PREVENTION AND REMEDIATION OF HYDRATE FORMATION IN SELECTED NATURAL GAS STREAMS

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CERTIFICATION

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DEDICATION

This work is dedicated to God Almighty for his infinite mercy, love, grace and ability to undertake and successfully complete this project.

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ABSTRACT

In this work, prediction of hydrate formation possibility in natural gas streams, prescription of the appropriate inhibition technique for hydrates in natural gas streams and evaluation of the effect of hydrate formation on gas flow rates through piping equipment were carried out. In order to perform these tasks, data for five natural gas streams were obtained from a gas field in the Niger Delta. While the data obtained for gas streams A to D showed that hydrate had not formed in the gas streams, that of gas stream E showed that hydrate had already formed and then the effect of this hydrate formation on the gas flow rate of this stream E was evaluated by computing the flow rates through the orifice before hydrate formation and after hydrate formation. Computer models were developed for the prediction of hydrate formation possibility in natural gas streams and the prescription of the appropriate inhibition technique for hydrates in natural gas streams. The results obtained showed that hydrate formation is not possible in gas stream A based on the evaluations but there is possibility of hydrate formation in natural gas streams B, C and D. Based on their variable flow rates and water contents, they had different appropriate inhibition techniques. The appropriate inhibition technique for gas stream B got from the results generated by the computer model is Heating the Gas Stream to High Temperatures; that for gas stream C is Passing the Gas Stream across Methanol or Ethylene Glycol to absorb the Water in the Gas; For gas stream C, PVTP, a reservoir engineering program was applied to determine the minimum weight % of glycol required to protect the gas up to 5000 psig at 50^0F as 29.8062% and that of methanol as 19.3878%. The results also showed that less methanol is required to protect the gas from forming hydrate at low temperatures than glycol. For gas stream D, the inhibition technique got from the results generated by the computer model is passing the Gas Stream through a Glycol Dehydrator Column. The amounts of water to be removed was estimated as 2.98 lbm/hr and the required glycol circulation rate as 0.075 gal/hr. The results got for gas Stream E showed that the flow rate through the orifice before hydrate formation was 2465829.4scf/hr and that after hydrate formation was 668146.4scf/hr. The implications of these results obtained showed that hydrate formation reduces the amount of flow through the orifice and to check the possibility of hydrate formation in a gas stream, the developed model can be used and if it is noticed that hydrate formation is possible, the model can still be used to determine the appropriate inhibition technique.

Key Words: Natural gas stream, flow rate, hydrate, water content, orifice, prediction, inhibition, prescription, glycol, temperature, dehydrator.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDY

Natural gas is found in deep underground natural rock formations or associated with other hydrocarbon reservoirs in coal beds and as methane clathrates. Petroleum is also another resource found in proximity to and with natural gas. Most natural gas was created over time by two mechanisms: biogenic and thermogenic. Biogenic gas is created by methanogenic organisms in marshes, bogs, landfills, and shallow sediments. Deeper in the earth, at greater temperature and pressure, thermogenic gas is created from buried organic material (US Energy Information Administration 2012).

Before natural gas can be used as a fuel, it must undergo processing to remove impurities, including water, to meet the specifications of marketable natural gas. The by-products of processing include ethane, propane, butanes, pentanes, and higher molecular weight hydrocarbons, hydrogen sulfide (which may be converted into pure sulfur), carbon dioxide, water vapor, and sometimes helium and nitrogen. Natural gas is often informally referred to simply as gas, especially when compared to other energy sources such as oil or coal (US Geological Survey 2012). Huge quantities of natural gas (primarily methane) exist in the form of hydrates (crystallized natural gas) under sediment on offshore continental shelves and on land in arctic regions that experience permafrost such as those in Siberia. Hydrates require a combination of high pressure and low temperature to be formed. It costs about twice as much to produce usable natural gas from crystallized natural gas economically from hydrates (Booths, 2010).

Gas hydrates are of great importance for a variety of reasons as shown in Fig 1.1. Per unit volume, gas hydrates contain a tremendous amount of gas. For example, 1 m^3 of hydrate disassociates at atmospheric temperature and pressure to form 164 m^3 of natural gas + 0.8 m^3 of water (Kvenvolden, 1993).

Considering the planet as a whole, the quantity of natural gas in sedimentary gas hydrates greatly exceeds the conventional natural gas resources. As a result, numerous studies have discussed the energy resource potential of gas hydrates (Kvenvolden, 1993).

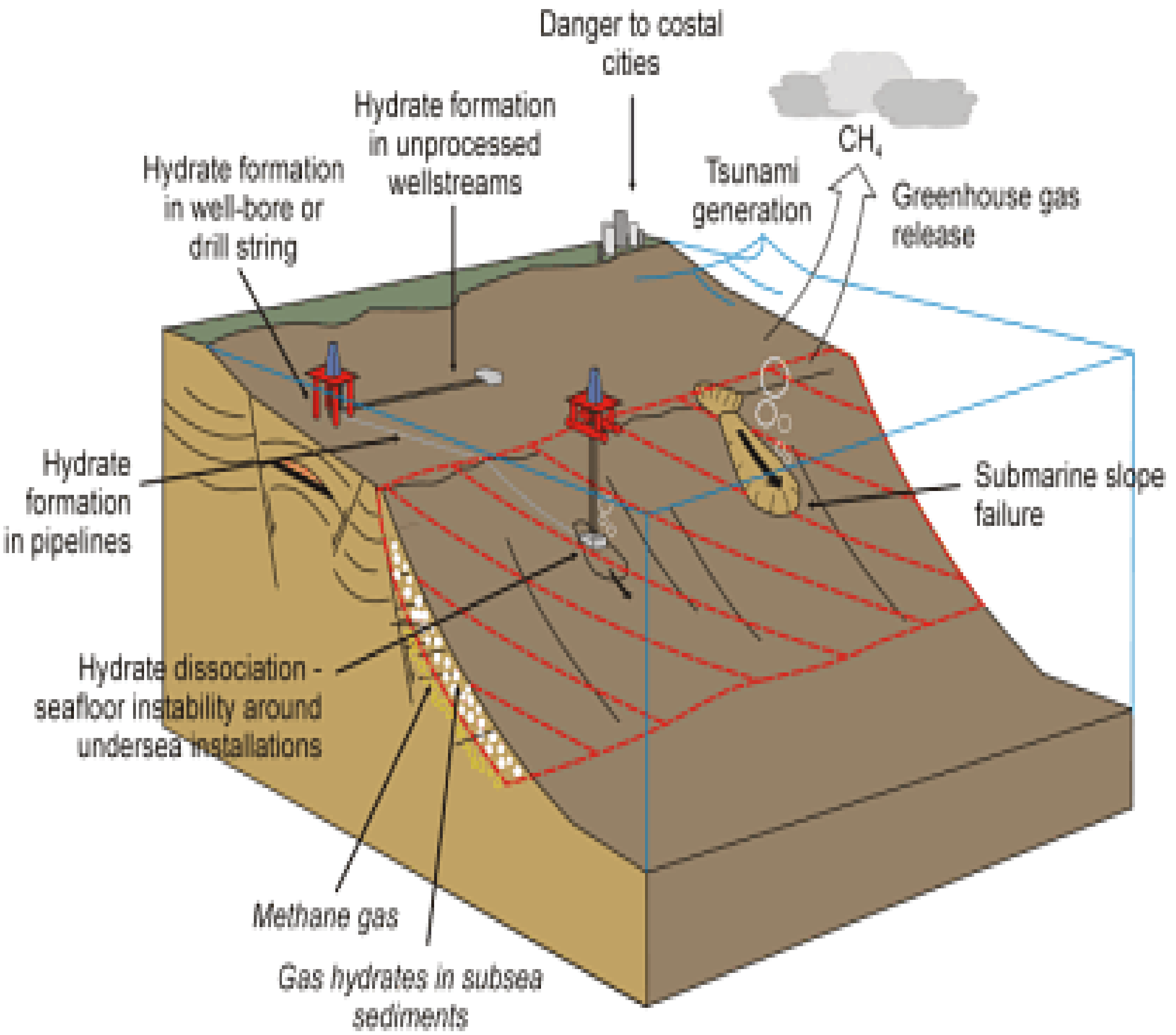


Fig 1.1: Major issues of gas hydrates.

Source: Heriot-Watt University Institute of Petroleum Engineering, (2013).

1.2 STATEMENT OF PROBLEM

Hydrate formation poses challenge to natural gas pipeline, some of which are:

- Flow restriction: Hydrate blockages are major problem in offshore and arctic operations. They can formed in subsea transfer lines, high residence time pipelines, gas expansion cross valves due to subcooling effect, etc. Hydrate formation is also common in hydrocarbon transmission lines such as ethane, propane and ethylene that are operating under low temperature environment.

- Ecological risks, as well as potential safety hazards to exploration and transmission personnel. The movement of hydrate at a very high velocity in a transmission line will rupture the line and also causes explosion of the line which may result to loss of life of personnel with corresponding spillage of the containment.

1.3 RESEARCH OBJECTIVES

This project is aimed at contributing to the assessment of hydrate formation in natural gas pipelines with emphasis on the challenges and evaluations. It focuses emphatically on the various techniques by which hydrates can be predicted so that they can be avoided.

In order to address these problems, the specific objectives of this research are:

i. To identify the occurrence and formation of hydrates in flowlines and storage systems.
ii. To evaluate the ways of inhibition of natural gas hydrates.
iii. To develop model for the prediction of possibility of hydrate formation in natural gas systems.
iv. To develop model for the prescription of the appropriate solution to any hydrate formation in natural gas streams.

1.4 JUSTIFICATION

Anthropogenically formed gas hydrates create reason that these substances are of interest. Gas hydrates can spontaneously form in petroleum production equipment and pipelines associated with deep-water petroleum production and arctic on-shore petroleum production. These unwanted hydrates can clog equipment, preventing the optimum production of hydrocarbons.

Study is conducted in this research work on predicting the possibility of the hydrate formation so that inhibition can be carried out on time.

Various methods are used to prevent hydrate formation in petroleum production and transportation equipment.

1.5 SCOPE OF STUDY

This research work covers the fundamental study of the evaluation of the formation of gas hydrates in natural gas streams.

It considers five natural gas samples for the purpose of prediction of the possibility of hydrate formation in the gas streams and prescription of the appropriate inhibition technique to already formed hydrate in the gas streams.

The data required from the gas samples include:

- Gas pressure
- Gas temperature
- Water content of the gas samples

- Gas specific gravity
- Flow rate of the gas stream

In this way, the possibility of hydrate formation in the natural gas stream can be predicted and the appropriate inhibition technique prescribed if hydrate is formed by the gas.

CHAPTER TWO

LITERATURE REVIEW

2.1 HISTORICAL BACKGROUND OF NATURAL GAS HYDRATE

According to King (2013), Methane hydrate is a crystalline solid that consists of a methane molecule surrounded by a cage of interlocking water molecules. Methane hydrate is an "ice" that only occurs naturally in subsurface deposits where temperature and pressure conditions are favorable for its formation. If the ice is removed from this temperature/pressure environment it becomes unstable. For this reason methane hydrate deposits are difficult to study. They cannot be drilled and cored for study like other subsurface materials because as they are brought to the surface the pressure is reduced and the temperature rises. This causes the ice to melt and the methane to escape. Several other names are commonly used for methane hydrate. These include: methane clathrate, hydromethane, methane ice, fire ice, natural gas hydrate, and gas hydrate. Most methane hydrate deposits also contain small amounts of other hydrocarbon hydrates. These include propane hydrate and ethane hydrate. Fig 2.1 is a diagram showing a large gas hydrate plug formed in an oil and gas pipeline.

Fig 2.1: A large gas hydrate plug formed in a subsea hydrocarbon pipeline.

Source: Heriot-Watt University Institute of Petroleum Engineering, (2013).

2.2 OCCURRENCE AND FORMATION OF NATURAL GAS HYDRATES

Gas hydrates occur naturally onshore in permafrost, and at or below the seafloor in sediments where water and gas combine at low temperatures and high pressures to form an ice-like solid substance. Methane, or natural gas, is typically the dominant gas in the hydrate structure. In a gas hydrate, frozen water molecules form a cage-like structure around high concentrations of natural gas. The gas hydrate structure is very compact. When heated and depressurized to temperatures and pressures typically found on the Earth’s surface (one atmosphere of pressure and 70^0 Fahrenheit), its volume expands by 150 to 170 times. Thus, one cubic foot of solid gas hydrate found underground in permafrost or beneath the seafloor would produce between 150 to 170 cubic feet of natural gas when brought to the surface (Folger, 2010).

An illustration of the deposit models for methane hydrate deposits at continental margins and under permafrost is shown in Fig 2.2.

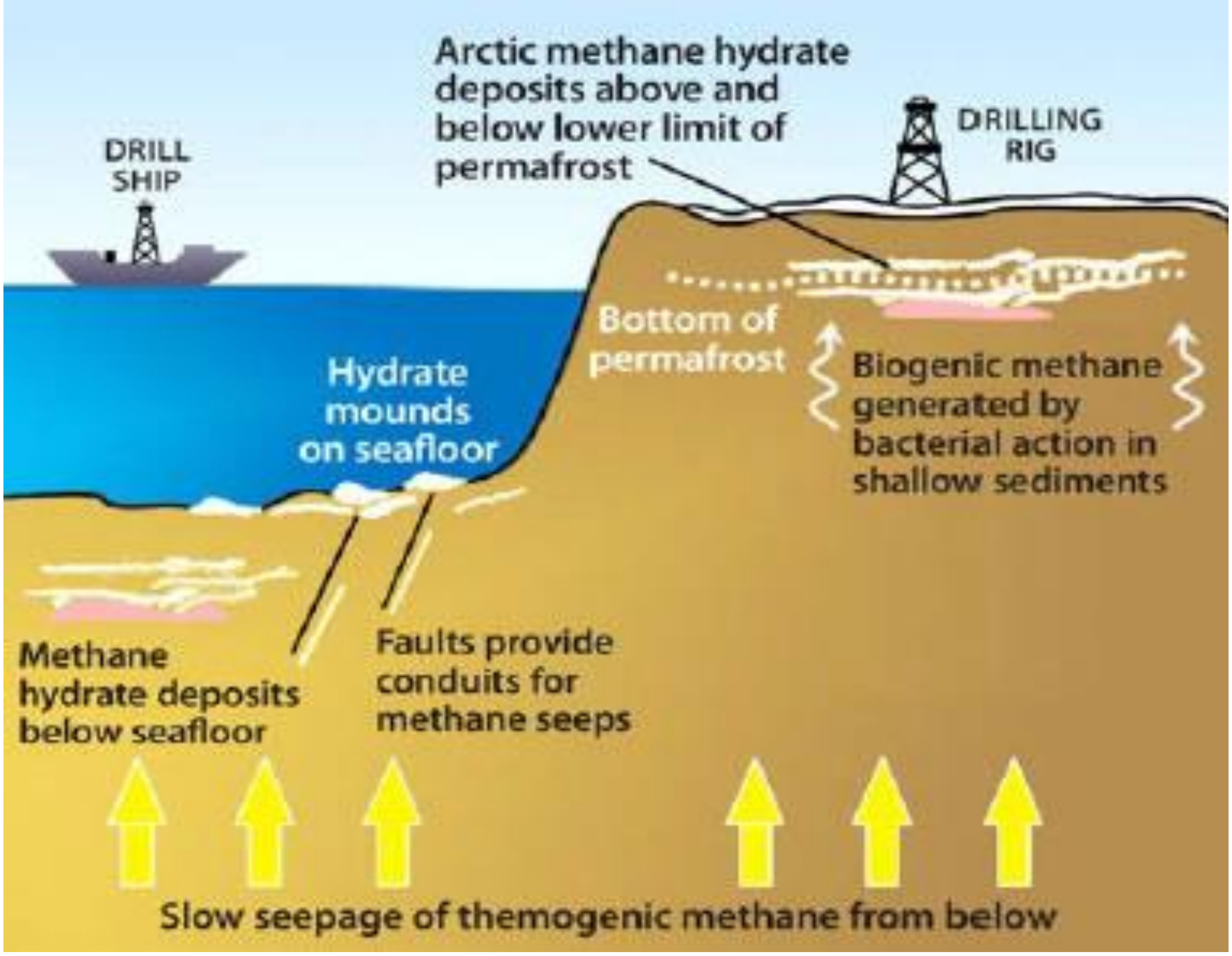


Fig 2.2: Deposit models for methane hydrate deposits at continental margins and under permafrost.

