters being equal, increasing the wellbore diameter decreases the heat transfer per area. As wellbore diameter influences circulation temperatures, time exposure to the open hole also influences the temperature profiles. Increase in wellbore diameter reduces the flowing velocity of the mud, and increases the time exposure to the formations. Three bit sizes, 12.5 in., 16 in., and 20 in., were used to simulate the wellbore diameter effect in a 5000 ft deep well. Changing the bit size from 12.5 in. to 16 in., a 28% increase, decreases the bottom hole temperature by 2%. On the other hand, a 25% increase in bit size, from 16 in. to 20 in., decreases the bottom hole temperature by 3%. Figure 6.7 illustrates the effect of wellbore diameter on circulating wellbore temperature distribution throughout the well.

Figure 6.7 Effect of bit size on wellbore temperature profile
6.3.2.5 Drill String Diameter

Drill string diameter determines the surface area between the drill string fluid and the annulus fluid available for heat transfer. As the drill string diameter increases, the surface area between the fluid in the drill string and the fluid in the annulus increases so that the heat transfer between the fluids that occupy these volumes is easier.

Two drill pipe diameters, 6-5/8 in., and 5 in., were used to simulate the temperature distribution in the well. All other parameters being equal, increasing the drill pipe diameter from 5 in. to 6-5/8 in. increased the bottom hole temperature by 2°C. Temperature in the deeper sections of the well increased with the increased drillpipe diameter, on the other hand flow line temperatures were almost equal, 77.1 °F for 6-5/8 in. drill pipe, and 77.4 °F for the 5 in. drill pipe. Figure 6.8 illustrates the effect of drill string diameter on the temperature distribution in the well.

![Figure 6.8 Effect of drill string diameter on temperature profile in the well](image-url)
6.3.2.6 Geothermal Gradient

Geothermal temperature gradient determines the undisturbed temperatures in the formations. The higher the gradient, the bigger is the increase in formation temperatures with respect to depth increments. As the formation temperatures get higher, the difference between the mud temperature and the formation temperature will increase, resulting a stronger heat flux between the formation and the wellbore fluids. This was illustrated using two different geothermal temperature gradients, 0.0127 °F/ft, and 0.0175 °F/ft. Using a surface temperature of 59.5°F, geothermal temperatures at 5,000 feet are 123°F, and 147°F respectively. The difference in the bottom hole temperature because of the different geothermal temperatures is less than 1°F. However, flow line temperatures differ by 2.5°F. Figure 6.9 shows the effect of the geothermal temperature gradient on the temperature distribution in the well.

![Diagram showing temperature distribution](Figure 6.9 Effect of temperature gradient on temperature distribution in the well)
6.3.2.7 Surface Temperature

The undisturbed geothermal temperature is a function of the temperature gradient in the well and the earth’s surface temperature. Any change in the surface temperature will shift the temperature profile throughout the well. For the base case simulation, a surface temperature of 59.5°F was used. The static bottomhole temperature was calculated to be 123°F using a geothermal gradient of 0.0127°F/ft.

In order to see the effect of earth’s surface temperature on the wellbore temperature profiles, simulations were carried out with two more surface temperatures, 50°F and 70°F, using the same geothermal gradient. 10°F difference in surface temperature changed the static bottomhole temperature by 10°F. However, the circulating bottomhole temperature changed only 2°F. In addition, flow line temperatures changed by 2.5°F in response to the change in the surface temperature. The mud inlet temperature was assumed to be 75°F in all cases. Figure 6.10 shows the effect of surface temperature change on the temperature profile in the well.

![Figure 6.10 Effect of surface temperature on temperature distribution in the well](image-url)
6.3.2.8 Stand Pipe Temperature

Stand pipe temperature is a key parameter for the heat transfer in the well. Three simulations were run with different stand pipe temperatures, 70°F, 75°F and 80°F respectively. A 5°F difference in the stand pipe temperature changed the bottom hole temperature by 4°F. Calculated bottom hole temperatures are 77°F, 81°F and 85°F respectively. Changing the stand pipe temperature by 5°F changed the flow line temperature about 3.5°F. However, the difference between the flow line temperature and stand pipe temperature increased with decreasing initial temperature, such that, the mud with 70°F stand pipe temperature gave a flow line temperature of 73.5°F, and the one with 80°F initial temperature had 80.8°F flow line temperature. Effect of stand pipe temperature on temperature distribution in the well is illustrated in Figure 6.11.

![Graph showing temperature distribution](image)

Figure 6.11 Effect of stand pipe temperature on temperature distribution in the well

6.3.2.9 True Vertical Depth

True vertical depth (TVD) determines the static geothermal temperature at the bottom of the well. All other parameters being equal, static geothermal temperature increases with depth.
Wellbore fluids are exposed to higher temperatures at the bottom of the well. In addition, time requirement for circulation and time exposure of the drilling fluid to high temperature formations is greater in deeper wells.

Computer simulations were carried out with, 4000 feet, 5000 feet, and 6000 feet TVS’s. Due to the geothermal gradient, static bottom hole temperature increased by 12.7°F for every 1000 feet drilled. On the other hand, circulating bottom hole temperatures increased only by 3-4°F. Figure 6.12 shows the effect of true vertical depth on temperature distribution in the well.

![Figure 6.12 Effect of true vertical depth on temperature distribution in the well](image)

### 6.3.2.10 Formation Properties

Four computer simulations were run with four different formation thermal properties. Formation properties used by Holmes and Swift\(^57\) were used to simulate the base case temperature distribution in the well. Shale, sandstone, and limestone properties were used as well. From the heat equation\(^60\) we know that \(\frac{\partial T}{\partial t} = \frac{k}{\rho c_p} \nabla^2 T\). According to this relationship, heat
Flow from or to the formation is directly proportional to the conductivity of the formation. However, density and thermal heat capacity of the formation are inversely proportional to the heat flow. Figure 6.13 shows the effect of formation type on the temperature distribution in the well. Table 6.4 shows the properties of different formations types, which were used for computer simulations.

![Diagram showing temperature distribution](image)

**Figure 6.13 Effect of formation type on temperature distribution**

**Table 6.4 Properties of different formations types.**

<table>
<thead>
<tr>
<th>Formation Type</th>
<th>Conductivity Btu/(ft-°F-hr)</th>
<th>Heat Capacity Btu/(lb-°F)</th>
<th>Density lb/cuft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>0.740</td>
<td>0.21</td>
<td>91.0</td>
</tr>
<tr>
<td>Shale</td>
<td>0.920</td>
<td>0.30</td>
<td>140.0</td>
</tr>
<tr>
<td>Sandstone</td>
<td>1.080</td>
<td>0.17</td>
<td>139.3</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.750</td>
<td>0.22</td>
<td>154.9</td>
</tr>
<tr>
<td>Base Case</td>
<td>1.300</td>
<td>0.20</td>
<td>165.0</td>
</tr>
</tbody>
</table>
In order to avoid hydrate dissociation during drilling in the open hole or behind the casing, the wellbore temperature at hydrate layers must be kept less than hydrate dissociation temperature. This parametric study was done to investigate the effects of different factors on the wellbore temperature distribution so that insight would be gained as to what parameters might be most efficiently adjusted to minimize hydrate dissociation. Although all of the parameters investigated in this study have impact on the wellbore temperature distribution, the significance of each parameter differ.

At the end of this parametric study, we conclude that the most significant parameter that affects the wellbore temperature profile is the mud inlet temperature. This is followed by the specific heat capacity of the drilling fluid. Geothermal properties, such as geothermal gradient and the surface temperature follow next. Although the circulation rate is not the most significant parameter for wellbore temperature, it determines the heat flux from the warm drilling fluid to the cooler formations.
7. APPLICATION OF THE MODEL TO THE LIMANKOY-1 WELL

This chapter shows the application of proposed dissociation model on the Limankoy-1 well, which was drilled in the Western Black Sea in 1999. Actual drilling parameters are used to investigate the temperature distribution and potential for hydrate dissociation in the Limankoy-1 well. Results are compared to the facts given in the daily reports section of the end of project report.

Limankoy-1 well was selected out of the two Western Black Sea exploration wells because this well had gas shows during the pilot hole and surface hole detected by the ROV camera. Table 7.1 gives the properties of the well.

Table 7.1 Limankoy-1 well drilling data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water depth, ft</td>
<td>2,887</td>
</tr>
<tr>
<td>Air gap, ft</td>
<td>85</td>
</tr>
<tr>
<td>Total depth, ft</td>
<td>9,039</td>
</tr>
<tr>
<td>Pilot hole total depth, ft</td>
<td>4,701</td>
</tr>
<tr>
<td>Pilot hole bit size, in</td>
<td>9.625</td>
</tr>
<tr>
<td>Pilot hole drilling fluid density, ppg</td>
<td>8.7</td>
</tr>
<tr>
<td>Surface hole total depth, ft</td>
<td>4,701</td>
</tr>
<tr>
<td>Surface hole bit size, in</td>
<td>16</td>
</tr>
<tr>
<td>Surface hole drilling fluid density, ppg</td>
<td>8.7</td>
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<tr>
<td>Surface casing size, in</td>
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<tr>
<td>Intermediate hole total depth, ft</td>
<td>5,663</td>
</tr>
<tr>
<td>Intermediate hole bit size, in</td>
<td>12.25</td>
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<tr>
<td>Intermediate hole drilling fluid density, ppg</td>
<td>9.4 – 10.3</td>
</tr>
<tr>
<td>Intermediate casing size, in</td>
<td>9.625</td>
</tr>
<tr>
<td>Open hole total depth, ft</td>
<td>9,039</td>
</tr>
<tr>
<td>Open hole bit size, in</td>
<td>8.5</td>
</tr>
<tr>
<td>Open hole drilling fluid density, ppg</td>
<td>10.2 – 10.3</td>
</tr>
<tr>
<td>Geothermal temperature gradient, °F/100 ft</td>
<td>2.52</td>
</tr>
</tbody>
</table>
7.1 Static Wellbore Temperatures in Limankoy-1

Temperature readings were recorded during drilling the intermediate hole, and the open hole section. The geothermal temperature trend was extended to the seafloor by linear extrapolation. Figure 7.1 shows the static wellbore temperature profile for Limankoy-1 well.

![Temperature profile diagram](image)

Figure 7.1 Limankoy-1 static temperature distribution

Daily drilling report summaries indicated that strong gas shows were observed by the remote operated vehicle (ROV) camera while drilling between 584 ft and 663 ft below seafloor. Although there were continuous small gas shows below this depth, a short trip at 1,043 ft below seafloor was made without any problems. A flow check was made, but well did not flow. The pilot hole was completed, filled with 10.5 ppg mud, and abandoned.

The surface hole was drilled riserless with seawater to a total depth of 4,701 ft with a 16” bit. Similar to the pilot hole, small gas shows were observed by the ROV camera between 351 feet (3,117 ft RKB) and 1,512 feet (4,314 ft RKB) below seafloor.
7.2 Hydrate Stability Analysis for Limankoy-1

According to the drilling report\textsuperscript{48}, there was not a productive sand or a shallow gas sand in this portion of the well. Therefore, a hydrate stability analysis was performed for this well using the Colorado School of Mines Hydrate Prediction Program, csmhyd98\textsuperscript{61}. Figure 7.2 shows the hydrate stability conditions obtained from csmhyd98 for Limankoy-1 well.