Source: United States Department of Energy, (2011).

Hydrates are solids resembling ice in appearance, which consist of a gas molecule surrounded by a cage of water molecules. Because of containing a large amount of methane, hydrates have been considered as a future energy resource. However, the formation of hydrates in the oil and gas pipelines has been a serious problem for a long time (Lysne and Larsen, 1995).

The formation of hydrates in a pipeline is common in seasonally cold or sub-sea environments with low temperatures and high pressures. In particular, hydrate blockages become a real menace to flow assurance in inadequately protected flowlines (Hunt, 1996).

Gas hydrates can form at the gas liquid interfaces along the entire length of the static pipeline. This can create small volumes of hydrate over time, but usually do not block the pipeline. However, when flow resumes, plugs can form at any point where the flow regime changes. Small-scale hydrate formation in the interface sometimes cannot be avoided in the pipeline. Moreover, under certain conditions, small-scale agglomerates are also observed in the bulk phase. Hydrate formation does not become a threat to pipe flow unless the agglomerates and hydrates formed at the interface start forming bridges. In such cases blockage occurs where the small accumulations of hydrates adhere to the walls and begin to bridge and reduce flow. This bridging can eventually shut down the entire pipeline or field until the hydrates have been removed (Austvik, 2000).

Like hydrate formation, dehydration of hydrates in the pipelines is another major operational safety risk (Mokhatab et al, 2007).

2.3 CONDITIONS FOR FORMATION OF HYDRATES

It is a result of the hydrogen bond that water can form hydrates. The hydrogen bond causes water molecules to align in regular orientations. The presence of certain compounds causes the aligned molecules to stabilise, and a solid mixture precipitates. The water molecules are referred to as the host molecules, and the other compounds, which stabilise the crystal, are called the guest molecules. The hydrate crystals have complex, threedimensional structures in which the water molecules form a cage, and the guest molecules are entrapped in the cages (Bahubali, 2010).

Hydrate Formation Phase Diagram is as shown in Fig 2.3. The phase diagram shows water depth (pressure) on the vertical axis and temperature on the horizontal axis. The dashed lines separate stability fields of water, water ice, gas and gas hydrate. The line labeled "hydrate to gas transition" is significant. Conditions for the formation of methane hydrate occur below this line. Above this line methane hydrate will not form. The red line traces a geotherm (the change of temperature with depth at a specific location). Note how, as depth increases, the geotherm crosses the hydrate to gas transition line. This means that gas hydrate in sediments usually overlie free gas. Graph modified after NOAA.

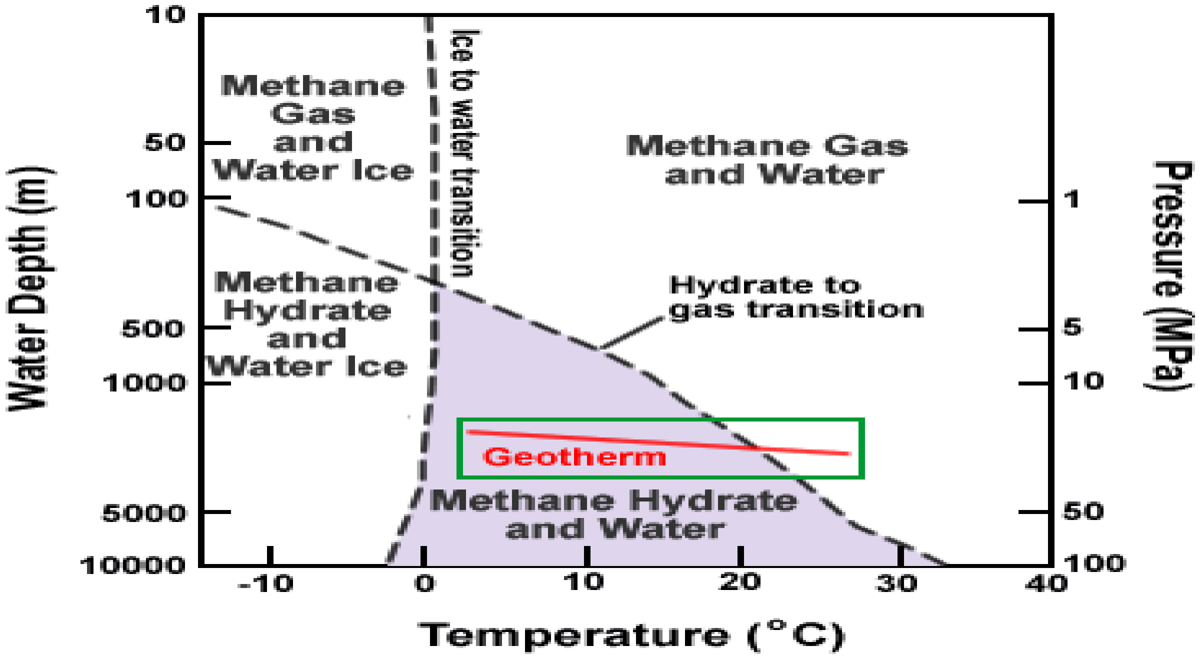


Fig 2.3: Gas Hydrates Formation Phase Diagram

Source: Ruppel, (2012).

Hydrates may exist far above the freezing point of water, and hence they can cause plugging of pipelines and nozzles. Also, they may cause many difficulties in deep water drilling platform because they could block mud line, choke, and blow out preventer (BOP). For over 160 years hydrates remained a mere scientific curiosity. Their importance to the oil and gas industry was realized in the early 1930's when Hammerschmidt discovered that the solid compounds, which frequently plugged the gas transmission lines during cold weather, were not ice but hydrates (Hammerschmidt, 1934).

It has been discovered under which conditions hydrates could form and how to prevent hydrate formation by the use of chemicals. During the recent years, the quest for long-distance transport of untreated or partly treated pipelines has caused an increased interest in the area of hydrate formation, hydrate crystallization, and hydrate mitigation (Dipl-Ing, 1967).

Hydrates form as a result of slow cooling of a fluid as in a pipeline or rapid cooling caused by depressurizing across valves or through turbo expanders. Studies have shown three conditions promote hydrate formation in gas pipelines and in petrochemical processes: Coexistence of water, natural gas components and low temperatures and high pressures. Other factors that favor hydrate formation can be listed as high fluid velocities, agitation, pressure, pulsations (or any source of fluid turbulence), the presence of CO_2 and H_2S (Carroll, 2003).

Gas molecules ranging from C_1 to C_4 and including CO_2, N_2 and H_2S are typical hydrate components. The water needed for hydrate formation can come from free water produced from the reservoir or from water vapor condensed by cooling the hydrocarbon fluid. At low temperature conditions, onshore pipelines suffer from hydrate formation during the winter months. Offshore, below 900 m of water depth and at the ocean bottom, the temperature is remarkably uniform around 3.8°C and the pipeline cools to this temperature within a few miles of the wellhead. This situation may lead to hydrate formation (Sloan and Bloys, 2000).

Gas hydrates are stable only under specific pressure-temperature conditions. Under the appropriate pressure, they can exist at temperatures significantly above the freezing point of water. The maximum temperature at which gas hydrate can exist depends on pressure and gas composition. For example, methane plus water at 600 psia forms hydrate at 41^0F, while at the same pressure, methane + 1% propane forms a gas hydrate at 49^0F. Hydrate stability can also be influenced by other factors, such as salinity (Edmonds et al., 1996).

According to Calvert, (2010), Gas hydrates form at temperatures above those of pure ice formation, which is an interesting point for discussion. Let us see if qualitative considerations can lead to an understanding of this. When ice forms from liquid water, the decrease in entropy is relatively small (0.292 Btu/lb-R) because water itself is fairly ordered, so the energy made available by the more efficient hydrogen bonding in ice relative to water is enough, when dissipated into the surroundings, to make the net entropy change positive, as it must be for a spontaneous process. At 4°C, methane forms hydrates above 551 psia. At 0°C, the required pressure falls to 370 psia. When a gas hydrate is formed, there is a considerable reduction in entropy because the gas is, in effect, condensed into a small volume. This is offset by the availability of the kinetic energy of the gas molecules, and a contribution from the van der Waals attraction between host and guest, which can be turned into entropy in the surroundings (exothermic reaction). The net result, as observed, is that the solid can be formed at temperatures above those of the formation of pure ice. It is reasonable that it is more difficult for small molecules, such as N_2 and CH_4, to form hydrates because their van der Waals interaction is weaker than for larger or more polarizable molecules such as H_2S or C_2H_6.

2.4 NATURAL GAS HYDRATES AS ENERGY SOURCE

There are at least three means by which commercial production of natural gas hydrates might eventually be achieved, all of which alter the thermodynamic conditions in the hydrate stability zone such that the gas hydrate decomposes. The first method is depressurization, akin to what may have happened at the Messoyakha Field. Its objective is to lower the pressure in the free-gas zone immediately beneath the hydrate stability zone, causing the hydrate at the base of the hydrate stability zone to decompose and the freed gas to move toward a wellbore. The second method is thermal stimulation, in which a source of heat provided directly in the form of injected steam or hot water or another heated liquid, or indirectly via electric or sonic means, is applied to the hydrate stability zone to raise its temperature, causing the hydrate to decompose. The direct approach could be accomplished in either of two modes: a frontal sweep similar to the steam floods that are routinely used to produce heavy oil, or by pumping hot liquid through a vertical fracture between an injection well and a production well. The third method is chemical inhibition, similar in concept to the chemical means presently used to inhibit the formation of water ice. This method seeks to displace the natural gas hydrate equilibrium condition beyond the hydrate stability zone's thermodynamic conditions through injection of a liquid inhibitor chemical adjacent to the hydrate (Energy Information Administration 1998).

The Global inventory of Natural Gas Hydrate Occurrence is shown in Fig 2.4 below.

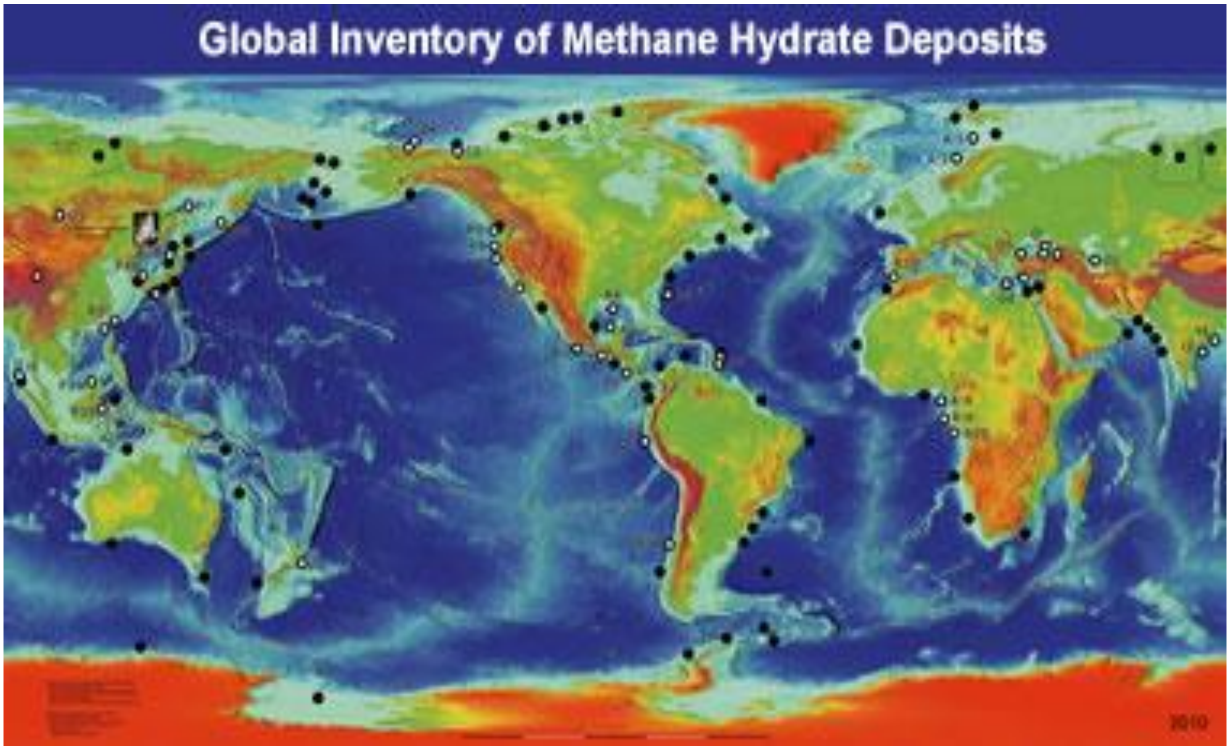


Fig 2.4: This map is a generalized version of locations in the USGS global inventory of natural gas hydrate occurrence database.
Source: Kvenvolden (1993)

Gas hydrates are a potentially huge global energy resource. The United States and other countries with territory in the Arctic or with offshore gas hydrates along their continental margins are interested in developing the resource. Countries currently pursuing national research and development programs include Japan, India, Korea, and China, among others. Although burning natural gas produces carbon dioxide (CO_2), a greenhouse gas, the amount of CO_2 liberated per unit of energy produced is less than 60% of the CO_2 produced from burning coal. In addition, the United States imports 20% of its natural gas consumed each year. Increasing the U.S. supply of natural gas from gas hydrates would decrease reliance on imported gas and reduce U.S. emissions of CO_2 if domestically produced gas hydrates substitute for coal as an energy source (US Department of Energy, 2011).

However, utilization of gas hydrates as an energy resource has been largely inhibited by the lack of economical methods for production for most hydrate accumulations, especially marine shelf hydrates. A variety of different mechanisms have been proposed for economically developing gas hydrates as an unconventional gas source (Goel et al., 2001).

2.5 PHYSICAL PROPERTIES OF NATURAL GAS HYDRATES

Natural gas hydrates are solids that form from a combination of water and one or more hydrocarbon or non-hydrocarbon gases. In physical appearance, gas hydrates resemble packed snow or ice. In a gas hydrate, the gas molecules are "caged" within a crystal structure composed of water molecules. Sometimes gas hydrates are called "gas clathrates". Clathrates are substances in which molecules of one compound are completely "caged" within the crystal structure of another. Therefore, gas hydrates are one type of clathrate (Weatherford, 2011).

Fig 2.5 is a schematic of the molecular structure of natural gas hydrate. Left: A ball-and-stick model of methane hydrate showing the central methane molecule surrounded by a "cage" of water molecules. Other hydrocarbon molecules such as pentane and ethane can occupy the central position in this structure.

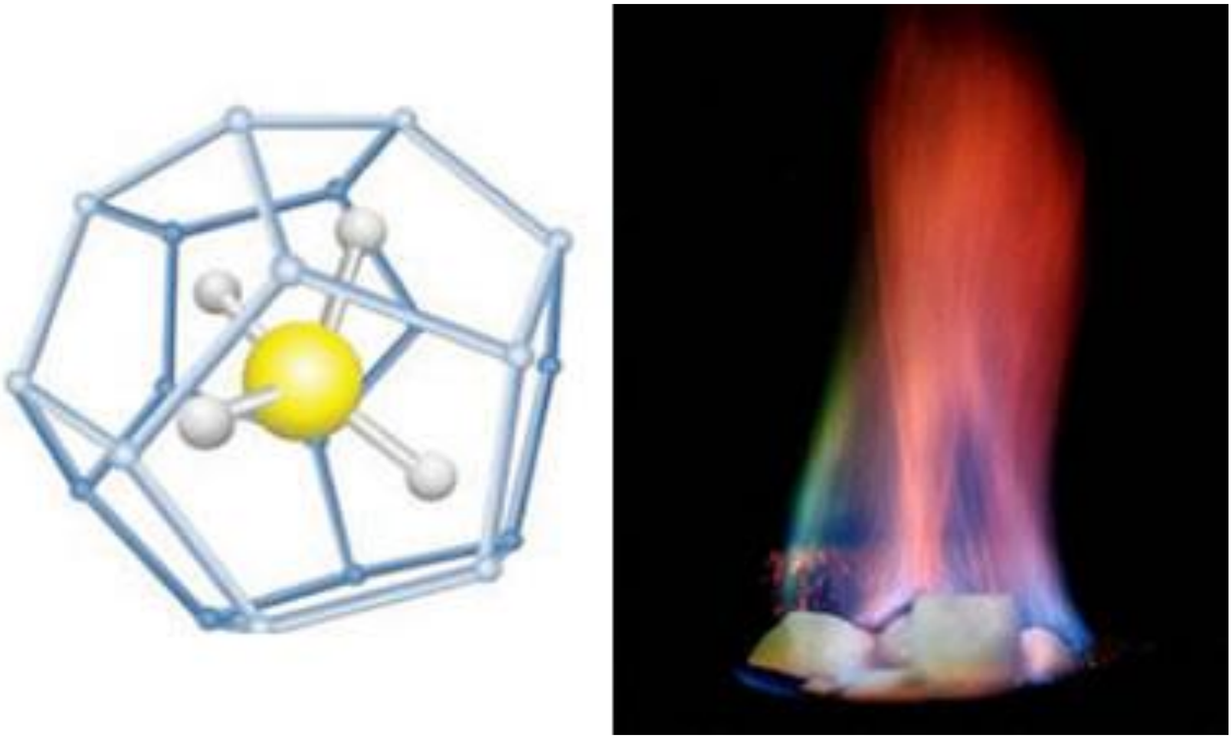


Fig 2.5: Molecular Structure of Methane Hydrate

Source: King, (2013).

NGH are solid materials which have higher densities than hydrocarbon components forming natural gas mixtures. In the open literature detailed investigation on NGH physical properties tend to focus mainly on mechanical, elastic and thermal properties. Compression deformation measurements on NGH sediments were conducted by Parameswaran et al., (1989) and Cameron et al., (1990) showed that strength of NGH is approximately similar to that of ice.

Later Stern et al., (1996) did compression deformation measurements at constant applied stress (creeping test) on NGH (methane hydrate) and his results showed the same trend as Parameswaran’s and Cameron’s. However, in 2003, Durham et al., (2003) showed that the impurities in previous studies effected the previous studies in creeping tests and they determined that NGH was 20 times more creep resistant than ice. Elastic properties of NGH can be estimated accurately since they are function of crystal structures and crystal structures are well defined.

Whalley, (1980) first proposed that the elastic properties of NGH are similar to that of ice in 1980. Later this theory was confirmed with first experimental studies conducted by Whiffen et al., (1982) and Pearson et al., (1984) based on experiments on simple hydrates via Brillouin spectroscopy method, which was later followed by Kiefte et al., (1985). More recently in 2002, Shimizu et al., (2002) performed in situ measurements on NGH via improved Brillouin spectroscopy technique and looked at the effect of pressure on shear stress as well as compression velocities. This study showed that the shear velocities of NGH (mainly methane hydrates) are similar to that of ice. First experimental studies on thermal properties of NGH were conducted by Stoll and Bryan, (1979) and they showed that the thermal conductivity of NGH as 0.393 Wm-1K-1 at 215.15 K which is 5 times less than that of ice (2.33 Wm-1K-1). Low thermal conductivity of NGH is confirmed with several studies later and a nice mapping of the thermal conductivity measurements from several experiments were recently published by Gupta (Gupta 2007).

Flow assurance can be defined as an operation that provides a reliable and controlled flow of fluids from the reservoir to the sales point. Flow assurance operation deals with formation, depositions and blockages of gas hydrates, paraffin, asphaltenes, and scales that can reduce flow efficiency of oil and gas pipelines. Due to significant technical difficulties and challenges, providing safe and efficient flow assurance needs interdisciplinary focus on the issue and joined efforts of scientists, engineers and operation engineers (Guo et al., 2005).

It was mentioned by Guo et al., (1993) that as a rule of thumb, methane caged NGH will form if the temperature is as high as 4.5^0C and pressures are as low as 11.7 bars. Mild conditions are required for NGH formations. NGH predictions can be determined by using simulation software and computational methods. However, predicting hydrate formation requires more detailed experimental studies for each reservoir fluid since the operating conditions and compositions vary vastly. As a result of both theoretical and experimental investigations, five different NGH prevention methods have been implemented to provide flow assurance (Makogon et al., 1997). These are:

i. Dehydration of wet gas and water removal (onshore or offshore)

ii. Avoid operation temperatures lower than the hydrate formation temperatures

iii. Avoid operation pressures higher than the hydrate formation pressures

iv. Injection of Thermodynamic Inhibitors (TI) such as methanol, glycol etc. to effectively decrease the hydrate formation temperature and inhibit or retard NGH crystal formation

v. Injection of Kinetic Inhibitors (KI) to prevent the aggregation of hydrate crystals 100% Mole

2.6 PROBLEMS POSED BY HYDRATES

Hydrates can easily influence various types of natural gas pipeline's internal corrosion which is a long-term problem through physical and chemical processes based on the hydrate size, stage and the contact period to wear off the pipe's protection films (Obanijesu et al., 2010).

H_2S, CO_2 and Cl - that are components of hydrate are acidic gases which have been established to contribute to internal gas pipeline corrosion rate. (Norsork Standard, 2005).

Methane is the major component of natural gas, as a reducing agent also aids metal corrosion (Yan et al., 2002).

Water is another known corrosive agent (Kritzer, 2004).

Gas hydrates are a significant hazard for drilling and production operations (Timothy et al., 2002).

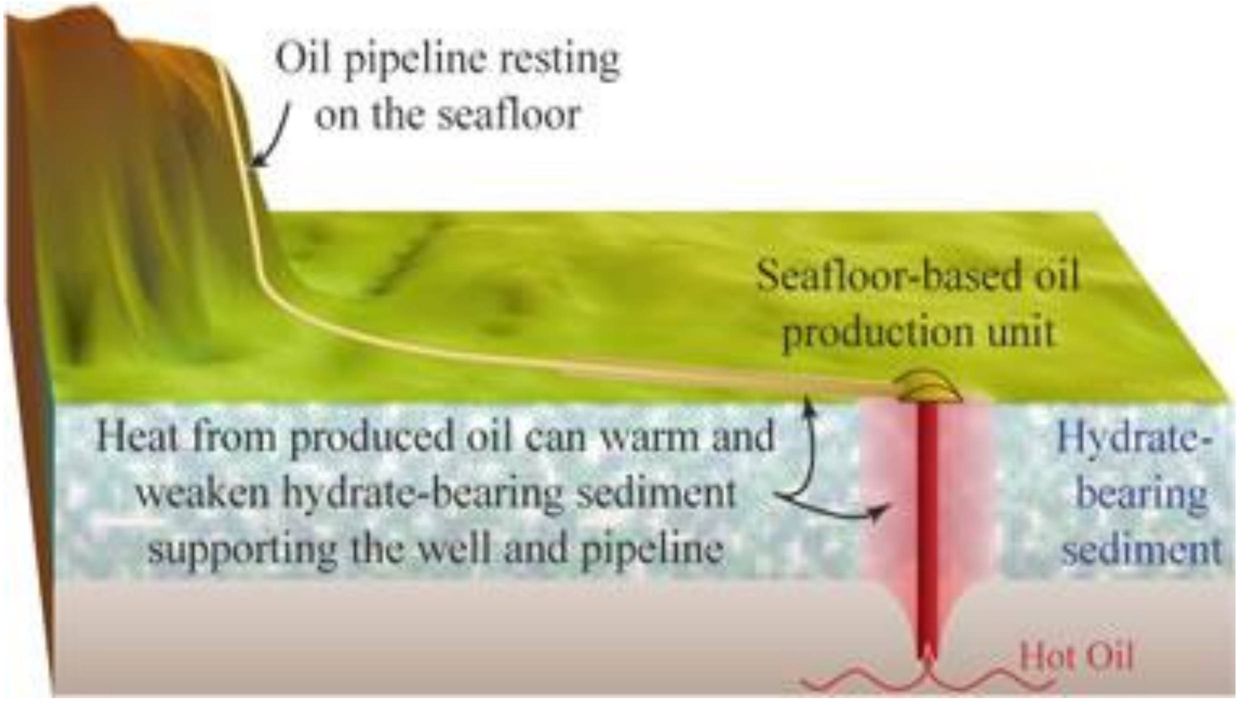


Fig 2.6: Hydrate-Bearing Sediments

Source: United States Geological Survey, (2007).

Fig 2.6 shows hydrate-bearing sediments. When oil wells are drilled through hydrate-bearing sediments, the warm temperature of the oil moving up through the frozen hydrate zone can cause melting. This can result in well failure. Warm pipelines running over frozen hydrate outcrops are also a hazard.

Gas hydrate production is hazardous in itself, as well as for conventional oil and gas activities that place wells and pipelines into permafrost or marine sediments. For activities in permafrost, two general categories of problems have been identified: (1) uncontrolled gas releases during drilling; and (2) damage to well casing during and after installation of a well. Similar problems could occur during offshore drilling into gas hydrate-bearing marine sediments. Offshore drilling operations that disturb gas hydrate-bearing sediments could fracture or disrupt the bottom sediments and compromise the wellbore, pipelines, rig supports, and other equipment involved in oil and gas production from the seafloor (Moridis, 2006).

Problems may differ somewhat between onshore and offshore operations, but they stem from the same characteristic of gas hydrates: decreases in pressure and/or increases in temperature can cause the gas hydrate to dissociate and rapidly release large amounts of gas into the well bore during a drilling operation.

According to Heriot-Watt University Institute of Petroleum Engineering, (2013), the aspect of gas hydrates which has the biggest implications for human welfare at present, is their potential as a geohazard. Of particular concern is the danger posed to deepwater drilling and production operations, and the large body of evidence which now exists linking gas hydrates with seafloor stability. With conventional oil and gas exploration extending into progressively deeper waters, the potential hazard gas hydrates pose to operations is gaining increasing recognition. Hazards can be considered as arising from two possible events: (1) the release of over-pressured gas (or fluids) trapped below the zone of hydrate stability, or (2) destabilization of in-situ hydrates. Conventional rotary drilling operations could cause rapid pressure, temperature or chemical changes in the surrounding sediment. An increase in temperature could be caused by a hot drill bit, warm drilling fluids, or later as high-temperature reservoir fluids rise through the well, while the addition of hydrate inhibitors to drilling muds (to prevent hydrate formation in the well-bore or drill string in the event of a gas-kick) could change sediment pore-fluid chemistry. Some, or all of these changes, could result in localized dissociation of gas hydrates in sediments surrounding wells. A similar case would apply to seafloor pipelines, where the transportation of hot fluids could cause dissociation of hydrates in proximal sediments. In a worst-case scenario, clathrate dissociation could lead to catastrophic gas release, and/or destabilization of the seafloor. The hazards associated with drilling in gas hydrate areas are exemplified by cases from the Alaskan Arctic, where subsurface permafrost hydrate destabilization has resulted in gas kicks, blowouts, and even fires.

2.7 PREDICTION OF HYDRATE FORMATION

2.7.1 Previous Methods of Predicting Hydrate Formation

2.7.1.1 The Gas Gravity Method

This was developed by Katz et al., (1945). It was known as the simplest method of determining the temperature and pressure of a gas mixture three-phase conditions. Gas gravity is defined as the molecular mass of the gas divided by that of air. Given as:

$$SG = M/28.966 \qquad 2.1$$

Where,

28.966 is the standard molar mass of air, and

M is the molecular weight of a gas (molar mass)

This method made use of the gas gravity chart. When calculating gas gravity of a gaseous mixture, either pressure or temperature is specified. The second intensive variable at which hydrate will be formed is traced from the chart. The limitation of this method is that it does not indicate the composition or type of the hydrate.

2.7.1.2 The Kvs Value Method

The K-factor method was devised by Carson and Katz, (1942). In their experiment they noted that the composition of the mixture changes at different temperatures and pressure in a manner indicative of hydrates. The concept of a solid solution enabled the notion of the mole fraction of a guest component in the solid phase hydrate mixture on a water-free basis. Carson and Katz defined a vapor-solid distribution coefficient (Kvsi) for each component as:

$$K_{vsi} = y_i/x_i \qquad 2.2$$

Where:

Y_i = mole fraction of component i in the water-free vapor

X_i = mole fraction of component i in the water-free solid hydrate.

This value is strictly a function of temperature and pressure. With the use of K-value chart one can easily determine in which phase a component can be found. For instance, methane and nitrogen have their K-values greater than unity. This implies that they concentrate in the vapor phase rather than in the hydrate. While components such as propane or butane normally have K-values less than unity are concentrated in the hydrate phase. The K-value can be used to determine the temperature or pressure for a three phase hydrate formation.

2.7.1.3 Baillie and Wichert Method

Baillie and Wichert, (1987) presented a chart method for calculating the hydrate temperature in sour gas mixtures. Their chart has a base temperature estimate calculated from the gravity of the gas and the H_2S concentration and a correction for propane content. This method is limited to gases with gravities between 0.6 and 1.0 and mixtures containing less than 50% H_2S, with an H_2S to CO_2 ratio between 10:1 and 1:3. In addition, this method is limited to pressures greater than 100 psia and less than

4000 psia. The method is not strictly for a sweet gas mixture containing CO_2, but may be accurate if the CO_2 is less than about 5 mol%.

2.8 INHIBITION OF NATURAL GAS HYDRATES

Methane hydrates are sensitive sediments. They can rapidly dissociate with an increase in temperature or a decrease in pressure. This dissociation produces free methane and water. The conversion of a solid sediment into liquids and gases will create a loss of support and shear strength. These can cause submarine slumping, landslides or subsidence that can damage production equipment and pipelines (United States Department of Energy, 2011).

Methane is a powerful greenhouse gas. Warmer Arctic temperatures could result in gradual melting of gas hydrates below permafrost. Warming oceans could cause gradual melting of gas hydrates near the sediment-water interface. Although many news reports have presented this as a potential catastrophe, USGS research has determined that gas hydrates are currently contributing to total atmospheric methane and that a catastrophic melting of unstable hydrate deposits is unlikely to send large amounts of methane into the atmosphere (Ruppel, 2012).

According to Sira et al., (1990), Gas hydrates are clathrate compounds in which each water molecule forms hydrogen bonds with its four nearest water molecules to build a solid crystalline lattice structure that encages gas molecules in its interstitial cavities. Hammerschmidt, (1934), determined that these solid gas hydrates form during transportation of natural gas and cause severe problems of blockages in pipelines. Since then, several methods of prevention of formation of gas hydrates were developed. The most commonly employed industrial methods include: removal of moisture content of natural gas by dew point lowering method, heating of a section containing hydrate plug to raise its temperature above hydrate dissociation temperature, depressurization of a hydrate plug simultaneously from both ends at a slow rate to a pressure below hydrate dissociation pressure, and injection of chemicals which act as hydrate inhibitors into the gas flow stream.

The term "hydrate inhibitor" is used for those chemicals which have ability to lower hydrate formation temperature (or shift hydrate equilibria). These chemicals include: methanol, glycols, ammonia, salts such as chlorides of sodium, potassium, calcium and magnesium. Several studies have been reported in literatures which provide experimental data on effect of inhibitor concentration on the thermodynamic phase equilibria of gas hydrates. Makogon (1981) and Sloan (1990) provided good review of these studies and a discussion on effectiveness and screening of these inhibitors for hydrate prevention. In general, the degree of inhibition is a function of the type of inhibitor, inhibitor concentration, pressure and composition of hydrate forming gas.

Recently published field experiments showed that hydrate blockage could form more readily in under-inhibited systems than in systems completely without inhibitor. On the basis of this experience, under-inhibited systems appear to be more likely to cause hydrate problems than systems completely without inhibitor. Consequently, the amount of the inhibitor in the pipeline must be maintained at such a level that hydrate formation will not be encountered (Austvik et al., 1995).