![Figure 7.2 Limankoy-1 hydrate stability conditions](image)

Figure 7.2 gives a hydrate stability interval approximately between 1,600 ft TVD and 3,700 ft TVD, which covers a depth of 700 – 800 ft of sediments below seafloor. In addition, it is known from the literature\textsuperscript{50,51} that Black Sea sediments contain naturally occurring gas hydrate layers. Hydrate layers will dissociate if they are exposed to an external heat source that brings the pressure and temperature conditions outside the stability conditions.

7.3 Pilot Hole Temperature Simulations

In order to predict the wellbore temperatures during circulation, a series of temperature simulations for the conditions given in Table 7.2 were executed with GTEMP\textsuperscript{8} wellbore
temperature simulator. In the Limankoy-1 well, drilling fluid reaches the bottom of the hole approximately 6 minutes after passing through the mud pump with the particular drill string configuration used in the well. The drilling records reported that the pilot hole was drilled within 24 hours. Therefore, the temperature simulations were done for a time range between 5 minutes and 24 hours.

The static bottom hole temperatures increase with increasing depth. For the worst-case highest temperature conditions, the temperature simulations were done for the surface casing setting depth. The results of the pilot hole wellbore temperature simulations are presented in Figure 7.3 as a function of time.

Table 7.2 Circulation and formation properties for Limankoy-1 pilot hole

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water depth, ft</td>
<td>2,887</td>
</tr>
<tr>
<td>Pilot hole total depth, ft</td>
<td>4,701</td>
</tr>
<tr>
<td>Pilot hole mud density, ppg</td>
<td>8.7</td>
</tr>
<tr>
<td>Mud thermal heat capacity, Btu/lb/°F</td>
<td>1.0</td>
</tr>
<tr>
<td>Circulating rate, gpm</td>
<td>500</td>
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<tr>
<td>Mud inlet temperature, °F</td>
<td>75</td>
</tr>
<tr>
<td>Circulation time, min</td>
<td>5 – 1440</td>
</tr>
<tr>
<td>Conductivity of sea water, Btu/hr/ft/°F</td>
<td>0.35</td>
</tr>
<tr>
<td>Heat capacity of sea water, Btu/lb/°F</td>
<td>1.0</td>
</tr>
<tr>
<td>Conductivity of drill string, Btu/hr/ft/°F</td>
<td>26.1</td>
</tr>
<tr>
<td>Heat capacity of drill string, Btu/lb/°F</td>
<td>0.11</td>
</tr>
<tr>
<td>Drill pipe OD, in</td>
<td>5.0</td>
</tr>
<tr>
<td>Drill pipe ID, in</td>
<td>4.276</td>
</tr>
<tr>
<td>Conductivity of formations, Btu/hr/ft/°F</td>
<td>0.750 – 1.080</td>
</tr>
<tr>
<td>Heat capacity of formations, Btu/lb/°F</td>
<td>0.17 – 0.30</td>
</tr>
<tr>
<td>Surface seawater temperature, °F</td>
<td>71</td>
</tr>
<tr>
<td>Seafloor temperature, °F</td>
<td>39</td>
</tr>
<tr>
<td>Static bottom hole temperature, °F</td>
<td>81</td>
</tr>
</tbody>
</table>
Simulation results indicated that, drill string mud temperatures start increasing after circulation starts, and stay almost constant after two hours of circulation. The predicted circulating bottom hole temperatures varied between 64°F and 75°F, 64°F being the bottom hole temperature after 5 minutes of circulation time.

![Temperature, deg F vs Depth, ft](image)

Figure 7.3 Limankoy-1 pilot hole temperature distributions as a function of time

The GTEMP temperature simulator can also predict the formation temperatures for given thermal properties. Unfortunately, the simulator cannot consider the latent heat spent for hydrate dissociation. Therefore, for the formation temperature distributions, it is assumed that there is no hydrate dissociation. Results of formation temperature simulations are plotted for the interval where insitu hydrates are possible for different circulation time periods. Figures 7.4, 7.5 and 7.6 illustrate the predicted temperature distributions in the formation at different distances from the center of the well: 4.9 in, 11.3 in and 21.2 in respectively.
The hydrate stability temperature for corresponding depths is also shown with results to allow for dissociation front predictions. Note that temperatures near the wellbore exceed the hydrate stability temperature shortly after circulation starts.

Figure 7.4 Limankoy-1 pilot hole formation temperature vs. time at r = 4.9 in

Figure 7.4 shows that the temperature at 4.9 in from the center of the well exceeds the hydrate stability temperature 10 minutes after circulation starts. On the other hand, at 11.3 in from the center of the well it takes approximately six hours to reach the hydrate stability temperature assuming no hydrate dissociation. Figure 7.5 shows the temperature distributions at 11.3 in from the center of the well for a variety of circulation times at the interval where insitu hydrates are possible.

Figure 7.6 shows the temperature distribution 21.2 in from the center of the well. It is obvious from the figure that the formation temperatures cannot reach the hydrate dissociation temperature at this distance within 24 hours given the assumption of no hydrate dissociation.
Figure 7.5 Limankoy-1 pilot hole formation temperature vs. time at r = 11.3 in

Figure 7.6 Limankoy-1 pilot hole formation temperature vs. time at r = 21.2 in
Figures 7.7, 7.8 and 7.9 show the simulated temperature distribution in the formations as a function of distance from the center of the well for various circulating times. Graphical illustrations were prepared for various depths between the sea floor and 800 ft below seafloor with increments of 200 ft. Figure 7.7 shows that at early times, after 10 minutes from the start of circulation, formation temperature stays below the hydrate dissociation temperature. However, temperature simulations presented in Figure 7.8 showed that after one hour of circulation formation temperatures exceed hydrate stability temperature at near wellbore.

The radius, where the hydrate stability temperature is exceeded, should also be the thawed zone radius. Consequently, these distributions can be used to imply the extent of hydrate dissociation. It is worth to repeat that the GTEMP simulator is a wellbore temperature simulator and cannot calculate hydrate dissociation. However, it may be used to predict the thawed zone radius. Ignoring the heat required to dissociate the hydrate, and assuming hydrates dissociate at all temperatures above the dissociation temperature, thawed zone radius can be used as the dissociation radius, which is the worst case that may happen.

![Figure 7.7 Limankoy-1 pilot hole temperature distribution after t = 10 min](image)
Figure 7.8 Limankoy-1 pilot hole temperature distribution after $t = 1$ hr

The simulated formation temperature distribution for 24 hours of circulation is presented in Figure 7.9. It is obvious from the figure that the thickness of the thawed zone after 24 hours is at least 7.5 inches.

Figure 7.9 Limankoy-1 pilot hole temperature distribution after $t = 24$ hr
7.4. Pilot Hole Dissociation Calculations

Hydrate dissociation was also predicted using the dissociation model presented in Chapter 5. This prediction should be more accurate than the predictions using the GTEMP simulator because the dissociation model considers the latent heat of hydrate dissociation. Location of the dissociation front, hole size, effective heat flux, and gas influx rate were calculated for Limankoy-1 pilot hole. Results of the dissociation calculations are presented in Figures 7.10 through 7.13.

The dissociation front location was calculated using eq. (5.78) given in Chapter 5. The heat flux was calculated for a circulation rate of 500 gpm, and a drilling fluid density of 8.7 ppg. It was assumed that the drilling fluid was seawater, so the thermal properties of the seawater were used. It was also assumed that the heat lost in the annulus was spent to increase the hydrate temperature to its dissociation temperature, and thereafter to dissociate the hydrate. The heat flux from the wellbore to the hydrate was calculated from the difference between the temperatures at the bottom and at the top of the expected insitu hydrates. The GTEMP simulator was used to predict the wellbore temperatures. The dissociation temperature was calculated for the corresponding hydrostatic pressure in the middle of the hydrate body by using the csmhyd98, the Colorado School of Mines Hydrate Prediction Model.

The temperature simulations showed that the temperature loss in the annulus, from 800 ft below seafloor to 200 ft below sea floor, was 0.62°F. This corresponds to a temperature loss gradient of 0.001033 °F/ft in field units, or 0.001883K/m in metric units. The heat flux to the hydrate at the beginning was calculated to be 338.15 W/m². However, as the dissociation front moves from the wellbore the contact area between the hydrate and the drilling fluid increases. This affects the effective heat flux into the hydrate zone.
Using the hydrostatic pressure at hydrate body, the dissociation temperature was predicted as 56.5°F. Geothermal temperature at 400 ft (center of hydrate layer) below the seafloor was used to represent the initial hydrate temperature. Predicted geothermal temperature at this depth was 49°F.

The location of the dissociation front was predicted using the 1-D linear dissociation equation and the predictions were used in the radial geometry to calculate the hole diameter, effective heat flux, and gas influx per ft of hydrate layer as presented in Chapter 5, Section 5.2.4, page 62. Figure 7.10 shows the actual model output for predicted location of the dissociation interface as a function of circulating time.

![Figure 7.10 Limankoy-1 pilot hole location of dissociation front as a function of time](image)

Figure 7.10 shows the diameter of the pilot hole as a function of time. The hole enlargement is due to hydrate dissociation. The hole diameter has increased approximately 5 inches, from 9.625 in to 14.5 in 24 hours after the circulation started. The wellbore diameter
reached 17.5 in after 48 hours of circulation. It is also seen from the figure that speed of
dissociation has decreased with time.

![Graph showing hole size vs. time](image)

Figure 7.11 Limankoy-1 pilot hole size vs. Time

The GTEMP temperature simulations had shown a 5 in thawed zone thickness after 24
hours of circulation, which corresponds to a 10 in increase in the wellbore diameter assuming all
of the hydrates within the thawed zone were dissociated. These predictions may be used for the
worst-case scenario. On the other hand, the amount of heat that is spent for hydrate dissociation
is significant. Ignoring this energy overestimates the amount of dissociation. Therefore,
dissociation model predictions are expected to be more accurate than the GTEMP predictions.

Effective heat flux at the dissociation interface was calculated by increasing the wellbore
diameter to the location of the dissociation front. As the wellbore diameter increased after start of
dissociation, the effective heat flux has significantly reduced. The effective heat flux at the
dissociation interface in the Limenkoy-1 pilot hole is presented in Figure 7.12.
Figure 7.12 Limankoy-1 pilot hole effective heat flux vs. time

Figure 7.13 shows the gas influx into the wellbore per ft of pure hydrate. The gas influx decreases rapidly at early time, but attains a constant value at larger times. Assuming a maximum hydrate thickness of 800 ft, the initial gas influx would be as high as 30 MScf/day.

Figure 7.13 Limankoy-1 pilot hole gas influx per ft of hydrate layer as a function of time
As mentioned earlier, the pilot hole was drilled with returns to the seafloor. There were strong gas shows observed by the ROV camera while drilling at depths between 584 ft and 683 ft below seafloor. The hydrate stability curve showed that this depth interval is within the hydrate stability conditions. The temperature simulations with a 75°F mud inlet temperature imply that the wellbore fluid temperature would exceed the hydrate stability temperature of approximately 56°F in this interval. Therefore, it is highly possible that these gas shows were due to hydrate dissociation.

Intermittent gas shows were observed during drilling the rest of the pilot hole. However, the well did not flow when a flow check was made. This phenomenon would be expected if the gas was from hydrates. After circulation is stopped, the wellbore temperatures tend to equalize with the formation temperatures. This decreases the heat flux to the formations, and finally, the heat flux stops after the temperatures are equalized. The negative flow check in the pilot hole was probably because of the insufficient heat flux into the hydrates to continue causing dissociation after circulation was stopped.

7.5 Surface Hole Temperature Simulations

The surface hole was also drilled riserless with sea water. Small gas shows were observed by the ROV camera between 351 ft and 1,512 ft below sea floor during drilling. The possible causes of the gas shows were shallow gas flows, shallow productive gas sands, cuttings gas, hydrate cuttings, or hydrate dissociation. The end of project report stated that there was not a productive sand or shallow gas sand in this portion of the well. However, pressure and temperature conditions in this section of the well promote naturally occurring gas hydrates.

In order to calculate hydrate dissociation, heat flux into the formations was determined. Similar to the pilot hole, temperature simulations were run to determine the heat flux into hydrate formations. The surface hole was drilled with the same drill string and drilling fluid. Therefore,
same properties, as given in Table 7.2, were used in the calculations. Total depth, bit size, circulation rate and initial circulation temperature are given in Table 7.3. The dissociation front prediction comparisons between the GTEMP and the dissociation model are presented.

Table 7.3 Circulation and wellbore properties for Limankoy-1 surface hole

| Surface hole total depth, ft | 4,701 |
| Surface hole bit size, in    | 16.0  |
| Surface hole mud density, ppg| 8.7   |
| Circulating rate, gpm        | 1,150 |

Figure 7.14 shows the static and circulating temperatures in Limankoy-1 surface hole. In addition, hydrate stability curve is shown on the figure to allow comparison for the temperature conditions in the wellbore.

Figure 7.14 Limankoy-1 surface hole temperature distribution as a function of time
It is seen from the figure that circulating temperatures exceeded the hydrate stability temperature immediately after circulation started. With a circulation rate of 1,150 gpm, it takes only 2-3 minutes for the drilling fluid to reach the bottom of the well. As the warm fluid was being circulated through the well, wellbore temperatures increased.

The temperature simulations with GTEMP showed that the thawed zone radius reached 16.3 inches after 24 hours of circulation. This corresponds to a thawed zone thickness of 8.3 inches. Compared to 7.5 inches in the pilot hole, it is seen that wellbore diameter and circulation rate do not have a significant effect on the thawed zone radius if the suction temperature is not changed. Figure 7.15 shows the temperature distribution in the possible insitu hydrate zone at 16.3 in from the center of the well as a function time. Further in this chapter, thawed zone radii will be compared to the dissociation model predictions.

![Figure 7.15 Limankoy-1 surface hole formation temperature vs. time at r = 16.3 in](image-url)
7.6 Dissociation Predictions for the Surface Hole

Similar to the pilot hole, dissociation calculations were made for the surface hole and model predictions are presented below in figures. The thawed zone radius and thickness predicted with the GTEMP simulator were plotted on the same graphs with the model predictions for dissociation front location and wellbore diameter after dissociation. This allows us to compare the output of the model to the GTEMP predictions and understand the importance of latent heat for dissociation calculations. Figure 7.16 shows the wellbore diameter predictions with the model and the GTEMP simulator.

![Figure 7.16 Limankoy-1 surface hole size vs. time](image)

Figure 7.16 shows the location of the dissociation front, which is an actual output of the dissociation model, and the predicted thawed zone thickness from the GTEMP simulator. The model predicted dissociated zone thicknesses as 2.5 inches and 4 inches for 12 hours and 24 hours respectively. On the other hand, the GTEMP simulator predicted the thawed zone thicknesses as 6 inches and 8.5 inches in for the same time periods. As seen from the figure, the
GTEMP predictions for the thawed zone thickness are almost two times greater than the dissociation front location estimated from the dissociation model. This is because the GTEMP does not account for the latent heat of dissociation, whereas, in reality, most of the heat is consumed for dissociation. For example, in the dissociation calculations, the ratio of latent heat of dissociation to the sensible heat was 45.7. Therefore, GTEMP predictions for thawed zone thickness cannot be used for hydrate dissociation predictions, but they can provide rough estimates whether dissociation will occur or not. From the same figure, we also see that the dissociation front moves fast in the early times, but its speed is almost constant after 24 hours.

Figure 7.17 Limankoy-1 surface hole location of the dissociation front vs. time

Gas influx calculations were also made for the surface hole assuming that the dissociation model results are correct. The calculations showed that the initial gas influx from the hydrates was 0.065 scf/min per foot of hydrate drilled. This equivalent to 100 scf/day per foot of hydrate thickness. Assuming that the hydrate stability interval, which is about 800 ft, was filled with pure hydrate, then the volume of the gas at surface would be 78 MScf/day. However, the dissociation
speed decreases with the increasing wellbore diameter. The gas influx after four hours was 71 MScf/day, 64 MScf/day after 12 hours, and almost constant at 59 MScf/day after 24 hours.

The gas influx into the well will be mixed with drilling fluid and reduce the hydrostatic pressure in the annulus. Once the rate of gas influx is determined, the reduction in the density of the drilling fluid and loss of hydrostatics can be calculated from eq (5.87) and (5.89). With a circulation rate of 1,150 gpm, the reduction in the hydroatatic would be only 1.5 psi. However, if the circulation rate is reduced to 500 gpm immediately, and the heat flux into the hydrate is still the same, then the loss of hydrostatics would be 3.2 psi. Even with a circulation rate of 100 gpm, the loss of hydrostatic would be only 7.5 psi.

Temperature simulations and hydrate dissociation predictions were made for the Limankoy-1 well pilot hole and surface hole sections. These sections were drilled riserless with the mud returns to the sea floor. The rest of the well was drilled with a 20” riser with the mud returns to the drilling vessel.

7.7. Dissociation Behind Casing

In order to predict the behavior of hydrates after they are cased off behind the 13-3/8” surface casing, the thermal wellbore simulator was used to predict the temperature distribution in the well during drilling below the surface casing. The temperature simulations were made assuming that the well was drilled to the TD of 9,039 ft with a 8.5 in bit, and 10.3 ppg mud was being circulated at a rate of 450 gpm. Temperature simulations were made for a time range from 5 minutes to 24 hours. The short time temperature distribution are not very important when it takes several days to drill to the next casing point. In addition, after 6 hours of circulation, the wellbore temperatures did not show a significant change. Therefore, only 1 hr and 6 hour temperature distributions were plotted. Figure 7.18 presents the predicted wellbore circulating temperatures, static temperatures and hydrate stability conditions for Limankoy-1 well.
Figure 7.18 Limankoy-1 well circulating temperatures and hydrate stability conditions

The wellbore temperatures are seen to be higher than the hydrate stability temperature during circulation. The higher temperature in the wellbore would cause a heat flux into the hydrate resulting in dissociation behind the casing. Insitu hydrates were expected at depths between the seafloor and 800 ft below the seafloor. Figure 7.19 shows Limankoy-1 circulating temperatures through the expected hydrate depth interval.

The surface hole was drilled in two days. The dissociation calculations have shown that the hydrates would have been dissociated 6 inches within two days. After the surface casing was run and cemented, the dissociated zone should be filled with cement. Figure 7.20 shows the temperature distribution predicted by GTEMP in the cement and the hydrate zone behind the surface casing after 24 hours of circulation. It is seen from the figure that temperatures behind the casing exceed the hydrate stability temperature.
Figure 7.19 Limankoy-1 circulating temperatures in expected hydrate depth interval

Figure 7.20 Temperature distribution in the hydrate zone behind the surface casing after 24 hours
Figure 7.20 indicates that hydrates behind the casing would be likely to dissociate during drilling of the intermediate hole. Dissociation products are water and gas. Because of the limited volume, dissociation causes pressure to increase, and dissociation continues until the pressure reaches the hydrate stability pressure at that particular temperature. If the pressure differential between the well and the dissociated gas exceeds the collapse rating of the casing, then significant risk of casing collapse occurs. Figure 7.21 illustrates the conceptual progress of dissociation with increasing formation temperature behind the surface casing in Limankoy-1 well. The collapse rating of Limankoy-1 well surface casing was 2260 psi.

Figure 7.21 Hydrate dissociation and formation conditions behind the surface casing, and illustration of risk of casing collapse

It is obvious from Figure 7.21 that formation temperatures above 72°F would potentially collapse the casing in the Limankoy-1 well. However, the drilling report indicated that the casing did not collapse. Figure 7.20 shows that the formation temperatures after 24 hours of circulation
at 600 ft, predicted using GTEMP, exceeded 71°F from the casing to a distance of 15 inches from the center of the well. Fortunately, the thickness of the cement around the casing at dissociated hydrate interval was approximately 7.5-8 inches extending about 14 inches from the center of the well. Apparently, formation temperature in the most likely hydrate bearing section from 584 ft to 663 ft did not exceed 72°F behind the casing, even after 24 hours of continuous circulation. Considering that the well depth, and therefore downhole temperatures were less than 75°F, the temperature behind the cement was probably lower than 71°F.

The overall conclusions from this chapter can be listed as follows.

The GTEMP wellbore temperature simulator may be used to make rough estimates for the temperature distribution in hydrates. However, it overpredicts the dissociation front radius. Therefore it should not be used for dissociation predictions.

Application of the dissociation model confirms that gas noted while drilling pilot and surface holes could be due to hydrate dissociation.

Hydrate dissociation may occur behind the surface casing. The casing may collapse if the pressure in the hydrate exceeds the differential collapse pressure. However, the volume created by the dissociation of hydrates may be filled with cement, and this may reduce the risk of casing collapse.

The method described herein, combining predictions of temperature distribution and hydrate dissociation, was successfully applied to real well conditions. The results are consistent with observations of gas in the mud returns to the seafloor. Although a rigorous quantitative assessment is not possible, it was concluded that this methodology can be used for predicting conditions in future wells.
8. RECOMMENDATIONS FOR HOPA-1 WELL

This chapter provides recommended practices for drilling the Hopa-1 well in the Eastern Black Sea Exploration Project. These recommendations are intended to help operator mitigate hydrate formation and dissociation problems. In order to understand the behavior of hydrates in Hopa-1 well, a hydrate stability plot was prepared. In order to make dissociation predictions, expected circulation temperatures were calculated with the GTEMP simulator and the dissociation model developed for this study was applied.

8.1 Hydrate Stability Conditions in Hopa-1

Hopa-1 lies in water depths between 5,000 ft and 6,000 ft, and is to reach an approximate total depth of 15,000 ft. A hydrate stability analysis was made with csmhyd98 for the expected pressure and temperature conditions in the Hopa-1 well. Figure 8.1 shows the expected static wellbore temperatures, and the hydrate stability temperatures assuming a water depth of 6,000 ft.

![Figure 8.1 Expected static temperatures and hydrate stability region for Hopa-1 well](image-url)
The figure shows that the pressure and temperature conditions in the water column below 1,400 ft and in the shallow sediments above 7,500 ft are favorable for hydrate formation. In addition, pressure and temperature conditions in the sediments below seafloor are suitable for the existence of in-situ hydrates over an interval up to 1,500 ft thick.