Yousif, (1996), Methanol injection has been used effectively to keep hydrates from forming as well as to release hydrate plugs restricting or stopping gas flow. Methanol is used as a means of preventing hydrate plugging or freezing in offshore hydrate control operations.

Inhibition experiments have been conducted using the methanol to inhibit hydrate formation in a pipeline. As the result, methanol had lower formation temperature than pure water but it was used as promoter to enhance the rate and amount of hydrate formation after the onset of hydrate formation.

These works can provide the predicting techniques of the hydrate plugging phenomena and hydrate control techniques by the inhibitor in the sub-sea pipeline system as well as flowlines of natural gas production system. Specifically, the results of this study can be applied to the selection of the prevention criteria and method of hydrate formation (Anderson et al., 1986).

CHAPTER THREE

METHODOLOGY

3.1 HYDRATE FORMATION PREDICTION

3.1.1 The Computer Model for Predicting Hydrate Formation

This involves the use of computer program developed with Microsoft Visual Basic Program for predicting the possibility of hydrate formation in a natural gas stream. The properties of the gas sample required for this evaluation are gas temperature, gas pressure and gas specific gravity. A sample of the Microsoft Visual Basic Program for predicting the possibility of hydrate formation in a natural gas stream is as shown in Fig 3.1.

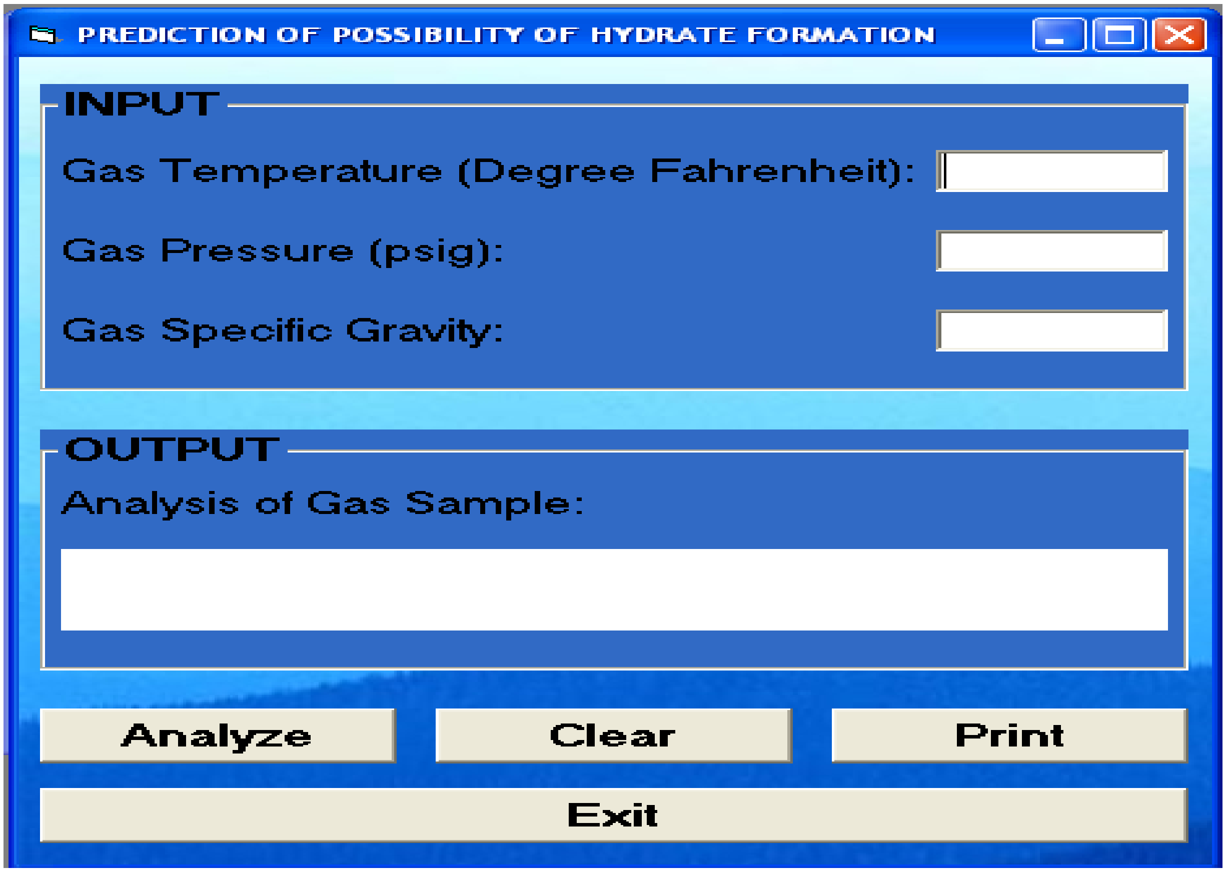


Fig 3.1: Microsoft Visual Basic Program for Prediction of Possibility of Hydrate Formation

3.2 HYDRATE MITIGATION AND REMEDIATION

The formation of hydrates requires four essential elements to occur: a supply of hydrate forming guest molecules, a supply of water and a combination of high pressure and/or low temperatures. Strategies for hydrate remediation and mitigation often modify one these elements to destabilize the hydrate and thus remove the problem.

Hydrates can also be prevented by the injection of chemical inhibitors which seek to modify the chemistry of hydrate formation such that the system is operated outside the hydrate envelope. There are various methods used in hydrate prevention:

- Temperature control
- Pressure control
- Water removal
- Insulation
- Thermodynamic inhibitors
- Low dosage hydrate inhibitors

Hydrate prevention using these techniques are reviewed, considering their application to deep water gas production systems for normal operation shutdown and restart. This review includes evaluation of the prevention techniques, considering technical issues associated with their application, level of protection, limitation, risk and cost of impact.

3.2.1 Temperature Control

Line heaters and insulated/heat traced lines will keep the temperature of flowing gas above the hydrate formation temperature within a specific range of gas flow rates- a very effective method for steady flow conditions. The use of insulation to maintain the temperature of the production fluids outside the hydrate envelope at system operating pressures is an established approach to hydrate prevention during normal operation. However, temperature control by passive insulation only offers hydrate control during normal operation when the system is being continually heated by hot production fluids. Following a shutdown the production fluid will cool down and enter hydrate formation envelope. The installation of active heating along a pipeline system has helped in alleviation of this type of problem.

3.2.2 Pressure Control

Design and operate the system with pressures low enough to maintain the fluid outside the hydrate envelope. This approach is seldom practical for normal operation since the pressure required for transportation of production fluids would usually exceed the hydrate formation pressure at the ambient temperature. However, for the removal of hydrates following unplanned shutdowns, depressurization outside the hydrate envelope is the normal practice (Mehta et al., 1996).

3.2.3 Removal of Water

The best method of hydrate prevention is by removal of water prior to transportation through the pipeline. The presence of water in a gas steam cannot be totally eliminated, in other words hydrate formation is inevitable in natural gas pipeline but it can be mitigated. Two processes are commonly used to lower the dew point by removing dissolved water.

In the first process, contacting the gas with a compound, typically tri-ethylene glycol (TEG), which removes water through hydrogen bonding, lowers the water concentration. In the second process, the gas is contacted with a solid such as molecular sieve, alumina or silica gel, which selectively adsorbs water.

3.2.4 Thermal Insulation

Heat conservation is common practice and is accomplished through insulation. Insulation provides hydrate control by maintaining the temperature above hydrate formation conditions. Insulation also provides a cool-down time before reaching the hydrate temperatures. This period gives operators time either to recover from the shutdown and restart a warm system or prepare the system from long-term shutdown.

3.2.5 Chemical Inhibitors

Frequently, inhibitors are injected into processing lines as a means of hydrate control by both the breakage of hydrate hydrogen bonds and the competition for available water molecules. Injecting chemical inhibitors into the system will modify the hydrate phase diagram or the kinetics/morphology of the formation. The injection of chemical inhibitors has also found widespread application. The various chemicals available for hydrate prevention fall into two classes: thermodynamic inhibitors and low dosage hydrate inhibitors.

3.3 PRESCRIPTION OF THE APPROPRIATE INHIBITION TECHNIQUE FOR HYDRATE FORMATION

This involves the use of computer program developed with Microsoft Visual Basic Program for prescribing the appropriate inhibition or prevention technique for hydrates.

The properties of the gas sample required for this evaluation are flow rate of the gas and the measured water content of the gas. A sample of the Microsoft Visual Basic Program for prescribing the appropriate inhibition or prevention technique for hydrates is as shown in Fig 3.3.

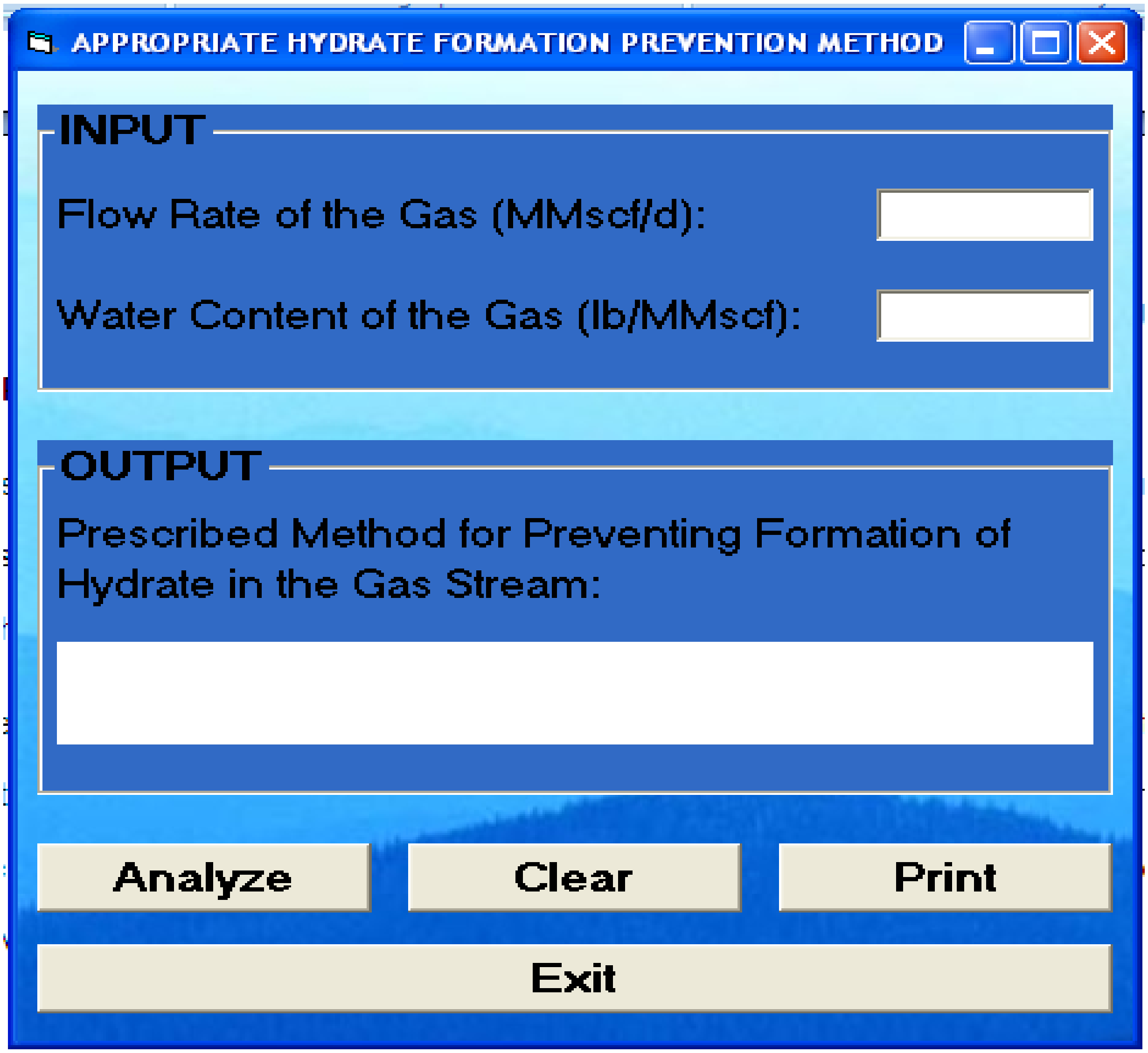


Fig 3.2: Microsoft Visual Basic Program for Prescribing the Appropriate Inhibition or Prevention Technique for Hydrate Formation

3.4 PROCEDURE FOR EVALUATION OF A GAS SAMPLE

The first step in evaluating a gas stream is to use the Microsoft Visual Basic Program shown in Fig 3.1 to perform analysis of the possibility of hydrate formation in the gas stream. If the result of the analysis is that hydrate is likely to form in the gas stream, perform analysis using the Computer Program shown in Fig 3.2 for the prescribed appropriate inhibition or prevention technique; ie whether the prevention technique required according to the computer program is Heating, Glycol Injection or Dehydration.

If the result of the analysis is Heating then heat is to be applied to the gas stream to bring it up to temperatures above which hydrate cannot form.

If the result is Glycol Injection, evaluate the weight % and mole % of the required glycol.

If the result is Dehydration, evaluate the amount of water in the gas to be removed to meet specification requirement and the required glycol circulation rate in the dehydration system.

In the case of the gas stream where hydrate has already formed within the orifice and the hydrate thickness has been obtained, then determine the effect of hydrate thickness on the gas flow rate through the orifice.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 CASES FOR PREDICTING HYDRATE FORMATION AND PRESCRIBING APPROPRIATE INHIBITION TECHNIQUE

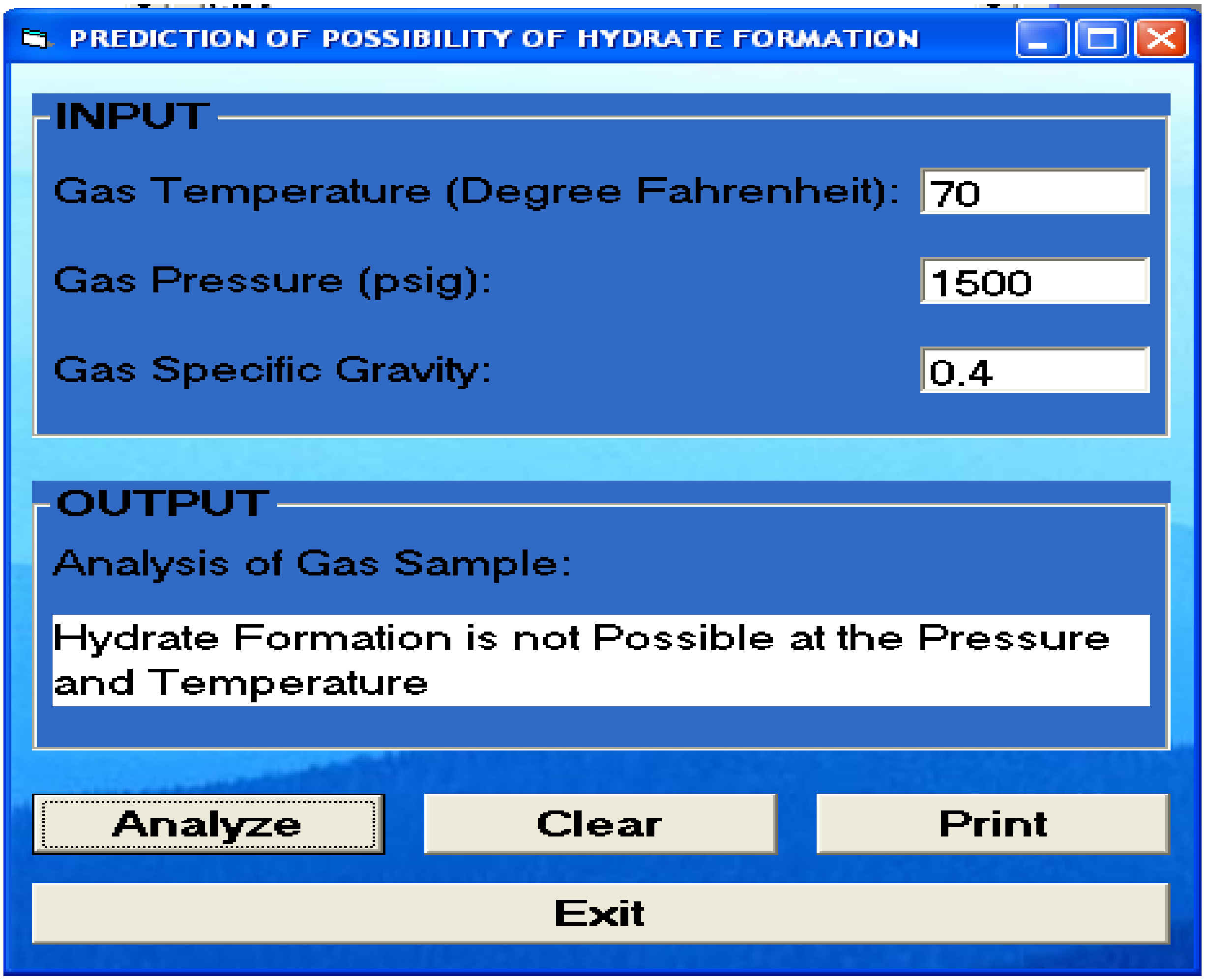
Data were collected for gas samples on four different natural gas streams flowing at different flow rates. The data are presented for the four natural gas streams in Tables 4.1, 4.2, 4.3 and 4.6.