8.2 Hydrate Dissociation in Hopa-1

While circulating, wellbore temperatures may exceed the hydrate stability temperature. In order to see the effect of mud inlet temperature on the circulating wellbore temperature profiles, three simulations were performed by using the GTEMP software with three different mud inlet temperatures, 100°F, 80°F and 60°F respectively. The input parameters for the temperature simulations are given in Table 8.1. The geothermal gradient for the Hopa-1 well is different than in the Western Black Sea wells, and was provided by the Turkish National Oil Company.

<table>
<thead>
<tr>
<th>Table 8.1 Temperature simulation input data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drilling depth, ft</td>
</tr>
<tr>
<td>Water depth, ft</td>
</tr>
<tr>
<td>Surface hole diameter, in</td>
</tr>
<tr>
<td>Initial circulating temperature, °F</td>
</tr>
<tr>
<td>Surface temperature, °F</td>
</tr>
<tr>
<td>Circulation rate, gpm</td>
</tr>
<tr>
<td>Geothermal gradient, °F/ft</td>
</tr>
</tbody>
</table>

Figures 8.2, 8.3 and 8.4 show the circulating temperatures in the Hopa-1 well surface hole section. It is obvious that cooling the mud down to 60°F at surface provides a lower temperature distribution in the wellbore. Even with the well depth at 10,000 ft, two hours of circulation the cool mud from the surface cools down the near wellbore area, and wellbore temperatures may be kept below the dissociation temperature.
Figure 8.2 Circulation temperature distributions with 100°F mud inlet temperature

Figure 8.3 Circulation temperature distributions with 80°F mud inlet temperature
Figure 8.4 Circulation temperature distributions with 60°F mud inlet temperature

The temperature decrease in the annulus around the expected hydrate layers was used to calculate the heat loss into the hydrate layers. The annular temperature loss was assumed to be spent into the surrounding formations. The heat flux into the formations was calculated from the annular temperature loss at depths between 200 ft below seafloor and 1400 ft below seafloor after two hours of circulation.

In the 24” hole with 1,150 gpm circulation rate, heat flux varied with initial circulating temperature. It was assumed that the surface hole was drilled riserless with seawater. The mud with 100°F initial circulating temperature gave an initial heat flux of 1,711 W/m². This heat flux can be used to calculate the location of dissociation front as described in Chapter 5. Predicted heat flux with 80°F initial circulation temperature was 1,285 W/m².

The wellbore temperatures with 60°F did not exceed the formation temperatures in most parts of this section of the well. However, while the warm mud at the bottom of the well was
being circulated up the annulus, wellbore temperatures were significantly higher than the formation temperature, and also higher than the dissociation temperature. The early time heat flux, before one hour of circulation, was significant, but did not last long. This early time heat flux into the hydrate would be likely to initiate dissociation, but after two hours the wellbore temperature was reduced below the dissociation temperature, and no dissociation would be anticipated.

The average dissociation temperature in the middle of the hydrate layer was calculated by using the pressure in the middle of the hydrate with the csmhyd98 model, and was 68°F. For the sake of simplicity, one representative initial hydrate temperature, 51°F, was selected for the dissociation calculations. The parameters that were used for the hydrate dissociation predictions are given in Table 8.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity of hydrate, $k$, W/m-K</td>
<td>0.5</td>
</tr>
<tr>
<td>Thermal diffusivity of hydrate, $\alpha$, m$^2$/s</td>
<td>$3.02 \times 10^{-7}$</td>
</tr>
<tr>
<td>Initial temperature of hydrate, $T_i$, K</td>
<td>282</td>
</tr>
<tr>
<td>Hydrate dissociation temperature, $T_d$, K</td>
<td>293</td>
</tr>
<tr>
<td>Heat Flux with $T_i = 100^\circ F$, Q, W/m$^2$</td>
<td>1,675</td>
</tr>
<tr>
<td>Heat Flux with $T_i = 80^\circ F$, Q, W/m$^2$</td>
<td>1,340</td>
</tr>
<tr>
<td>Heat Flux with $T_i = 60^\circ F$, Q, W/m$^2$</td>
<td>0</td>
</tr>
</tbody>
</table>

In order to compare the effect of mud cooling at surface on hydrate dissociation, heat flux and dissociation model calculations were performed for the three inlet mud temperatures. Results are presented in figures below. Figure 8.5 gives the location of dissociation front versus time, and Figure 8.6 gives the hole enlargement due to dissociation for the three suction pit temperatures.
Figure 8.5 Effect of initial circulating temperature on hydrate dissociation

Figure 8.6 Hole enlargement due to hydrate dissociation for different mud inlet temperatures
The heat flux is from the formation to the wellbore if the circulating temperatures are less than the formation temperatures. Therefore the dissociation front in Figure 8.5 did not move after two hours of circulation. Figure 8.6 shows that there is an insignificant amount of dissociation at early times. This was due to the warm fluid being circulated up the annulus. After the temperatures reached steady-state, the wellbore temperatures were below the dissociation temperature and there was no dissociation for an inlet mud temperature of 60°F. As a result, the wellbore diameter would remain constant with that inlet mud temperature. Figure 8.7 presents the gas influx volume at surface conditions per ft of hydrate.

![Graph showing gas influx at different temperatures](image)

Figure 8.7 Effect of inlet mud temperature on gas influx from hydrate layers

The gas influx from the hydrates approaches a steady rate after several hours, as observed in previous simulations. In Hopa-1, the worst case thickness of the hydrate may be 1,500 ft. Circulating a 100°F fluid in the well would cause a rate of 0.22 scf/min of gas per ft of hydrate, which is equivalent to 64 MScf/day at surface conditions. For 80°F, the volume of the gas at surface would be 35 MScf/day.
8.2.1 Dissociation of Cuttings

As discussed in Chapter 5, most of the cuttings are carried to the seafloor by the drilling fluid before they dissociate. However, the density of hydrate cuttings is less than the density of water. Therefore, the cuttings float in the seawater, and they are carried to the sea surface by buoyancy forces. For the sake of simplicity, it was assumed that the cuttings dissociate immediately when the pressure and temperature conditions are no longer favorable for the hydrate stability. Figure 8.1 shows that pressure and temperature conditions in the Black Sea are not within the hydrate stability at water depths above 1500 ft. Therefore, the hydrate cuttings generated in Hopa-1 well are expected to dissociate at a water depth of 1500 ft.

The rate of dissociation of cuttings is a function of the rate of cuttings generation, and proportional to the rate of penetration. The hydrate cuttings disperse in the seawater while they rise up. When they come up to 1500 ft water depth, the dissociation starts and hydrate cuttings break into water and gas. The cuttings and gas from hydrate should create a plume. According to a previous study, the radius of the plume varies from 16% to 100% of the water depth. For the worst case, 16% radius was assumed in this study, which is 960 ft. Figure 8.8 is an illustration of the cuttings and gas plume in the seawater.

Figure 8.8 Hydrate cuttings and gas plume
The dispersed cuttings and gas tend to reduce the water density underneath the drilling vessel. Since the cuttings and gas are dispersed in a very wide area, the reduction in the seawater density is insignificant. The maximum predicted density reduction was observed with 200 ft/hr rate of penetration, and was only 0.17 ppg at the sea surface. Figure 8.9 below shows the distribution of the seawater density in the affected zone.

![Water density, ppg](image)

Figure 8.9 Seawater density reduction due to dissociation of cuttings

### 8.2.2 Surface Gas Hazards

The reduction in the seawater density due to cuttings dissociation is not significant. Therefore, a significant effect on the buoyancy is not expected. However, acoustic-based dynamic positioning (DP) systems do not function efficiently in gas-aerated water. If a DP vessel is utilized where a gas boil is present at surface, thruster efficiency is also reduced due to the aeration of the water\(^63\). Some vessels have shallow suction for main engine salt water cooling system that would also be affected.
The gas at sea surface may catch fire from the heat sources around the rig. This may endanger the safety of the personnel and the equipment. Also, fire at sea surface adversely affects positioning a floating vessel. Extinguishing the fire is almost impossible.

8.3 Hydrate Mitigation Recommendations for Hopa-1

The pressure and temperature conditions in Hopa-1 well are favorable for hydrate formation and there are natural gas hydrates in the shallow sediments of the deep Black Sea. A series of precautions are recommended to minimize the impact of hydrates on well operations and personnel.

1. If the dissociation radius is likely to create wellbore instability problems, the risk of hydrate dissociation while drilling should be minimized by reducing the stand pipe temperature down to 60°F.

   o While drilling the surface hole with returns to the seafloor this can be achieved by using a mud-cooler unit or by taking the suction of the pump deep in the seawater where the temperature is below 60°F. In the Eastern Black Sea, the seawater temperature goes below this temperature at a water depth of 250 ft. Therefore, lowering the suction of the pump down to 250 ft in the sea could greatly reduce the risk of dissociation due to thermal effects.

   o While drilling below the surface hole, the well is drilled with mud with returns back to the drilling vessel. To prevent hydrate dissociation behind casing, a mud-cooler unit should be used to reduce the standpipe temperature.

2. The wellbore temperature opposite a hydrate layer is expected to increase as the well goes deeper. This may lead dissociation of hydrates behind the casing, and increase formation pressures may cause casing collapse. The maximum expected differential collapse pressure before formation fracture in Hopa-1 well is 1500 psi. Therefore, to
prevent collapse of casing from further dissociation of hydrates behind the casing, a casing string with a minimum collapse rating of 1,500 psi should be run and cemented.

3. The hydrate stability temperature at seafloor is 60°F, however, the seawater temperature is 36°F. Therefore, hydrate inhibitors should be mixed in the mud after the hydrate zones are cased off. Mixing salt in the mud will reduce the risk of hydrate formation in the wellbore. It is known from a previous study\textsuperscript{53} that 20% sodium chloride salt in mud will suppress the hydrate formation temperature by 24°F.

4. To reduce the risk of casing collapse or venting to seafloor, heat transfer through the cement should be minimized. This may be achieved by using a low thermal conductivity cement. Cement with perlite provides a low thermal conductivity (0.096 Btu/h-ft·°F) compared to the regular cement (0.840 Btu/h-ft·°F).

5. Drilling a pilot hole is highly recommended when in-situ hydrates are expected. The smaller pilot hole and lower mud flow rates result in lower gas flux rates released by hydrate dissociation as shown herein. In addition, filling the hole with cold fluid will be faster. The use of a small pilot hole will also improve the quality of formation evaluation based on LWD. Pilot holes are also recommended by IADC\textsuperscript{63} for areas of unknown pore pressure because in the smaller hole it is easier to perform a dynamic kill and requires smaller kill mud volumes in the event of a kick.

6. The drilling crew should carefully watch for indications of hydrates. Hydrates can be detected with change in rate of penetration and with gas shows and/or buoyant cuttings at the remote operated vehicle (ROV) camera.
   
   - In a hydrate zone, the relative drilling rate decreases.
   - The hydrate cuttings density is less than the water density, so they float in the seawater. The ROV camera should be watched carefully for hydrate cuttings.
7. A logging program for the pilot hole should be designed to detect and quantify the presence of hydrates to allow effective planning of further drilling, completion and production operations. Hydrates can be detected with several logs including caliper, sonic, neutron porosity, spontaneous potential and dual induction logs. The caliper log in a hydrate interval usually indicates an oversized wellbore due to spalling from the decomposition of a hydrate. Sonic logs indicate an increase in acoustic velocities in a hydrate zone to a range from 3.1 km/s to 4.4 km/s. Neutron porosity increases in contrast to a normal apparent reduction in neutron porosity in a free gas. The hydrate limits the penetration of mud filtrate, thus reduces the negative spontaneous potential. There is a relatively high resistivity spike on the dual induction log in a hydrate zone, ranging from 50 ohm-m to 1,000 ohm-m. Due to thawing next to the wellbore, the long normal separates from the short normal. An example log plot is provided in Figure 8.10 below.

Figure 8.10 Characteristics of hydrates in log data
9. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes this study of hydrate related concerns and solutions for deepwater Black Sea drilling. It states the overall conclusions from the study and recommendations for the future research.

9.1 Summary

Enhanced technology in deepwater drilling enables operators to explore, develop and produce deepwater offshore hydrocarbon fields. With the increasing water depth, the pressure and temperature operating conditions fall within hydrate stability boundaries, and naturally occurring gas hydrates may be encountered during drilling. The warm drilling fluid being circulated through the annulus can lead to hydrate dissociation. If the dissociation is rapid and significant, a gas kick will occur. If dissociation is extensive, the wellbore may become unstable. Furthermore, if dissociation occurs behind the casing, the casing may collapse due to the increased pressure in the gas resulting from dissociation. While the value of gas hydrates as a future energy resource remains uncertain, the hazards they pose to exploration and production of conventional energy are more evident.

A one-dimensional, linear, analytical, dissociation model was developed to predict the degree of hydrate dissociation during drilling. The model was used to calculate the location of the dissociation front versus time and wellbore temperature. This allowed wellbore enlargement due to dissociation to be calculated. The reduction of effective heat flux due to hole enlargement and its effect on dissociation rate were addressed. This method was applied to both past and planned deepwater wells in the Turkish Black Sea. The resulting gas influx volumes and the density reduction in the drilling fluid due to gas influx was calculated.

A series of wellbore temperature simulations were made by using GTEMP, a thermal wellbore temperature simulator, to investigate the effects of several parameters on temperature
distribution in the well. Results of the temperature simulations were used to calculate the temperature in, and temperature reduction along the annulus over an assumed hydrate interval, which was used to determine the heat influx into the hydrates.

The thermal model presented in this study provides a tool for prediction of hydrate dissociation rates and gas influx rates for a given set of hydrate reservoir and drilling conditions. The model is useful for selecting the mud temperatures and mud circulation rates to be used for drilling through hydrates.

9.2 Conclusions

1. Agreement between the linear dissociation model predictions and an experimental study done by others is within 15%.

2. The model presented in this study can be used for hydrate dissociation predictions during drilling. This model can be applied to any well where naturally occurring hydrates are expected to be encountered.

3. Gas shows observed in Black Sea wells occurred within depths where in-situ hydrates could exist. In addition, the well logs confirmed that there were no gas sands within this interval. Application of the dissociation model indicates that any hydrates encountered while drilling pilot and surface holes would have experienced dissociation and could be the cause of the gas shows.

4. The dissociation front speed is predicted to decrease with time given the assumption that the total heat flow into the hydrate is constant. The primary parameter affecting dissociation is the heat flux provided to the hydrate face. As the location of the dissociation interface moves away from the wellbore, the face area becomes larger resulting a decrease in the effective heat flux. Reduction in the heat flux reduces the speed of dissociation.
5. The dissociation of hydrates in deepwater wells causes observable gas influx rates at the seafloor; however, it has almost no impact on well pressures. Therefore, well control problem due to hydrate dissociation is not likely to occur. Also, the gas volume at the surface is small and therefore is not likely to cause a fire or a vessel instability problem. Under these circumstances, the main concern with dissociation of hydrates in the open hole appears to be wellbore instability.

6. The standpipe temperature is the most significant controllable parameter affecting the wellbore temperature profiles. The most effective way of controlling hydrate dissociation is to force the wellbore temperature to be lower than the temperature required for hydrate dissociation. Reducing the mud inlet temperature at surface by using a mud cooler, or by other means such as using cold make up water, can provide wellbore temperatures that are below the dissociation temperature in situations where this cooling is adequate to offset heat gained from the higher temperature formations below the hydrate.

7. Hydrate dissociation behind casing raises two concerns. The increase in volume of reservoir fluids due to hydrate dissociation causes increased formation pressure. Dissociation will continue until the formation pressure reaches the hydrate stability pressure at that particular temperature, and establishes new equilibrium conditions. An additional increase in temperature will result in further dissociation until a new equilibrium is reached. One concern is that the increase in formation pressure creates a differential casing collapse pressure, which would cause casing with an insufficient collapse rating to collapse. The other concern is that the increase in formation pressure could exceed the fracture pressure, which would lead to gas venting at the seafloor. These problems can occur during both drilling and production.
9.3 Recommendations

The overall recommendations for the future research are:

8. The analytical model was developed to address the impact of natural gas hydrates for the assumed worst case conditions. Further development of the model presented in this study should consider the following recommendations

   ○ The model should be developed to account for hydrate dissociation in porous sediments.

   ○ An early time solution of the model could not be obtained analytically, and the late time solution of the model was used for predictions at early times. Compared to the duration of drilling, the early time period of a few minutes or less is not significant. Therefore, development of an early time solution is not recommend.

   ○ The dissociation model presented here is a 1-D linear model, and it was applied to a radial geometry. The model should be adapted to a true radial geometry for more accurate results.

   ○ Further work is needed to validate the predictions of the model. Well logging records and drilling records from deepwater wells should be acquired and examined for the existence of in-situ hydrates and information on wellbore and surface temperatures and hole enlargement in hydrates to compare actual enlargement to predicted enlargement.

   ○ The calculation steps used in this study are not user friendly. First, temperature profiles were obtained from GTEMP. Temperature profiles were then used to calculate the heat flow into the hydrates. The dissociation interface location was calculated with the analytical model. A temperature model should be integrated with the dissociation model to resolve this difficulty and improve prediction
accuracy. The temperature model should consider the change in the wellbore radius as the hydrate dissociates.

- The hydrate layer was assumed to be isolated from the adjacent formations so that interactions with these formations were ignored. A detailed study of fluid and/or heat flow from and/or into the surrounding formations should be performed to predict the effects of these interactions on hydrate dissociation.

- Hydrate dissociation due to depressurization was ignored in the analytical model. The combined effects of thermal stimulation and depressurization on dissociation should be investigated.

9. The main concern with hydrate dissociation in the open hole seems to be wellbore instability. Therefore, the effect of hydrate dissociation while drilling on open hole wellbore instability should be investigated to develop a method to establish the maximum allowable enlargement for a given wellbore.

10. Most of the heat flow from the drilling fluid into a hydrate formation is spent for hydrate dissociation. A simple calculation should be made to compare the dissociation front location predicted by a simple balance between heat input and latent heat versus the front location predicted by the analytical model. This could provide a means for faster and simpler dissociation predictions.
REFERENCES


55. Namli, S., Louisiana State University, Mathematics Department, personal communication.


APPENDIX – A: DERIVATION OF THE HYDRATE DISSOCIATION MODEL

Let \( t_d \) be the time required for the boundary surface to reach the equilibrium temperature. When the wellbore temperature is considerably higher than the hydrate dissociation temperature, \( t_d \) is fairly small. Thus, for \( t < t_d \) the problem may be considered as a fixed boundary problem. The fixed boundary problem may be then regarded as a heating problem preceding dissociation. The appropriate differential equations for the fixed-boundary problem, and associated boundary conditions and initial conditions are given by:

\[
\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}, \quad 0 < x < \infty, \quad t > 0 \quad \text{................................. (A.1)}
\]

Inner boundary condition:

\[
-k \frac{\partial T}{\partial x} = Q, \quad x = 0, \quad t > 0 \quad \text{................................. (A.2)}
\]

Outer boundary condition

\[
T = T_i, \quad x = \infty, \quad t > 0 \quad \text{................................. (A.3)}
\]

Initial Condition

\[
T = T_i, \quad 0 < x < \infty, \quad t = 0 \quad \text{................................. (A.4)}
\]

Integrating (A.1) with respect to \( x \) over the interval \([0, \delta(t)]\)

\[
\frac{d}{dt} \left( \int_{x=0}^{x=\delta(t)} Tdx - T_i\delta \right) = \alpha \left( \frac{\partial T}{\partial x} \right)_{x=0}^{\delta(t)} \left( \frac{\partial T}{\partial x} \right)_{x=0}^{\delta(t)} - \frac{\partial T}{\partial x} \left|_{x=\delta(t)}^{x=0} \right.
\]

\[
\frac{d}{dt} \left( \int_{x=0}^{x=\delta(t)} Tdx - T_i\delta \right) = \alpha \left( \frac{\partial T}{\partial x} \right)_{x=\delta(t)}^{0} - \frac{\partial T}{\partial x} \left|_{x=0}^{x=\delta(t)} \right.
\]

\[
\frac{d}{dt} \left( \int_{x=0}^{x=\delta(t)} Tdx - T_i\delta \right) = -\alpha \frac{\partial T}{\partial x} (0, t) \quad \text{................................. (A.5)}
\]

Let \( T = c_4x^4 + c_3x^3 + c_2x^2 + c_1x + c_0 \) \quad \text{................................. (A.6)}
Five conditions to determine the coefficients, \( c_i \) are given by

\[
\frac{\partial T}{\partial x}(0, t) = -\frac{Q}{k} \quad \text{(A.7)}
\]

\[
T(\delta, t) = T_i \quad \text{(A.8)}
\]

\[
\frac{\partial T}{\partial x}(\delta, t) = 0 \quad \text{(A.9)}
\]

\[
\frac{\partial^2 T}{\partial x^2}(\delta, t) = 0 \quad \text{(A.10)}
\]

\[
\frac{\partial^3 T}{\partial x^3}(\delta, t) = 0 \quad \text{(A.11)}
\]

Taking the first derivative of (A.6), and applying (A.7)

\[
\frac{\partial T}{\partial x}(0, t) = 4c_4 x^3 + 3c_3 x^2 + 2c_2 x + c_1 = -\frac{Q}{k}
\]

\[
c_1 = -\frac{Q}{k} \quad \text{(A.12)}
\]

Applying (A.8) to (A.6)

\[
T(\delta, t) = c_4 \delta^4 + c_3 \delta^3 + c_2 \delta^2 - \frac{Q}{k} \delta + c_0 = T_i \quad \text{(A.13)}
\]

Applying (A.9) to (A.6)

\[
\frac{\partial T}{\partial x}(\delta, t) = 4c_4 \delta^3 + 3c_3 \delta^2 + 2c_2 \delta - \frac{Q}{k} = 0 \quad \text{(A.14)}
\]

Applying (A.10) to (A.6)

\[
\frac{\partial^2 T}{\partial x^2}(\delta, t) = 12c_4 \delta^2 + 6c_3 \delta + 2c_2 = 0 \quad \text{(A.15)}
\]

Applying (A.11) to (A.6)

\[
\frac{\partial^3 T}{\partial x^3}(\delta, t) = 24c_4 \delta + 6c_3 = 0 \quad \text{(A.16)}
\]
Solving (A.16)

\[ 24c_4\delta + 6c_3 = 0 \Rightarrow c_3 = -4c_4\delta \]  
\[ \text{……………………………………………………… (A.17)} \]