4.1.1 Case 1: Natural Gas Stream A

Table 4.1: Data for Natural Gas Stream A

Gas Temperature, ^{0}F	70
Gas Pressure, psig	1500
Gas Specific Gravity	0.4
Gas Flow Rate, MMscf/d	0.60
Water Content of the Gas, lb/MMscf	0.30

Using the data in Table 4.1 for Natural Gas Stream A, the possibility of hydrate formation can be predicted with Fig 3.1 as shown in Fig 4.1 below:



Gas Temperature (Degree Fahrenheit): 70

Gas Pressure (psig): 1500

Gas Specific Gravity: 0.4

Analysis of Gas Sample:

Hydrate Formation is not Possible at the Pressure and Temperature

Fig 4.1: Prediction of the Possibility of Hydrate Formation in Natural Gas Stream A.

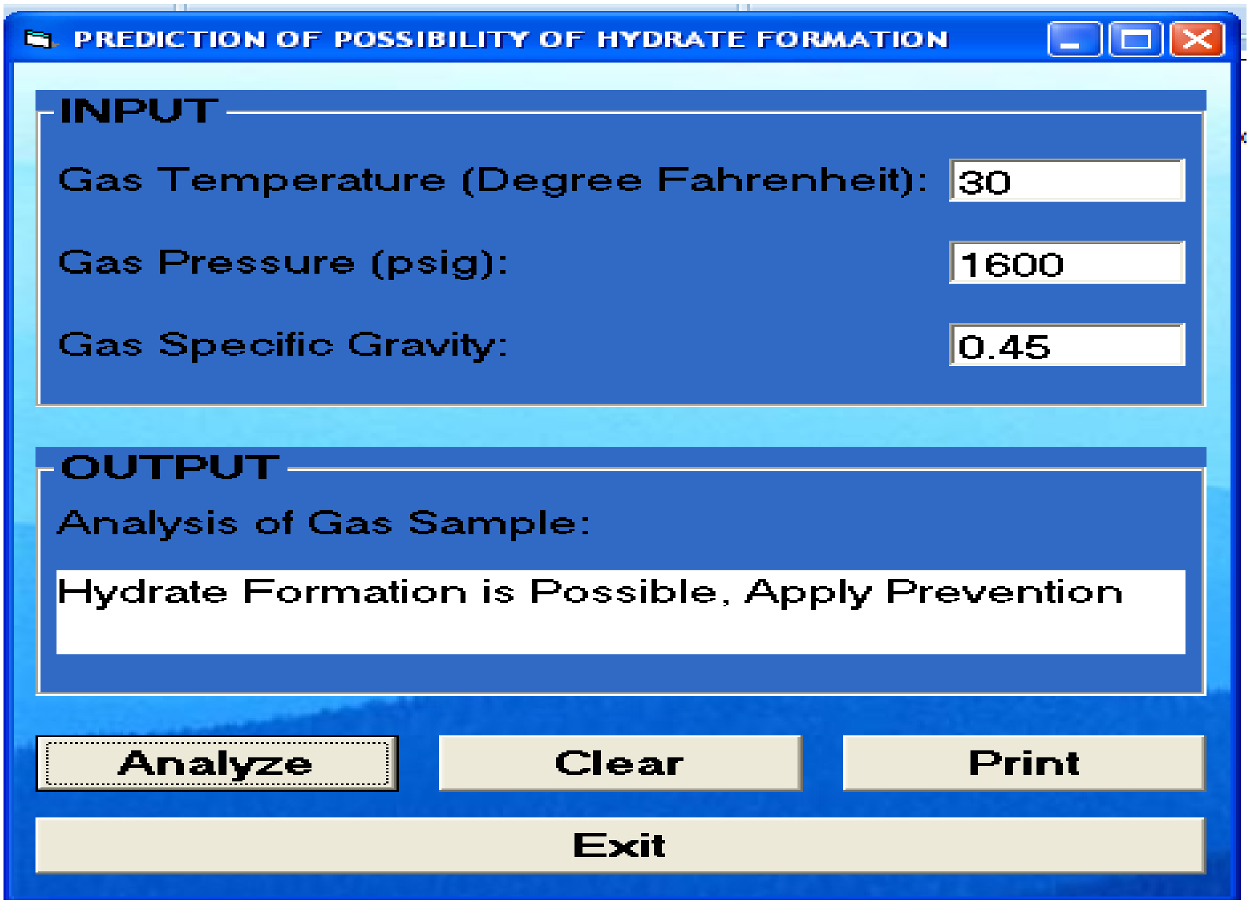
From Fig 4.1, it is observed that hydrate formation is not possible at the given temperature and pressure of the gas. Therefore no threat is being posed by this natural gas stream.

4.1.2 Case 2: Natural Gas Stream B

Table 4.2: Data for Natural Gas Stream B

Gas Temperature, ^{0}F	30
Gas Pressure, psig	1600
Gas Specific Gravity	0.45
Gas Flow Rate, MMscf/d	0.66
Water Content of the Gas, lb/MMscf	11

Using the data in Table 4.2 for Natural Gas Stream B, the possibility of hydrate formation can be predicted with Fig 3.1 as shown in Fig 4.2 below:


PREDICTION OF POSSIBILITY OF HYDRATE FORMATION

INPUT

Gas Temperature (Degree Fahrenheit): 30

Gas Pressure (psig): 1600

Gas Specific Gravity: 0.45

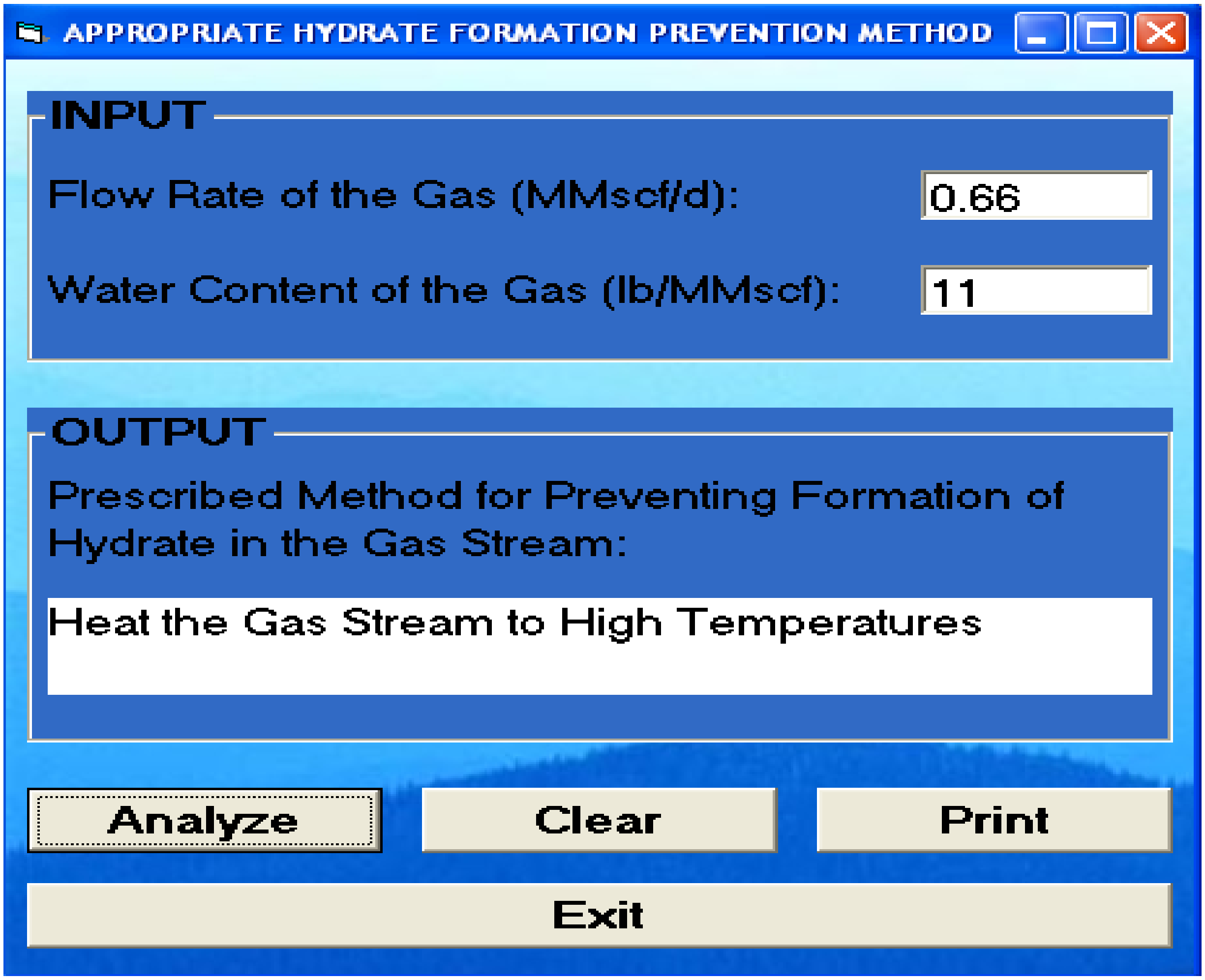
OUTPUT

Analysis of Gas Sample:

Hydrate Formation is Possible, Apply Prevention

Fig 4.2: Prediction of Possibility of Hydrate Formation in Natural Gas Stream B.

From Fig 4.2, it is observed that hydrate formation is possible at the given temperature and pressure of the gas. This is a threat being posed by this natural gas stream. Fig 3.2 is applied to evaluate the prescribed appropriate prevention technique for hydrate formation in the natural gas stream. This is as shown in Fig 4.3.


APPROPRIATE HYDRATE FORMATION PREVENTION METHOD

INPUT

Flow Rate of the Gas (MMscf/d): 0.66

Water Content of the Gas (lb/MMscf): 11

OUTPUT

Prescribed Method for Preventing Formation of Hydrate in the Gas Stream:

Heat the Gas Stream to High Temperatures

Fig 4.3: Prescription of the Appropriate Hydrate Formation Prevention Technique for Natural Gas Stream B.

A Reservoir Engineering Program, PVTP was applied to produce a chart of the Hydrate Formation Pressures of Natural Gas Stream B at various Gas

Temperatures and the plot of Hydrate Formation Pressure against Gas Temperature is shown in Fig 4.4 below.

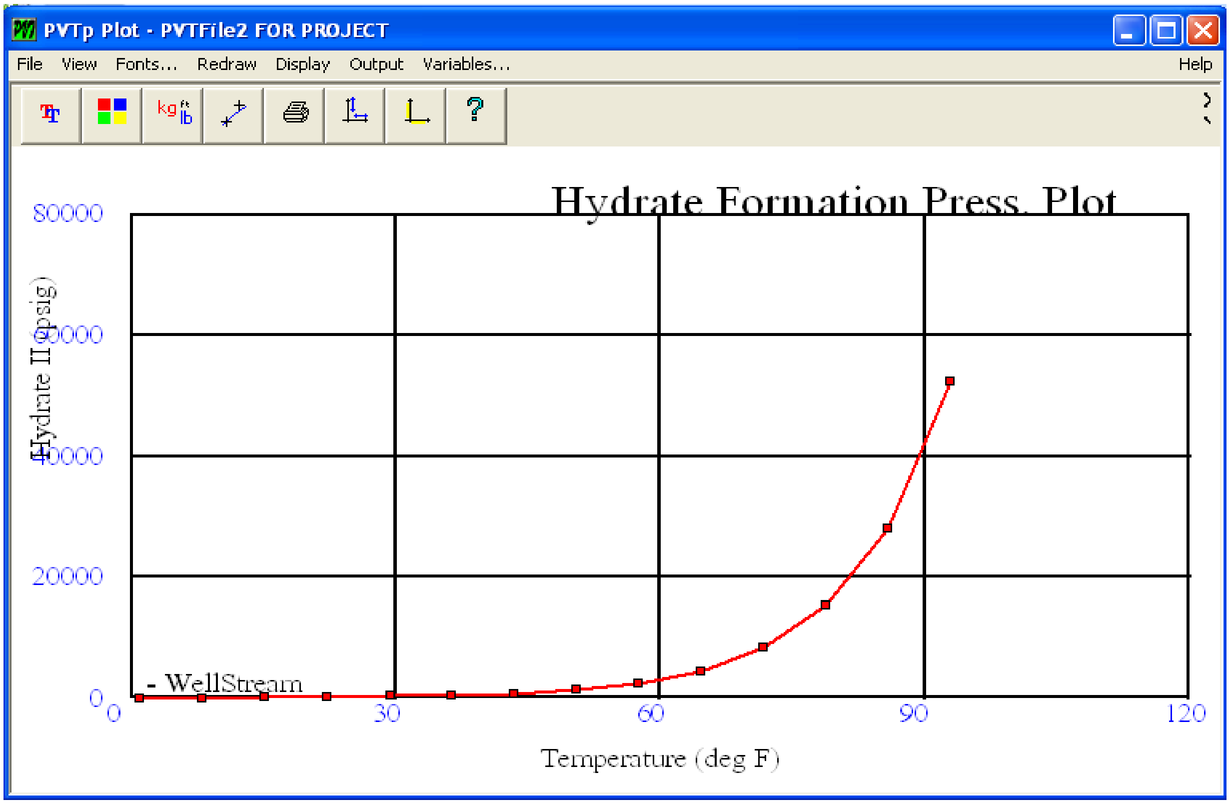


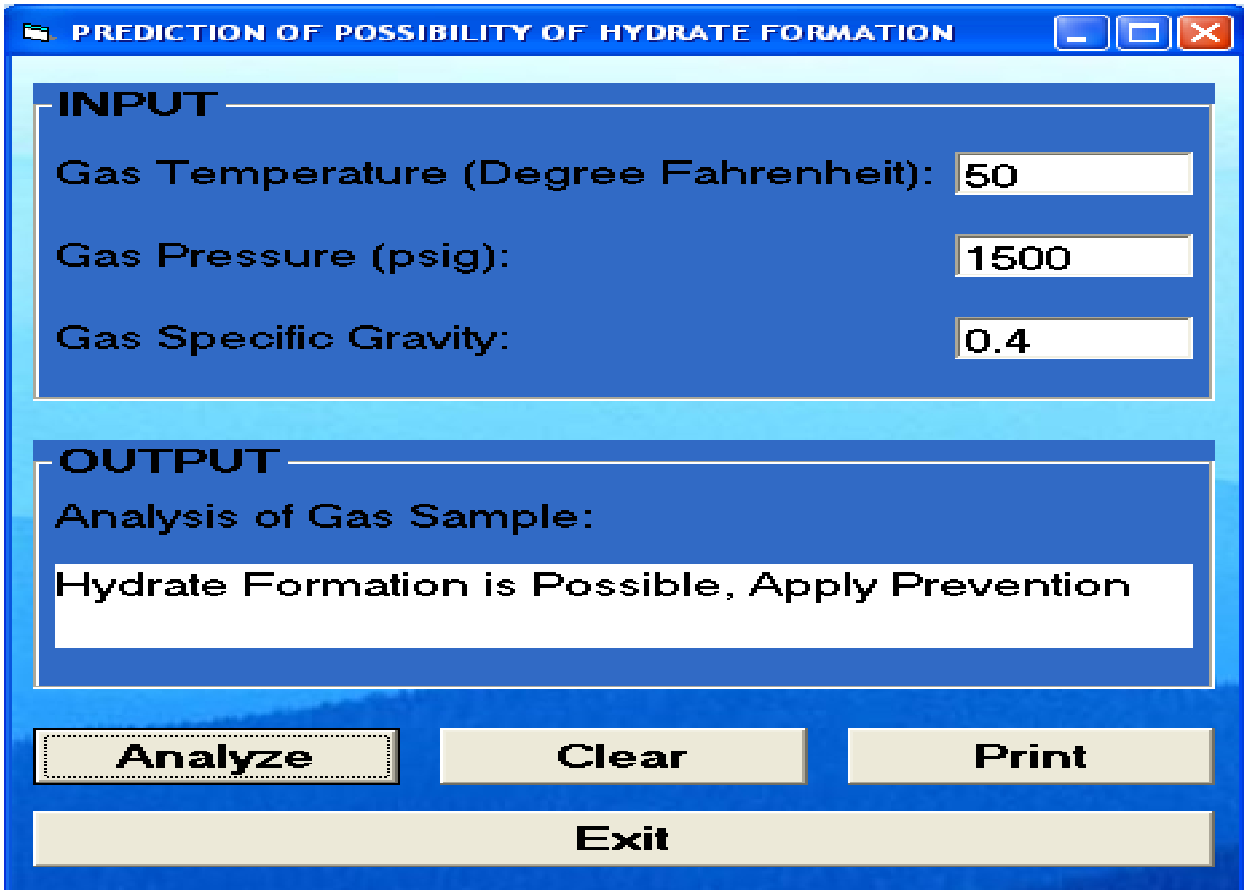
Fig 4.4: Plot of Hydrate Formation Pressure against Gas Temperature for Natural Gas Stream B.