Writing \(c_3\) into (A.15)

\[ 12c_4\delta^2 - 24c_4\delta^2 + 2c_2 = 0 \Rightarrow c_2 = 6c_4\delta^2 \]  
\[ \text{……………………………………………………… (A.18)} \]

Writing \(c_2\) and \(c_3\) into (A.14)

\[ 4c_4\delta^3 - 12c_4\delta^3 + 12c_4\delta^3 - \frac{Q}{k} = 0 \Rightarrow c_4 = \frac{1}{4} \frac{Q}{k\delta^3} \]  
\[ \text{……………………………………………………… (A.19)} \]

Writing (A.19) into (A.17)

\[ c_3 = -4c_4\delta \Rightarrow c_3 = -\frac{Q}{k\delta^2} \]  
\[ \text{……………………………………………………… (A.20)} \]

Writing (A.19) into (A.18)

\[ c_2 = 6c_4\delta^2 \Rightarrow c_2 = \frac{3}{2} \frac{Q}{k\delta} \]  
\[ \text{……………………………………………………… (A.21)} \]

Writing (A.12), (A.19), (A.20) and (A.21) into (A.13)

\[ T(\delta, t) = \frac{1}{4} \frac{Q}{k\delta^3} \delta^4 - \frac{Q}{k\delta^2} \delta^3 + \frac{3}{2} \frac{Q}{k\delta} \delta^2 - \frac{Q}{k} \delta + c_0 = T_0 \]

After doing the necessary substitutions

\[ \frac{Q}{k} \delta \left[ \frac{1}{4} - \frac{3}{2} \right] + c_0 = T_0 \Rightarrow c_0 = T_0 + \frac{1}{4} \frac{Q}{k} \delta \]  
\[ \text{……………………………………………………… (A.22)} \]

Writing the coefficients, \(c_1\), into the forth degree polynomial equation

\[ T(x, t) = \frac{1}{4} \frac{Q}{k\delta^3} x^4 - \frac{Q}{k\delta^2} x^3 + \frac{3}{2} \frac{Q}{k\delta} x^2 - \frac{Q}{k} x + T_0 + \frac{1}{4} \frac{Q}{k} \delta \]  
\[ \text{……………………………………………………… (A.23)} \]

Rearranging (A.23)

\[ T(x, t) = \frac{Q}{k} \delta \left[ \frac{1}{4} \left( \frac{x}{\delta} \right)^4 - \left( \frac{x}{\delta} \right)^3 + \frac{3}{2} \left( \frac{x}{\delta} \right)^2 - \left( \frac{x}{\delta} \right) + \frac{1}{4} \right] + T_0 \]  
\[ \text{……………………………………………………… (A.24)} \]
Writing (A.24) into (A.5)
\[
\frac{d}{dt} \left[ \int_0^\delta \left( \frac{Q}{k} \delta \left[ \frac{1}{4} \left( \frac{x}{\delta} \right)^4 - \frac{3}{2} \left( \frac{x}{\delta} \right)^2 - \frac{1}{4} \right] + T_i \right] dx - T_i \delta \right] = -\alpha \frac{\partial T}{\partial x}(0,t) \quad \text{(A.25)}
\]

Solving the LHS of (A.25)
\[
\frac{d}{dt} \left( \frac{Q}{k} \delta \left[ \frac{1}{20} \delta^4 - \frac{1}{4} \delta^3 + \frac{1}{2} \delta^2 + \frac{1}{4} \delta \right] + T_i \delta \right) \Bigg|_{x=\delta(t)} - T_i \delta \Bigg|_{x=0}
\]

After doing the necessary substitutions
\[
\frac{d}{dt} \left( \frac{1}{20} \frac{Q}{k} \delta^2 \right) = -\alpha \frac{\partial T}{\partial x}(0,t) \quad \text{................................................................. (A.26)}
\]

Applying the power rule to the LHS of (A.26), and combining with (A.7)
\[
\frac{d}{dt} \left( \frac{1}{20} \frac{Q}{k} \delta^2 \right) = \frac{1}{20} \frac{Q}{k} 2\delta \frac{d\delta}{dt} = \alpha \frac{Q}{k}
\]

After doing the substitutions
\[
\delta d\delta = 10\alpha dt \quad \text{................................................................. (A.27)}
\]

Integrating (A.27)
\[
\frac{\delta^2}{2} = 10 \alpha t \Rightarrow \delta^2 = 20 \alpha t \Rightarrow \delta = \sqrt{20 \alpha t} \quad \text{................................................................. (A.28)}
\]

Writing \( x = 0 \) into (A.23)
\[
T(0,t) = \frac{1}{4} \frac{Q}{k} \delta + T_i \quad \text{................................................................. (A.29)}
\]

Writing (A.28) into (A.29)
\[
T(0,t) = \frac{1}{4} \frac{Q}{k} \sqrt{20 \alpha t} + T_i
\]
\[ T(0, t) = \frac{Q}{k} \sqrt[5]{\frac{5}{4}} \alpha t + T_i \]  
…………………………………………………… (A.30)

Hydrate dissociation starts when \( T(0, t) = T_d \) at \( t = t_d \), then

\[ T(0, t_d) = T_d = \frac{Q}{k} \sqrt[5]{\frac{5}{4}} \alpha t_d + T_i \]  
…………………………………………………… (A.31)

Solving (A.31) for \( t_d \)

\[ t_d = \frac{4}{5} \frac{k^2}{\alpha Q^2} (T_d - T_i)^2 \]  
…………………………………………………… (A.32)

When \( t > t_d \) the problem becomes a moving boundary problem. The appropriate differential equations for the moving-boundary problem, and associated boundary conditions and initial conditions are given by:

\[ \frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \]  
\[ X_D(t) < x < \infty, \quad t > 0 \]  
……………………………… (A.33)

Moving boundary conditions:

\[ T = T_s \]  
\[ x = X_D(t), \quad t > 0 \]  
……………………………… (A.34)

\[ -k \frac{\partial T}{\partial x} + \rho L \frac{dX}{dt} = Q \]  
\[ x = X_D(t), \quad t > 0 \]  
……………………………… (A.35)

Outer boundary condition

\[ T = T_i \]  
\[ x = \infty, \quad t > 0 \]  
……………………………… (A.36)

Initial Condition

\[ T = f(x) \]  
\[ 0 < x < \infty, \quad t = t_d \]  
……………………………… (A.37)

Where, the function \( f(x) \) is obtained from the solution of the fixed-boundary problem.

Integrating (A.33) with respect to \( x \) over the interval \([X(t), \delta(t)]\)
\[ \int_{x=X_0(t)}^{x=\delta(t)} \frac{\partial T}{\partial t} \, dx = \int_{x=X_0(t)}^{x=\delta(t)} \alpha \frac{\partial^2 T}{\partial x^2} \, dx \quad \text{.................................} \quad (A.38) \]

Solving the LHS

\[ \int_{X_0(t)}^{\delta(t)} \frac{\partial T}{\partial t} \, dx = \int_{x=0}^{x=\delta(t)} \frac{\partial T}{\partial t} \, dx - \int_{x=0}^{x=X_0(t)} \frac{\partial T}{\partial t} \, dx \]
\[ = \frac{d}{dt} \left[ \int_{x=0}^{x=\delta(t)} T \, dx - T_1 \delta \right] - \frac{d}{dt} \left[ \int_{x=0}^{x=X_0(t)} T \, dx - \left( T_{sd} + \rho L \frac{\alpha}{k} \right) X_D(t) \right] \]
\[ \int_{X_0(t)}^{\delta(t)} \frac{\partial T}{\partial t} \, dx = \frac{d}{dt} \left[ \int_{x=X_0(t)}^{x=\delta(t)} T \, dx - T_1 \delta + \left( T_{sd} + \rho L \frac{\alpha}{k} \right) X_D(t) \right] \quad \text{.................................} \quad (A.39) \]

Solving the RHS

\[ \int_{X_0(t)}^{\delta(t)} \alpha \frac{\partial^2 T}{\partial x^2} \, dx = \alpha \left( \frac{\partial T}{\partial x} \right) \bigg|_{X_0}^{\delta} \]
\[ = \alpha \left( \frac{\partial T}{\partial x} \bigg|_{x=\delta(t)} - \frac{\partial T}{\partial x} \bigg|_{x=X_0(t)} \right) \]

\[ T(\delta, t) = T_1 \Rightarrow \frac{\partial T}{\partial x} \bigg|_{x=\delta(t)} = 0 \]

By the help of the moving boundary, (A.35),

\[ \frac{\partial T}{\partial x} \bigg|_{x=X_0(t)} = \frac{\rho L}{k} \frac{dX_D}{dt} \bigg|_{x=X_0(t)} - \frac{Q}{k} \]
\[ \frac{dX}{dt} \bigg|_{x=X_0(t)} = 0 \]
\[ \frac{\partial T}{\partial x} \bigg|_{x=X_0(t)} = -\frac{Q}{k} \]

So, RHS of the equation can be expressed as follows:

\[ \int_{X_0(t)}^{\delta(t)} \alpha \frac{\partial^2 T}{\partial x^2} \, dx = \alpha \frac{Q}{k} \quad \text{.................................} \quad (A.40) \]
Combining the LHS and the RHS equations, (A.33) becomes:

\[
\frac{d}{dt} \left[ \int_{x=x_0(t)}^{x_0(t)} T \, dx - T_1 \delta + \left( T_d + \frac{\rho L \alpha}{k} \right) X_D(t) \right] = \frac{Q}{k} \]  \tag{A.41}

Similarly let the temperature \( T \) at any point be a forth order polynomial represented by the equation below.

\[
T = c_4 x^4 + c_3 x^3 + c_2 x^2 + c_1 x + c_0 \]  \tag{A.42}

Five conditions to determine the coefficients, \( c_i \)

\[
T(X_D, t) = T_d \]  \tag{A.43}

\[
T(\delta, t) = T_i \]  \tag{A.44}

\[
\frac{\partial T}{\partial x}(\delta, t) = 0 \]  \tag{A.45}

\[
\frac{\partial^2 T}{\partial x^2}(\delta, t) = 0 \]  \tag{A.46}

\[
\frac{\partial^3 T}{\partial x^3}(\delta, t) = 0 \]  \tag{A.47}

With the help of (A.43)

\[
T = c_4 X_D^4 + c_3 X_D^3 + c_2 X_D^2 + c_1 X_D + c_0 = T_d \]  \tag{A.48}

With the help of (A.44)

\[
T = c_4 \delta^4 + c_3 \delta^3 + c_2 \delta^2 + c_1 \delta + c_0 = T_i \]  \tag{A.49}

Taking the first derivative of (A.42) and solving for \( T(x, t) = T(\delta, t) \)

\[
\frac{\partial T}{\partial x}(\delta, t) = 4c_4 x^3 + 3c_3 x^2 + 2c_2 x + c_1 = 0 \]  \tag{A.50}

Taking the second derivative of (A.42) and solving for \( T(x, t) = T(\delta, t) \)
\[
\frac{\partial^2 T}{\partial x^2} (\delta, t) = 12c_4 \delta^2 + 6c_3 \delta + 2c_2 = 0 \quad \text{.................................................... (A.51)}
\]

Taking the third derivative of (A.42) and solving for \( T(x, t) = T(\delta, t) \)

\[
\frac{\partial^3 T}{\partial x^3} (\delta, t) = 24c_4 \delta + 6c_3 = 0 \quad \text{.................................................... (A.52)}
\]