4.1.3 Case 3: Natural Gas Stream C

Table 4.3: Data for Natural Gas Stream C

Gas Temperature, ^{0}F	50
Gas Pressure, psig	1500
Gas Specific Gravity	0.4
Gas Flow Rate, MMscf/d	0.70
Water Content of the Gas, lb/MMscf	23.5

Using the data in Table 4.3 for Natural Gas Stream C, the possibility of hydrate formation can be predicted with Fig 3.1 as shown in Fig 4.5 below:



Gas Temperature (Degree Fahrenheit): 50

Gas Pressure (psig): 1500

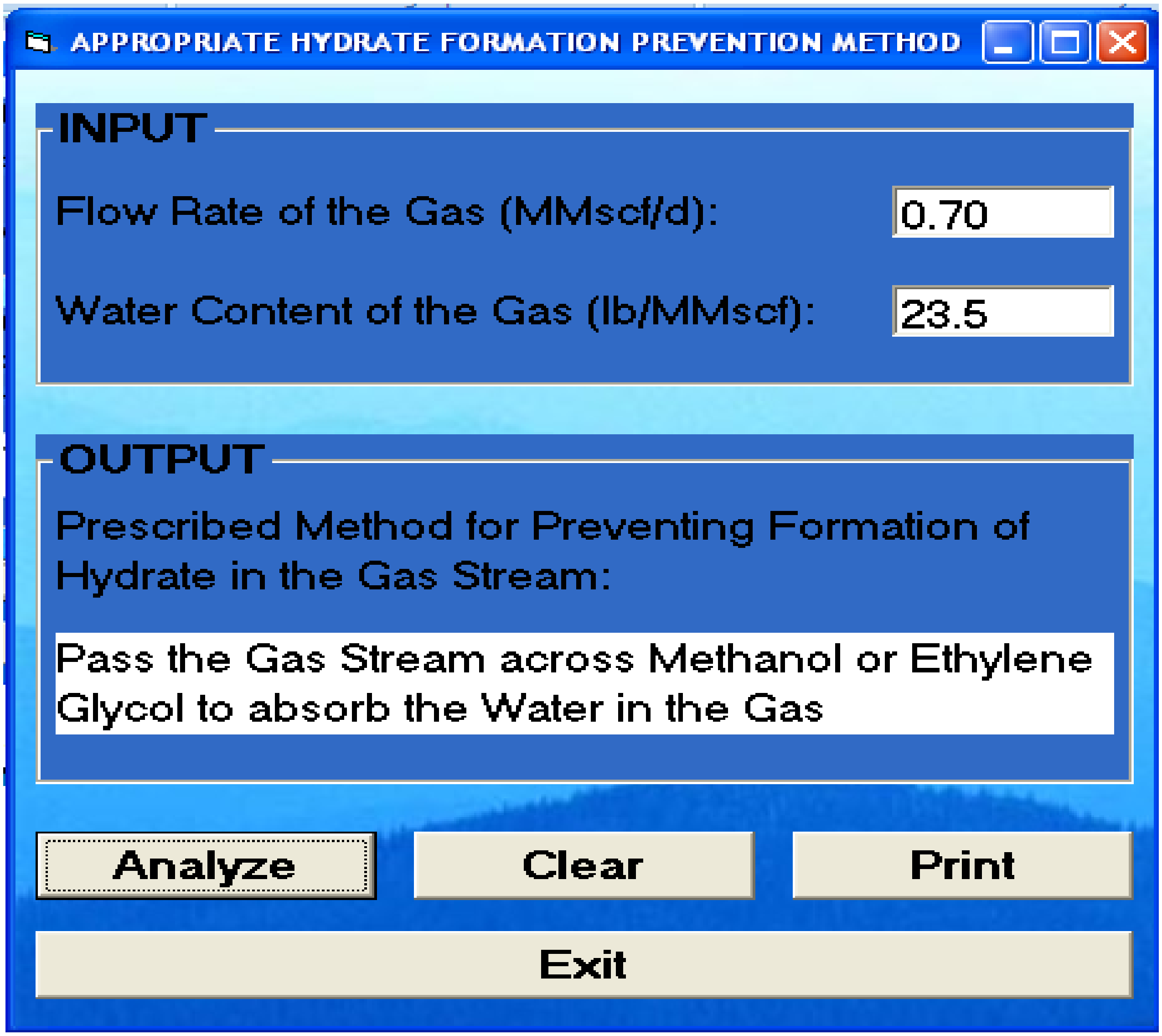
Gas Specific Gravity: 0.4

Analysis of Gas Sample:

Hydrate Formation is Possible, Apply Prevention

Fig 4.5: Prediction of Possibility of Hydrate Formation in Natural Gas Stream C.

From Fig 4.5, it is observed that hydrate formation is possible at the given temperature and pressure of the gas. This is a threat being posed by this natural gas stream. Fig 3.2 is applied to evaluate the prescribed appropriate prevention technique for hydrate formation in the natural gas stream. This is as shown in Fig 4.6.



Flow Rate of the Gas (MMscf/d): 0.70

Water Content of the Gas (lb/MMscf): 23.5

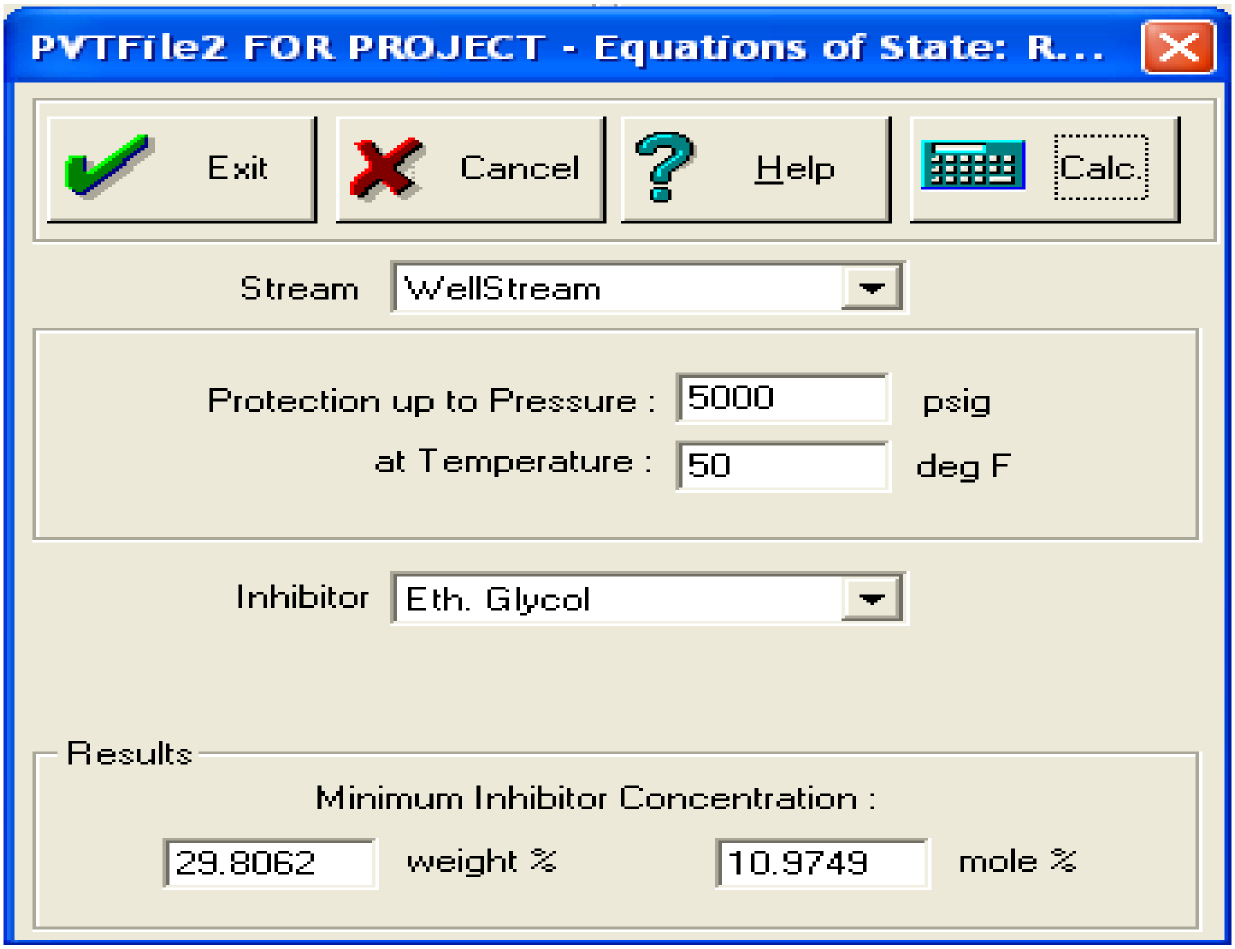
Prescribed Method for Preventing Formation of Hydrate in the Gas Stream:

Pass the Gas Stream across Methanol or Ethylene Glycol to absorb the Water in the Gas

Fig 4.6: Prescription of the Appropriate Hydrate Formation Prevention Technique for Natural Gas Stream C.

From Fig 4.6, the prescribed prevention technique is passing the gas stream across glycol or methanol.

A reservoir engineering program, PVTP is used to determine the minimum ethylene glycol concentration in weight % and mole % required to inhibit the hydrate formation and protect the gas stream up to 5000 psig at the same temperature as shown in Fig 4.7



Stream WellStream

Protection up to Pressure : 5000 psig

at Temperature : 50 deg F

Inhibitor Eth. Glycol

Results

Minimum Inhibitor Concentration :

29.8062 weight %

10.9749 mole %

Fig 4.7: Minimum Ethylene Glycol required for protecting the gas from Hydrate Formation up to 5000 psig at the same Temperature for Natural Gas Stream C.

Using Fig 4.7, the minimum glycol concentration in weight % required to protect the gas stream from hydrate formation up to 5000 psig at various gas temperatures were evaluated and presented in Table 4.4 which was used to generate plot of Minimum Glycol Concentration in weight % against Gas Temperature as shown in Fig 4.8.

Table 4.4: Minimum Ethylene Glycol Concentration at various Gas Temperatures

Gas Temperature, ^{0}F	Minimum Glycol Conc, wt %
10	62.57
20	56.69
30	49.56
40	40.98
50	29.81
60	15.78
70	0.97
80	0.97
90	0.97
100	0.97

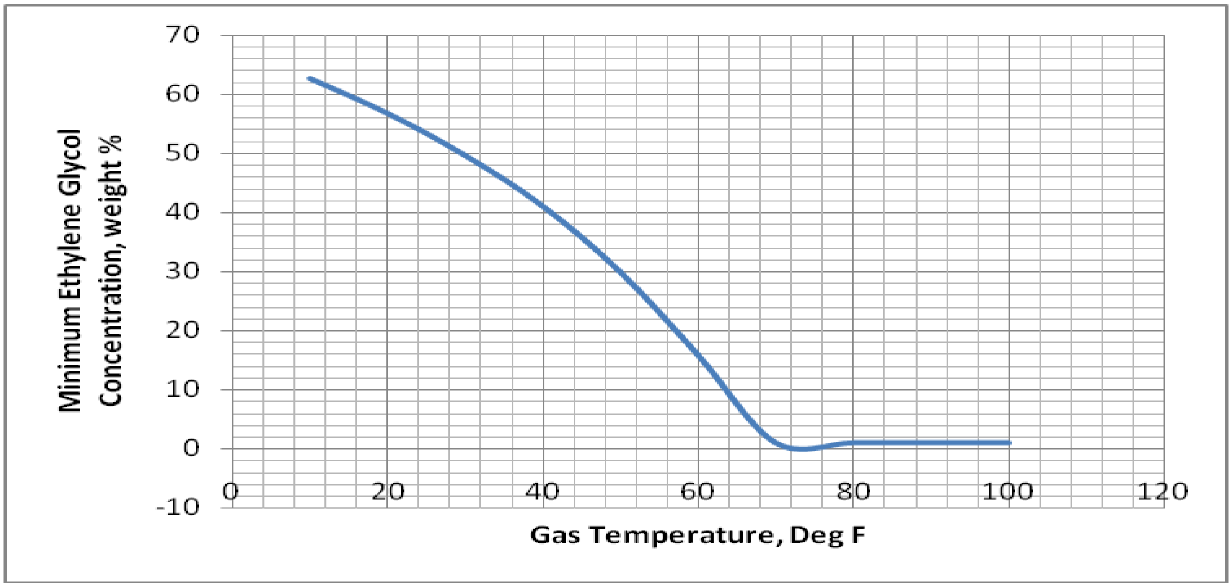
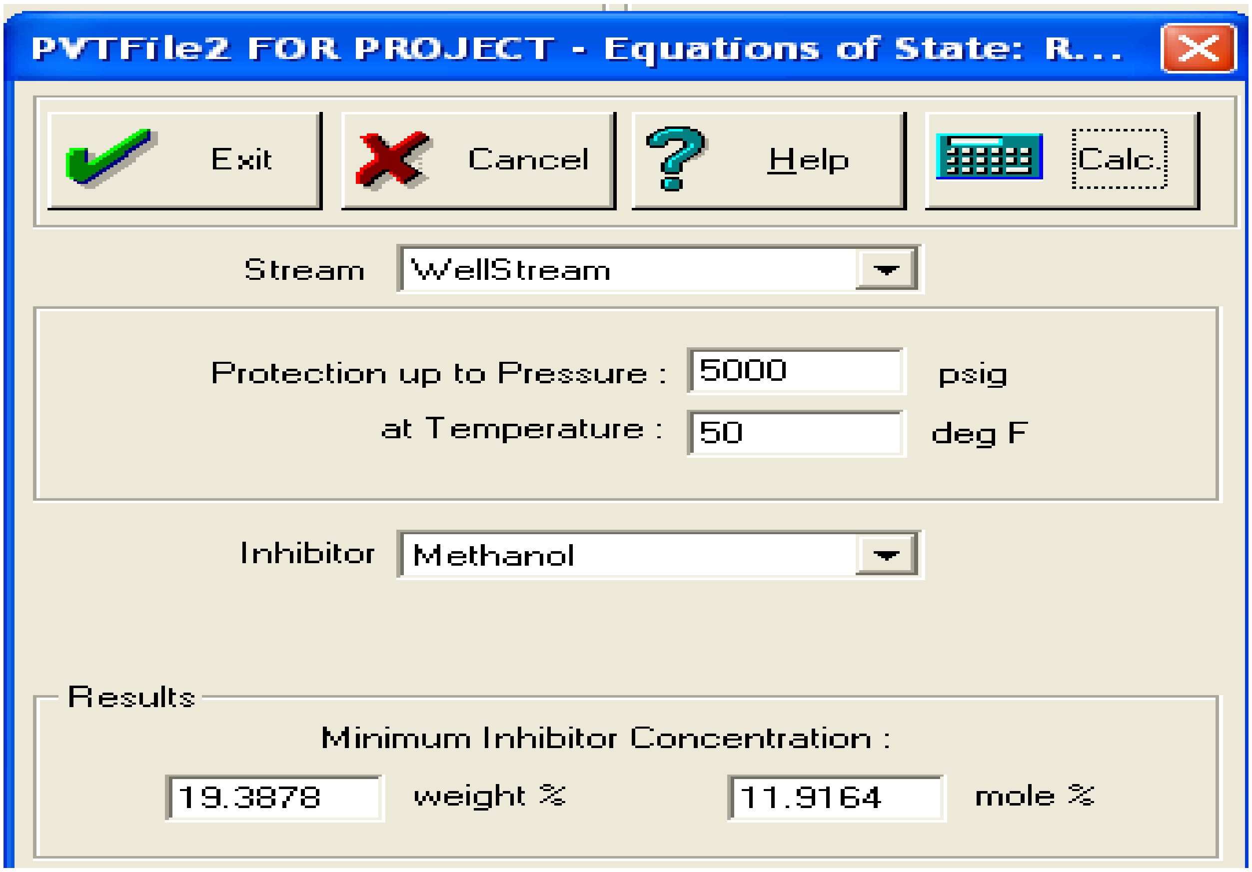


Fig 4.8: Minimum Glycol Concentration at various Gas Temperatures

The minimum methanol concentration in weight % and mole % required to inhibit the hydrate formation and protect the gas stream up to 5000 psig at the same temperature as shown in Fig 4.9.