Solving (A.52) we get

\[
24c_4 \delta + 6c_3 = 0 \Rightarrow c_3 = -4c_4 \delta \quad \text{.................................................... (A.53)}
\]

Writing \( c_3 \) into (A.51) we get

\[
12c_4 \delta^2 - 24c_4 \delta^2 + 2c_2 = 0 \Rightarrow c_2 = 6c_4 \delta^2 \quad \text{.................................................... (A.54)}
\]

Writing \( c_2 \) and \( c_3 \) into (A.50) we get

\[
4c_4 x^3 + 3c_3 x^2 + 2c_2 x + c_1 = 0 \Rightarrow c_1 = -4c_4 \delta^3 \quad \text{.................................................... (A.55)}
\]

Writing \( c_1, c_2, c_3 \) and \( c_4 \) into (A.48) and (A.49), and eliminating \( c_0 \) we get

\[
T_i - T_d = c_4 (\delta^4 - X_D^4) - 4c_4 (\delta^4 - \delta X_D^3) + 6c_4 (\delta^4 - \delta^2 X_D^2) - 4c_4 (\delta^4 - \delta^3 X_D)
\]

\[
T_i - T_d = c_4 (\delta - X_D)^4
\]

\[
c_4 = -\frac{T_i - T_d}{(\delta - X_D)^4} \quad \text{.................................................... (A.56)}
\]

\[
c_3 = -4c_4 \delta \Rightarrow c_3 = 4\delta \frac{T_i - T_d}{(\delta - X_D)^4} \quad \text{.................................................... (A.57)}
\]

\[
c_2 = 6c_4 \delta^2 \Rightarrow c_2 = 6\delta^2 \frac{T_i - T_d}{(\delta - X_D)^4}
\]

(A.58)

\[
c_1 = -4c_4 \delta^3 \Rightarrow c_1 = 4\delta^3 \frac{T_i - T_d}{(\delta - X_D)^4} \quad \text{.................................................... (A.59)}
\]
\[
c_0 = -\delta^4 \frac{T_i - T_d}{(\delta - X_D)^4} + T_i \quad \text{................................. (A.60)}
\]

Writing all coefficients in (A.42) we get
\[
T = -\frac{T_i - T_d}{(\delta - X_D)^4} x^4 + 4\delta \frac{T_i - T_d}{(\delta - X_D)^4} x^3 - 6\delta^2 \frac{T_i - T_d}{(\delta - X_D)^4} x^2 \\
+ 4\delta^3 \frac{T_i - T_d}{(\delta - X_D)^4} x - \delta^4 \frac{T_i - T_d}{(\delta - X_D)^4} + T_i 
\]

\[
\text{................................. (A.61)}
\]

Rearranging (A.61) we get
\[
T = -\frac{T_i - T_d}{(\delta - X_D)^4} \left[ x^4 + 4\delta x^3 - 6\delta^2 x^2 + 4\delta^3 x - \delta^4 \right] + T_i 
\]

\[
\text{................................. (A.62)}
\]

Integrating (A.62) with respect to \( x \) over the interval \([X(t), \delta(t)]\)
\[
\int_{x=X_D}^{x=\delta} Tdx = \left\{ \frac{T_i - T_d}{(\delta - X_D)^4} \left[ \frac{-x^5}{5} + 2\delta x^4 - 2\delta^2 x^3 - 2\delta^3 x^2 - \delta^4 x \right] + T_i x \right\}_{x=X_D}^{x=\delta(t)} .... (A.63)
\]

Rearranging (A.63)
\[
\int_{x=X_D}^{x=\delta} Tdx = \frac{T_i - T_d}{(\delta - X_D)^4} \left[ \frac{\delta - x}{5} + T_i x \right]_{x=X_D}^{x=\delta(t)} = -\frac{T_i - T_d}{5} (\delta - X_D)^5 + T_i \delta - T_i X_D .. (A.64)
\]

Then (A.41) becomes
\[
\frac{d}{dt} \left[ -\frac{T_i - T_d}{5} (\delta - X_D) - T_i X_D + \left( T_d + \rho L \frac{\alpha}{k} \right) X_D(t) \right] = \alpha \frac{Q}{k} \quad \text{............... (A.65)}
\]

Rearranging (A.65)
\[
\frac{d}{dt} \left[ (\delta - X_D) + 5 \left( 1 + \frac{\rho L \alpha}{k(T_d - T_i)} \right) X_D \right] = \frac{5\alpha Q}{k(T_d - T_i)} \quad \text{...................... (A.66)}
\]

Rearranging (A.66) we get
\[
\frac{d}{dt} (\delta - X_D) + 5 \left( 1 + \frac{\rho L \alpha}{k(T_d - T_i)} \right) dX_D = \frac{5\alpha Q}{k(T_d - T_i)} \quad \text{...................... (A.67)}
\]
Stefan number is known as the ratio of latent to sensible heat, and is defined as:

\[ \nu = \frac{L}{C_p \Delta T} = \frac{L}{C_p(T_d - T_i)} = \frac{\rho L \alpha}{k(T_d - T_i)} \]  \hspace{1cm} (A.68)

Writing Stefan number in (A.67) we get

\[ \frac{d}{dt}(\delta - X_d) + 5(1 + \nu)\frac{dX_d}{dt} = \frac{5\alpha Q}{k(T_d - T_i)} \]  \hspace{1cm} (A.69)

Rearranging (A.35)

\[ \rho L \frac{dX_d}{dt} = Q + k \frac{\partial T}{\partial x} \bigg|_{x=X_o(t)} \]  \hspace{1cm} (A.70)

If we write (A.62) into (A.70) we get

\[ \rho L \frac{dX_d}{dt} = Q + k \frac{T_i - T_d}{(\delta - X_d)^4} \left[ x^4 + 4\delta x^3 - 6\delta^2 x^2 + 4\delta^3 x - \delta^4 \right] + T_i \bigg|_{x=X_o(t)} \]

\[ \rho L \frac{dX_d}{dt} = Q + k \left( \frac{T_i - T_d}{\delta - X_d} \right)^3 \bigg|_{x=X_o(t)} \]

\[ \rho L \frac{dX_d}{dt} = Q - 4k \left( \frac{T_d - T_i}{\delta - X_d} \right) \]

\[ \frac{dX_d}{dt} = \frac{Q}{\rho L} - \frac{4k(T_d - T_i)}{\rho L \left( \delta - X_d \right)} \]  \hspace{1cm} (A.71)

Equations (A.69) and (A.71) are two simultaneous differential equations for \( \delta - X_D \) and \( X_D \). The initial conditions are

\[ X_D = 0 \] at \( t = t_d \)  \hspace{1cm} (A.72)

\[ \delta = \frac{4k(T_d - T_i)}{Q} \] at \( t = t_d \)  \hspace{1cm} (A.73)

Writing (A.71) in (A.69) we get
\[ \frac{d}{dt}(\delta - X_D) + 5(1 + \nu) \left( \frac{Q}{\rho L} - \frac{4k(T_d - T_i)}{\rho L(\delta - X_D)} \right) = \frac{5\alpha Q}{k(T_u - T_i)} \]  \hspace{1cm} (A.74)

\[
\frac{d}{dt}(\delta - X_D) - 5(1 + \nu) \left( \frac{4k(T_d - T_i)}{\rho L(\delta - X_D)} \right) + 5 \left( 1 + \frac{\rho L \alpha}{k(T_u - T_i)} \right) \left( \frac{Q}{\rho L} \right) - \frac{5\alpha Q}{k(T_d - T_i)} = 0
\]

(A.74) becomes

\[
\frac{d}{dt}(\delta - X_D) - 5(1 + \nu) \frac{4k(T_d - T_i)}{\rho L(\delta - X_D)} + \frac{5Q}{\rho L} = 0
\]

Multiplying both sides of the equation by \( \frac{\rho L}{5Q} \) we get

\[
\frac{\rho L}{5Q} \frac{d}{dt}(\delta - X_D) - (1 + \nu) \frac{4k(T_d - T_i)}{Q(\delta - X_D)} + 1 = 0 \]  \hspace{1cm} (A.75)

Dimensionless thickness of the thawed zone, \( \varepsilon \), can be defined as:

\[
\varepsilon = \frac{Q(\delta - X_D)}{4k(T_d - T_i)} \]  \hspace{1cm} (A.76)

Then

\[
d\varepsilon = \frac{Q}{4k(T_d - T_i)} d(\delta - X_D)
\]

\[
d(\delta - X_D) = \frac{4k(T_d - T_i)}{Q} d\varepsilon \]  \hspace{1cm} (A.77)

Writing (A.77) in (A.75) we get

\[
\frac{4k(T_d - T_i)\rho L}{5Q^2} \frac{d\varepsilon}{dt} \left( 1 + \nu \right) \frac{1}{\varepsilon} + 1 = 0 \]  \hspace{1cm} (A.78)

A dimensionless time, \( \tau \), can be defined as:

\[
\tau = \frac{5Q^2}{4k(T_d - T_i)\rho L} t \]  \hspace{1cm} (A.79)

Then

\[
d\tau = \frac{5Q^2}{4k(T_d - T_i)\rho L} dt
\]
Writing (A.80) in (A.78) we get
\[
\frac{d\varepsilon}{d\tau} - \left(1 + \nu\right) \frac{1}{\varepsilon} + 1 = 0 \quad \text{........................................... (A.81)}
\]

Writing the initial conditions, (A.72) and (A.73), in (A.76) we get
\[
\varepsilon = \frac{Q(\frac{4k(T_d - T_i)}{Q} - 0)}{4k(T_d - T_i)} = 1 \quad \text{........................................... (A.82)}
\]

Writing (A.79) at \(t = t_d\)
\[
\tau_d = \frac{5Q^2}{4k(T_d - T_i)\rho L} \quad t_d = \frac{5Q^2}{4k(T_d - T_i)\rho L} \frac{4k^2(T_d - T_i)^2}{5\alpha Q^2}
\]
\[
\tau_d = \frac{k(T_d - T_i)}{\rho L} = \frac{1}{\nu} \quad \text{........................................... (A.83)}
\]

Rearranging (A.81) we get
\[
\frac{d\varepsilon}{d\tau} = \left(1 + \nu\right) \frac{1}{\varepsilon} - 1
\]

This function is hard to integrate so,
\[
\frac{d\tau}{d\varepsilon} = \frac{\varepsilon}{(1 + \nu)\varepsilon - \varepsilon},
\]
\[
\int_{\tau_i}^{\tau} d\tau = \int_{\varepsilon}^{\varepsilon} \frac{\varepsilon}{(1 + \nu)\varepsilon - \varepsilon} d\varepsilon \quad \text{........................................... (A.84)}
\]

Integrating (A.84) we get
\[
\int_{\tau_i}^{\tau} d\tau = \int_{\varepsilon}^{\varepsilon} \frac{\varepsilon}{(1 + \nu)\varepsilon - \varepsilon} d\varepsilon
\]

Solution of this integral is
\[
\tau \bigg|_{\tau_i}^{\tau} = \left(- (1 + \nu) \ln(1 + \nu - \varepsilon) - \varepsilon\right) \bigg|_{\varepsilon}
\]
\[
\tau - \tau_d = \left[ -(1+\nu)\ln(1+\nu-\varepsilon) + (1+\nu)\ln(1+\nu-1+1) \right]
\]

\[
\tau - \tau_d = 1 - \varepsilon + (1+\nu)\ln\left( \frac{\nu}{1+\nu-\varepsilon} \right)
\]

(A.85)

If we write (A.76) and (A.80) in (A.71) we get

\[
\frac{\rho L}{Q} \frac{dX_D}{4k(T_d-T_i)\rho L} \frac{d\tau}{d\varepsilon} = 1 - \frac{1}{\varepsilon}
\]

(A.86)

Dimensionless position of the dissociation interface can be defined as:

\[
X^* = \frac{5QX_D}{4k(T_d-T_i)}
\]

(A.87)

Writing (A.87) in (A.86) and rearranging the equation we get

\[
\frac{dX^*}{d\tau} = \frac{\varepsilon - 1}{\varepsilon}
\]

(A.88)

with the initial condition

\[
X^* = 0 \quad \text{at} \quad \tau = 0
\]

(A.89)

It is hard to solve (A.88) in this form. If we multiply and divide the LHS of (A.88) by \(d\varepsilon\) we get

\[
\frac{dX^*}{d\varepsilon} = \frac{\varepsilon - 1}{d\tau}
\]

(A.90)

Rearranging and taking the reciprocal of (A.81) inverse

\[
\frac{d\tau}{d\varepsilon} = \frac{1}{(1+\nu)\frac{1+\nu-\varepsilon}{\varepsilon} - 1} = \frac{\varepsilon}{1+\nu-\varepsilon}
\]

(A.91)

Writing (A.91) in (A.90) we get
\[
\frac{dX^*}{d\varepsilon} = \frac{\varepsilon - 1}{\varepsilon} \quad \frac{1}{1 + \nu - \varepsilon}
\]

After doing substitutions, and rearranging the equation

\[
\frac{dX^*}{d\varepsilon} = \frac{\varepsilon - 1}{1 + \nu - \varepsilon} \quad \text{………………………………………………………………………………….. (A.92)}
\]

with

\[
X^* = 0 \quad \text{at} \quad \varepsilon = 1 \quad \text{………………………………………………………………………………….. (A.93)}
\]

In (A.92)

\[
\frac{\varepsilon - 1}{1 + \nu - \varepsilon} = \frac{\varepsilon - 1 + \nu - \nu}{1 + \nu - \varepsilon} = \frac{\nu - (1 + \nu - \varepsilon)}{1 + \nu - \varepsilon} = \frac{\nu}{1 + \nu - \varepsilon} - 1
\]

Substituting this expression in place and integrating (A.92)

\[
\int_0^{X^*} dX^* = \int_1^{\varepsilon} \left( \frac{\nu}{1 + \nu - \varepsilon} - 1 \right) d\varepsilon,
\]

Solution of this integral is

\[
X^*|_0^{X^*} = \left( -\nu \ln(1 + \nu - \varepsilon) - \varepsilon \right)|_1^{\varepsilon}
\]

\[
X^* - 0 = \left[ (-\nu \ln(1 + \nu - \varepsilon) - \varepsilon) + (\nu \ln(1 + \nu - 1) + 1) \right]
\]

\[
X^* = 1 - \varepsilon + \nu \ln \left( \frac{\nu}{1 + \nu - \varepsilon} \right) \quad \text{………………………………………………………………………………….. (A.94)}
\]

The speed of interface decreases with time, eventually attaining a constant value. Thus, a

long-time solution for large \( t \) can be obtained by setting \( \frac{dX_D}{dt} \) equal to a constant, which is

\[
\frac{dX_D}{dt} = \frac{1}{1 + \nu} \frac{\alpha Q}{k(T_d - T_i)} \quad \text{………………………………………………………………………………….. (A.95)}
\]
The heat balance equations can be written and illustrated separately for the drill pipe and for the annulus for a small control volume, with a thickness of \(dz\). Figure B.1 illustrates the heat balance equations for the drillpipe.

Heat balance equations for the drill pipe are as follows.

\[
\dot{Q}_{pz} - \dot{Q}_{p(z+dz)} = 2\pi r_p h_p (T_p - T_a)dz \\
\dot{Q}_{pa} = 2\pi r_p h_p (T_p - T_a)dz \\
\dot{Q}_{p(z+dz)} = mC_p T_{p(z+dz)}
\]

Heat balance for the annulus can be written and illustrated similarly. Figure B.2 illustrates the heat balance equations for the annulus.
Heat balance equations for the annulus can be written as follows.

\[ \dot{Q}_{az} - \dot{Q}_{a(z+dz)} + 2\pi r_p h_p (T_p - T_a)dz = 2\pi r_w h_w (T_a - T_f)dz \]  \hspace{1cm} \text{(B.4)}

\[ mC_p T_p - mC_p T_{p(z+dz)} + 2\pi r_p h_p (T_p - T_a)dz = 2\pi r_w h_w (T_a - T_f)dz \]  \hspace{1cm} \text{(B.5)}

\[ mC_p \frac{dT_a}{dz} + 2\pi r_p h_p (T_p - T_a) = 2\pi r_w h_w (T_a - T_f) \]  \hspace{1cm} \text{(B.6)}

Dividing both sides of (B.3) and (B.6) into \( 2\pi r_p h_p \),

\[ \frac{mC_p}{2\pi r_p h_p} \frac{dT_p}{dz} = (T_p - T_a) \]  \hspace{1cm} \text{(B.7)}

\[ \frac{mC_p}{2\pi r_p h_p} \frac{dT_a}{dz} + (T_p - T_a) = \frac{2\pi r_w h_w}{2\pi r_p h_p} (T_a - T_f) \]  \hspace{1cm} \text{(B.8)}

Define \( A = \frac{mC_p}{2\pi r_p h_p} \), \( B = \frac{r_w h_w}{r_p h_p} \), and \( T_f = T_s + Gz \)

Then \( A \frac{dT_p}{dz} = (T_p - T_a) \)  \hspace{1cm} \text{(B.9)}
\[ A \frac{dT_a}{dz} + (T_p - T_a) = B(T_a - T_s - Gz) \quad \text{...........................................} \quad (B.10) \]

Rearranging (B.9) and (B.10)

\[ \frac{dT_p}{dz} - \frac{1}{A} T_p = -\frac{1}{A} T_a \quad \text{...........................................} \quad (B.11) \]

\[ \frac{dT_a}{dz} - \left( \frac{B+1}{A} \right) T_a = \frac{1}{A} (T_p - BT_s - BGz) \quad \text{...........................................} \quad (B.12) \]

These are the equations of the linear heat transfer model, and they are first order ordinary differential equations. The solution for these kind ordinary differential equations is:

\[ T_p = K_1 e^{C_1z} + K_2 e^{C_2z} + Gz + T_s - GA \quad \text{...........................................} \quad (B.13) \]

\[ T_a = K_1 C_3 e^{C_1z} + K_2 C_4 e^{C_2z} + Gz + T_s \quad \text{...........................................} \quad (B.14) \]

Where

\[ C_1 = \frac{B}{2A} \left( 1 + \sqrt{1 + \frac{4}{B}} \right), \]

\[ C_2 = \frac{B}{2A} \left( 1 - \sqrt{1 + \frac{4}{B}} \right), \]

\[ C_3 = 1 + \frac{B}{2} \left( 1 + \sqrt{1 + \frac{4}{B}} \right), \text{ and} \]

\[ C_4 = 1 + \frac{B}{2} \left( 1 - \sqrt{1 + \frac{4}{B}} \right) \]

Solving the equation at the boundary conditions we can find integration constants.

At \( z = 0 \), \( T_p = T_{pi} \), and at \( z = H \), \( T_p = T_a \)

Then \( K_1 = T_{pi} - K_2 - T_s + GA \), and

\[ K_2 = \frac{GA - [T_{pi} - T_s + GA] e^{C_1 H (1 - C_3)}}{e^{C_1 H (1 - C_4)} - e^{C_1 H (1 - C_3)}} \]
APPENDIX – C: NOMENCLATURE

A : Coefficient, ratio \( mC_p/2\pi r_p h_p \)
B : Coefficient, ratio \( r_w h_w/r_p h_p \)
\( C_p \) : Heat capacity (specific heat) of hydrate
\( d \) : Hole diameter
\( D \) : Depth
\( f_g \) : fraction of gas in the drilling fluid
\( G \) : Geothermal gradient
\( h_d \) : Hydrate layer thickness
\( h_p \) : Heat transfer coefficient of the drillpipe
\( h_w \) : Heat transfer coefficient of the well
\( H \) : Total depth of the well
\( k \) : Thermal conductivity of hydrate layer
\( L \) : Dissociation heat of hydrate
\( m \) : Mass flow rate through the drillpipe
\( M \) : Molecular weight of gas
\( n \) : Number of mole of gas
\( n \) : Gas influx due to dissociation
\( N \) : Cumulative gas influx due to dissociation
\( P \) : Pressure
\( P_{st} \) : Standard pressure
\( q_c \) : Rate of cuttings generation
\( q_g \) : Gas volumetric rate at standard conditions due to dissociation
\( Q \) : Effective heat flux into the hydrate face
\( Q_a \) : Heat flux in the annulus
\( Q_{af} \) : Heat flux from the annulus to the formation
\( Q_{pa} \) : Heat flux from the drillpipe to the annulus
\( R \) : Gas constant
\( r_p \) : Drillpipe radius
\( r_w \) : Wellbore radius
\( t \) : Time
\( t_d \) : Time at start of dissociation
\( T \) : Temperature
\( T_a \) : Temperature in the annulus
\( T_i \) : Initial hydrate layer temperature
\( T_d \) : Hydrate dissociation temperature
\( T_f \) : Formation temperature
\( T_p \) : Temperature in the drillstring
\( T_s \) : Surface temperature
\( T_{st} \) : Standard temperature
\( T_w \) : Wellbore temperature
\( x \) : Direction of the dissociation
\( X_D \) : Distance between the dissociation front and the wellbore
\( X^* \) : Dimensionless position of the dissociation interface
\( Z_D \) : Dissociated zone
\( Z_S \) : Solid hydrate zone
\( \alpha \) : Thermal diffusivity of the hydrate
\( \varepsilon \) : Dimensionless thickness of the thermally disturbed zone as defined in eq. (5.57)
\( \delta \) : Thermally disturbed zone distance from the wellbore
\( \nu \) : Stefan number (ratio of latent heat to sensible heat)
\( \rho \) : Density of hydrate
\( \rho_g \) : Density of gas in drilling fluid
\( \rho_i \) : Density of the drilling fluid
\( _\rho \) : Mean drilling fluid density
\( \tau \) : Dimensionless time
\( \tau_d \) : Dimensionless start of dissociation time
VITA

Erdem Catak, son of Gulluzar Catak and Etem Catak, was born in Kirklareli, Turkey, on January 2, 1979. He attended Technical University of Istanbul, receiving a Bachelor of Science degree with honors in petroleum and natural gas engineering in 2001. After doing graduate studies in the Institute of Science and Technology in Technical University of Istanbul he was awarded a Master of Science scholarship by Turkish Petroleum Corporation. In 2003, he enrolled at Louisiana State University to start his studies for a master’s degree. He specializes in drilling, drilling fluids and well control.