Stream: WellStream

Protection up to Pressure : 5000 psig

at Temperature : 50 deg F

Inhibitor: Methanol

Results

Minimum Inhibitor Concentration :

19.3878 weight %

11.9164 mole %

Fig 4.9: Minimum Methanol required for protecting the gas from Hydrate Formation up to 5000 psig at the same Temperature for Natural Gas Stream C.

Using Fig 4.9, the minimum methanol concentration in weight % required to protect the gas stream from hydrate formation up to 5000 psig at various gas temperatures is presented in Table 4.5 and used to generate plot of Minimum Methanol Concentration in weight % against Gas Temperature as shown in Fig 4.10.

Table 4.5: Minimum Methanol Concentration at various Gas Temperatures

Gas Temperature, ^{0}F	Minimum Methanol Conc, wt %
10	47.2
20	41.3
30	34.76
40	27.48
50	19.39
60	10.41
70	2.26
80	2.26
90	2.26
100	2.26

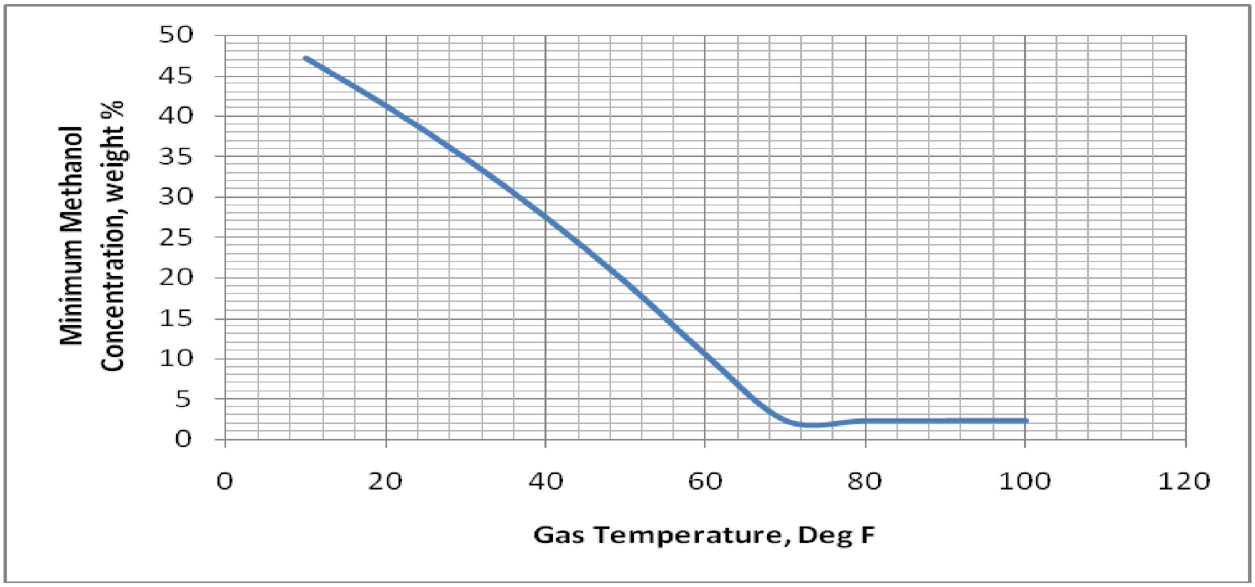


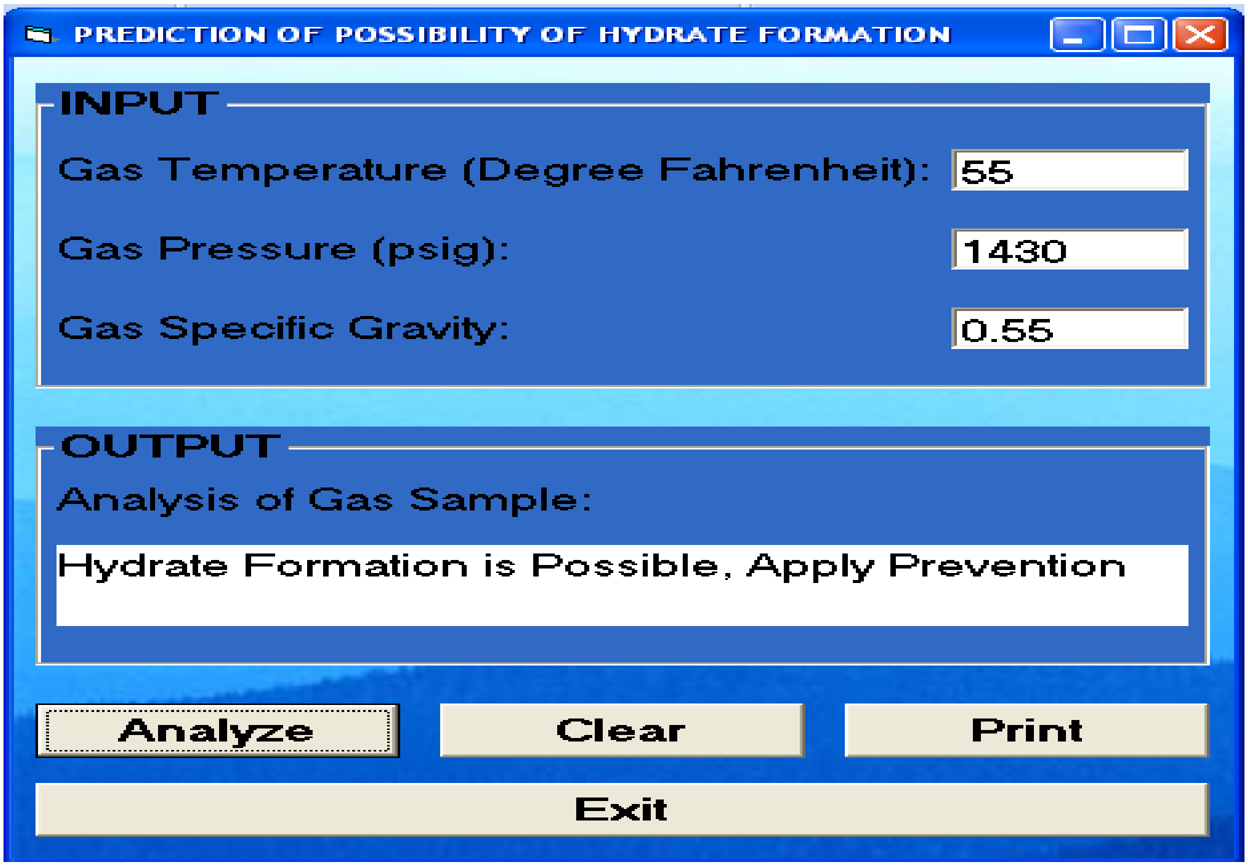
Fig 4.10: Minimum Methanol Concentration at various Gas Temperatures

4.1.4 Case 4: Natural Gas Stream D

Table 4.6: Data for Natural Gas Stream D

Gas Temperature, ^{0}F	55
Gas Pressure, psig	1430
Gas Specific Gravity	0.55
Gas Flow Rate, MMscf/d	2
Water Content of the Gas, lb/MMscf	36

Using the data in Table 4.6 for Natural Gas Stream D, the possibility of hydrate formation can be predicted with Fig 3.1 as shown in Fig 4.11 below.



PREDICTION OF POSSIBILITY OF HYDRATE FORMATION

INPUT

Gas Temperature (Degree Fahrenheit): 55

Gas Pressure (psig): 1430

Gas Specific Gravity: 0.55

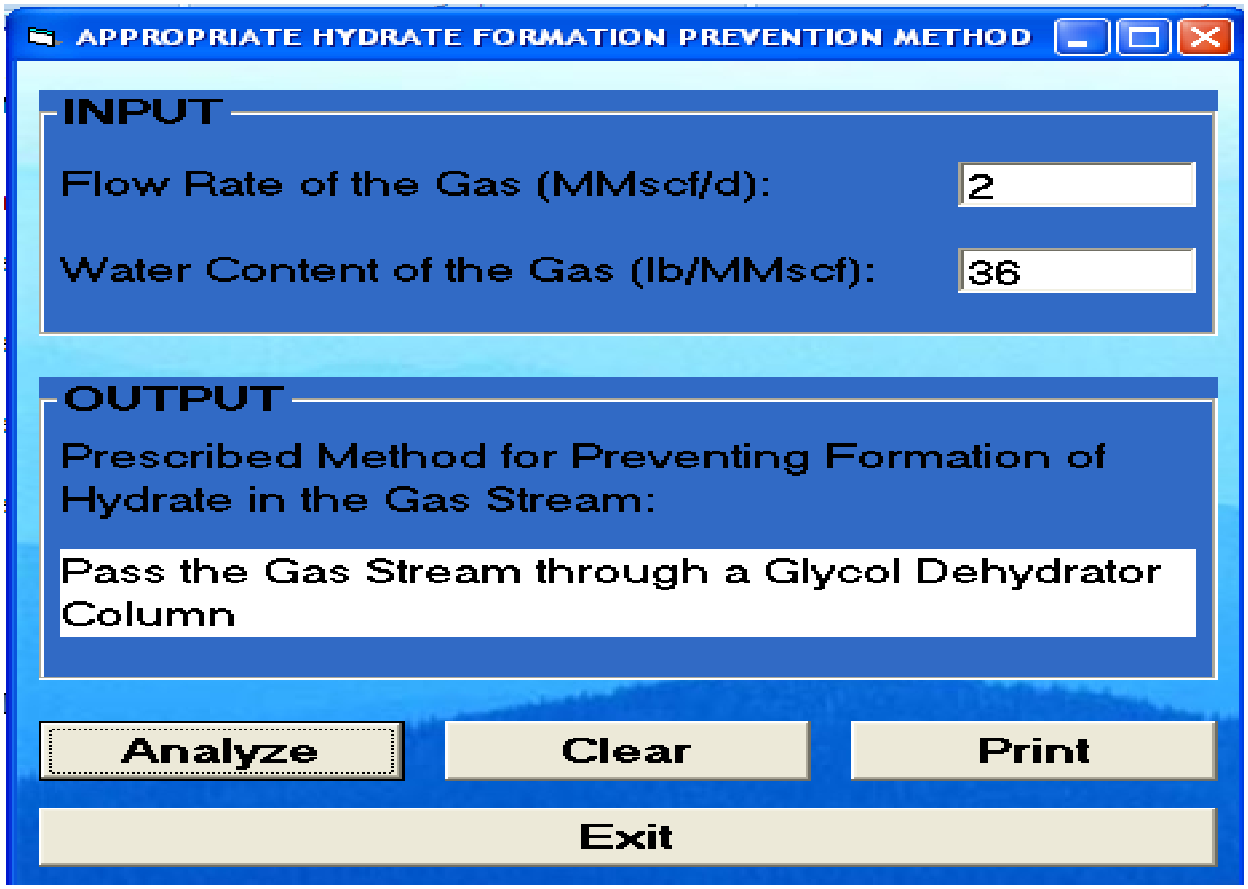
OUTPUT

Analysis of Gas Sample:

Hydrate Formation is Possible, Apply Prevention

Fig 4.11: Prediction of Possibility of Hydrate Formation in Natural Gas Stream D.

From Fig 4.11, it can be read that hydrate formation is possible at the given temperature and pressure of the gas. This is a threat being posed by this natural gas stream. Fig 3.2 is applied to evaluate the prescribed appropriate prevention technique for hydrate formation in the natural gas stream. This is as shown in Fig 4.12.



Flow Rate of the Gas (MMscf/d): 2

Water Content of the Gas (lb/MMscf): 36

Prescribed Method for Preventing Formation of Hydrate in the Gas Stream:

Pass the Gas Stream through a Glycol Dehydrator Column

Fig 4.12: Prescription of the Appropriate Hydrate Formation Prevention Technique for Natural Gas Stream D.

From Fig 4.12, the prescribed prevention technique is passing the gas stream through glycol dehydrator column.

The Amount of Water in lb_m/hr to be removed from the gas to meet specification is estimated using Eq as:

Amount of water to be removed = $(C_{wi} – C_{wo})q/24$ 4.1

Where C_{wi} = Water content of inlet gas, $lb_mH_2O/MMscf$

C_{wo} = Water content of outlet gas to meet specification, 0.3 $lb_mH_2O/MMscf$

q = Gas flow rate, MMscf/d

From eq 4.1, Amount of water removed = (36 – 0.3)*2/24 = 2.98 lb_m/hr

The Glycol Circulation Rate in gal/hr is determined using Eq as:

$q_G = (GWR)C_{wi}q/24$ 4.2

where GWR = Glycol to Water ratio, 3 gal.TEG/lb_mH_2O

From eq 4.2, Glycol Circulation Rate = 3 * 0.3 * 2/24 = 0.075 gal/hr

Using eq 4.2, the Glycol Circulation Rate at various Water Content of the inlet gas is computed and presented in Table 4.7 and used to generate plot of Glycol Circulation Rate against Water Content as shown in Fig 4.13.

Table 4.7: Glycol Circulation Rate at various Water Content

Water Content, lb/MMscf	Glycol Circulation Rate, gal/hr
0.3	0.075
3.3	0.825
13	3.25
23	5.75
33	8.25
43	10.75
53	13.25
63	15.75

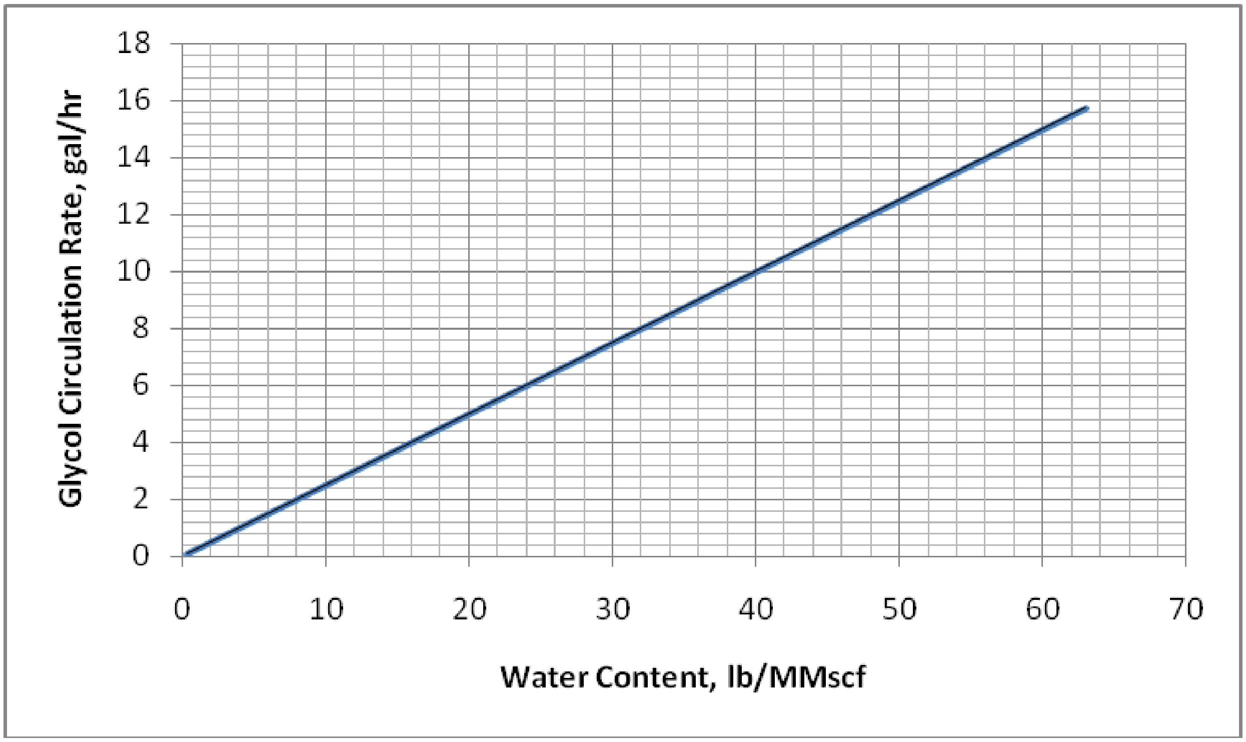


Fig 4.13: Glycol Circulation Rate at various Water Content

4.2 EFFECT OF HYDRATE FORMATION ON FLOW

In order to evaluate the effect of hydrate formation on the flow of gas through flow areas, Natural Gas Stream E was taken into consideration and the work station report was obtained. The report states that hydrate is known to have formed in the orifice and the thickness of the hydrate is obtained as 2.25’’. The effect of the hydrate formation on the flow of gas through the orifice is evaluated thus.

4.2.1 Natural Gas Stream E

Table 4.8: Data for Natural Gas Stream E

Gas Temperature, T, ^{0}F	35
Gas Pressure, P, psig	1200
Gas Specific Gravity, SG	0.70
Orifice Gas Flow Rate without hydrate, Q, scf/hr	129167
Water Content of the Gas, C_w, lb/MMscf	39.3
Differential Pressure at 60^{0}F, h_w, in	65
Absolute Static Pressure, P_f, psia	2000
Orifice Size, d, in	4.75
Pipe Size, D, in	11.376
Absolute Base Pressure, P_b, psia	14.65
Absolute Base Temperature, T_b, ^{0}F	60
Gas Compressibility Factor, z	0.7
Atmospheric Pressure, P_{atm}, psia	14.4
Gravitational Acceleration, g, ft/s^2	32.1418
Temperature During Orifice Boring, T_m, ^{0}F	25

The flow rate through the orifice without hydrate formation is computed with eq 4.3 shown below:

$$Q = C^i(h_wP_f)^{0.5} \qquad 4.3$$

Where C^i is the Orifice Flow Constant expressed in eq 4.4 below:

$$C^i = F_b{*}F_r{*}Y{*}F_{pb}{*}F_{tb}{*}F_{tf}{*}F_g{*}F_{pv}{*}F_m{*}F_l{*}F_a \qquad 4.4$$

F_b = Base Orifice Factor read from the Orifice Meter Table shown in Fig 4.15 at pipe size of 11.376 as 4653.4

F_r = Reynold's Number Factor given by eq 4.5 as:

$$F_r = 1+b/(h_wP_f)^{0.5} \qquad 4.5$$

b is read from Fig 4.16 at d = 4.75 and D = 11.376 as 0.0178

$F_r = 1+0.0178/(65*2000)^{0.5} = 1.000049368$

Y = Expansion Factor read from the Orifice Meter Table shown in Fig 4.17 at d/D of 4.75/11.376 which is 0.418 and h_w/P_f of 0.03 as 0.99964

F_{pb} = Pressure Base Factor given by eq 4.6 as:

$$F_{pb} = 14.73/P_b \tag{4.6}$$

$F_{pb} = 14.73/P_b = 14.73/14.65 = 1.00546$

F_{tb} = Temperature Base Factor given by eq 4.7 as:

$$F_{tb} = (T_b + 460)/520 \tag{4.7}$$

$F_{tb} = (60 + 460)/520 = 1$

F_{tf} = Flowing Temperature Factor given by eq 4.8 as:

$$F_{tf} = [520/(T + 460)]^{0.5} \tag{4.8}$$

$F_{tf} = [520/(35 + 460)]^{0.5} = 1.02494$

F_g = Specific Gravity Factor given by eq 4.9 as:

$$F_g = (1/SG)^{0.5} \tag{4.9}$$

$F_g = (1/0.7)^{0.5} = 1.195$

F_{pv} = Supercompressibility Factor given by eq 4.10 as:

$$F_{pv} = (1/z)^{0.5} \tag{4.10}$$

$F_{pv} = (1/0.7)^{0.5} = 1.195$

F_m = Manometer Factor given by eq 4.11 as:

$$F_m = [(62.3663 - (P_{atm} + (h_w/27.707))/192.4)/62.3663]^{0.5} \tag{4.11}$$

$F_m = [(62.3663 - (14.4 + (65/27.707))/192.4)/62.3663]^{0.5} = 0.9993$

F_l = Gauge Location Factor given by eq 4.12 as:

$$F_l = (g/32.17405)^{0.5} \tag{4.12}$$

$F_l = (32.1418/32.17405)^{0.5} = 0.9995$

F_a = Orifice Thermal Expansion Factor given by eq 4.13 as:

$$F_a = 1 + 0.000018(T - T_m) \tag{4.13}$$

F_a = 1 + 0.000018(35 - 25) = 1.00018

From eq 4.4, C^i = 4653.4 * 1.000049368 * 0.99964 * 1.00546 * 1 * 1.02494 * 1.195 * 1.195 * 0.9993 * 0.9995 * 1.00018 = 6839

From eq 4.3, Q = 6839 * $(65 * 2000)^{0.5}$ = 2465829.4 scf/hr

2465829.4scf/hr is the flow rate through the orifice without hydrate formation.

The flow rate through the orifice after hydrate formation is computed as follows:

The New Orifice Size, d_2 = Orifice Size – Hydrate Thickness 4.14

d_2 = 4.75 – 2.25 = 2.5

The New Base Orifice Factor F_{b2} is read from the Orifice Meter Table shown in Fig 4.15 at pipe size of 11.376 as 1260.8

For the New Reynold's Number Factor:

The New b is read from Fig 4.16 at d = 2.5 and D = 11.376 as 0.0342

The New F_r, F_{r2} = $1+0.0342/(65*2000)^{0.5}$ = 1.000094854

The New Expansion Factor, Y_2 read from the Orifice Meter Table shown in Fig 4.17 at d/D of 2.5/11.376 which is 0.22 and h_w/P_f of 0.03 as 0.99967

The New Flow Constant is computed as follows:

C^i = 1260.8 * 1.000094854 * 0.99967 * 1.00546 * 1 * 1.02494 * 1.195 * 1.195 * 0.9993 * 0.9995 * 1.00018 = 1853.1

The flow rate after hydrate formation is then evaluated using eq 4.3 as:

Q = 1853.1 * $(65 * 2000)^{0.5}$ = 668146.4 scf/hr

Using eq 4.3, the Orifice Flow Rate at various Hydrate Thicknesses is computed and presented in Table 4.9 and used to generate plot of Orifice Flow Rate at various Hydrate Thicknesses as shown in Fig 4.13.

Table 4.9: Orifice Flow Rate at various Hydrate Thicknesses

Hydrate Thickness, in	Orifice Flow Rate, scf/hr
0	0.075
0.5	0.825
1	3.25
1.5	5.75
2	8.25
2.5	10.75
3	13.25
3.5	15.75

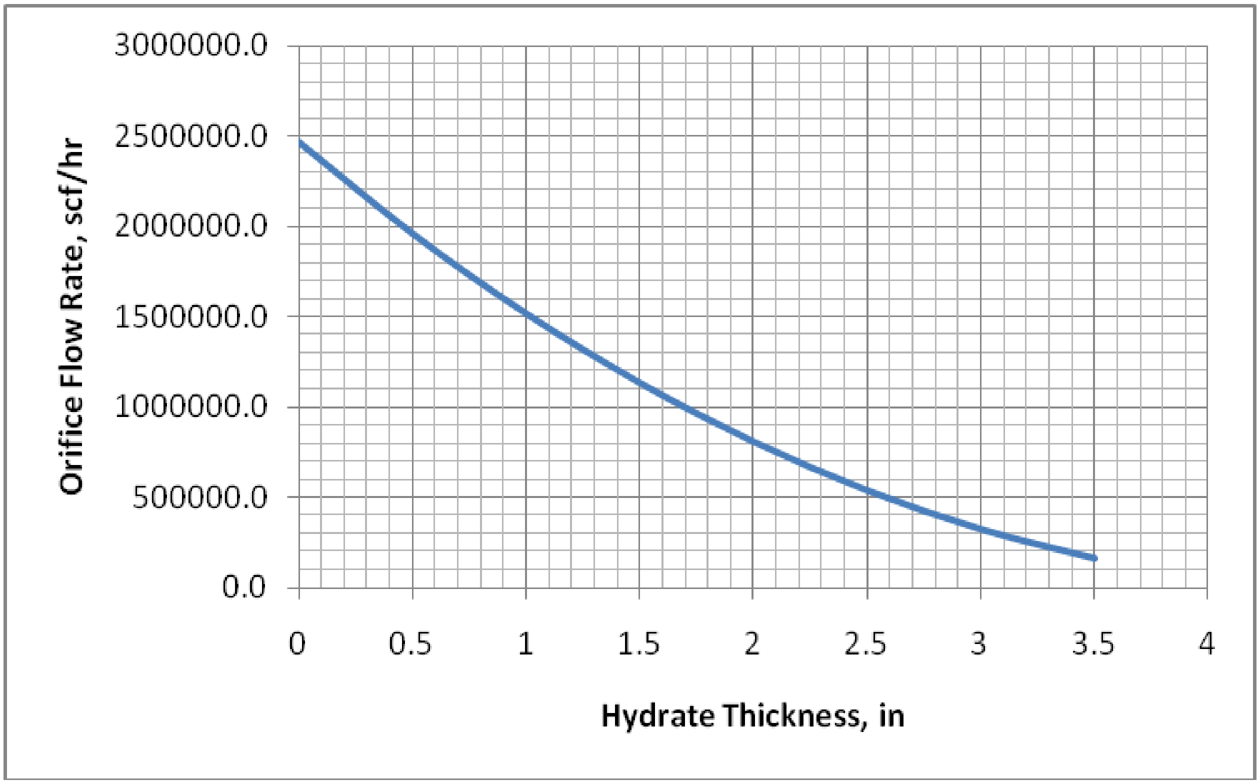


Fig 4.14: Orifice Flow Rate at various Hydrate Thicknesses

4.3 DISCUSSION

The data that were collected for the four natural gas streams were used for the evaluation of the gas samples.

The analysis on Gas Stream A showed that hydrate formation was not possible at the temperature and pressure of the gas stream, therefore no further evaluations were conducted on Gas Stream A.

The hydrate formation prediction analysis on Gas Stream B showed that hydrate could form in that gas stream and it advised that prevention should be applied. Based on the flow rate and water content of the gas which were rather low, the prevention method prescription program prescribed heating the gas stream to high temperatures. This is shown in Fig 4.3. Fig 4.4 shows the plot of the Temperatures at which gas needs to be heated to in order to avoid hydrate formation at the corresponding pressure.

The hydrate formation prediction analysis on Gas Stream C also showed that hydrate could form in that gas stream and according to Fig 4.5, it is advised that prevention be applied. Based on the flow rate and water content of the gas which were not too high, the prevention method prescription program, as shown in Fig 4.6, prescribed passing the gas stream across Methanol or Ethylene Glycol to absorb the water in the gas. A reservoir engineering program, PVTP was used to determine the minimum ethylene glycol concentration and minimum methanol concentration in weight % and mole % required to inhibit the hydrate formation and protect the gas stream up to 5000 psig at the same temperature. The evaluations are shown in Figs 4.7 and 4.9. The minimum weight % of glycol required to protect the gas up to 5000 psig at 50^0Fis 29.8062 whereas that of methanol is 19.3878. From the evaluations and Figs 4.8 and 4.10, it is seen that less methanol is required to protect the gas from forming hydrate at low temperatures than glycol. It is then suggested that it is more advisable to use methanol when protecting the gas from forming hydrate at low temperatures than to use glycol.

The hydrate formation prediction analysis on Gas Stream D also showed that hydrate could form in that gas stream. Based on the flow rate and water content of the gas which were high, the prevention method prescription program, as shown in Fig 4.12, prescribed passing the gas stream through a Glycol Dehydrator Column. The necessary computations made were computations for the amount of water to be removed to meet specification and the circulation rate of the glycol in the dehydration system needed to remove that amount of water. The amount of water to be removed is gotten as 2.98 lb_m/hr and the required glycol circulation rate is 0.075 gal/hr. A plot of glycol circulation rate against water content of the gas was generated as shown in Fig 4.13.

The effect of hydrate formation on flow was also evaluated by using the Orifice Flow equations, eqs 4.3 and 4.4, to compute the Gas Stream E flow rates through the orifice before hydrate formation and after hydrate formation. From the computations and Fig 4.14, it is seen that hydrate formation reduces the amount of flow through the orifice. The flow rate through the orifice before hydrate formation was 2465829.4scf/hr but after hydrate of about 2.25’’ thickness was formed the flow rate reduced to 668146.4scf/hr. Also, from Fig 4.14, as the thickness of the hydrate increases, the flow rate of gas through the orifice decreases.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Hydrate formation analyses on gas streams A to D were carried out in this research work. The result of the analyses has shown that only gas stream A is likely not to form hydrate if transported through the piping systems at that very temperature and pressure, but hydrate formation is very possible in gas streams B, C and D. The report gotten from the work station regarding gas stream E shows that hydrate had formed in the orifice. Equations and computer models were used for predicting the possibility of hydrate formation in the natural gas stream and for prescribing the appropriate inhibition or prevention technique to be applied in the gas streams to stop hydrate from forming. The effect of hydrate formation on the flow of gas through the orifice was also evaluated.

From the evaluations conducted using the equations, computer models and charts, the following conclusions may be drawn:

1. At low pressures and high temperatures, hydrate is less likely to form in natural gas stream than at low temperatures and high pressures. If a gas sample is evaluated to be susceptible to hydrate formation then heating the gas to high temperatures can cushion the problem of hydrate formation.
2. When the water content of the gas sample is not too high and the flow rate is high then heating the gas to high temperatures may not likely be the long-lasting inhibition technique to the formation of hydrate in the gas stream. It is then advisable to pass the gas stream through glycol/methanol or even send the gas into a glycol dehydrator

column which is the ideal inhibition technique for gas streams with high water content and high flow rate.

3. It is less material-utilizing to use methanol when protecting the gas from forming hydrate at low temperatures than to use glycol since less methanol is required to protect the gas from hydrate formation up to any given pressure at low temperatures.
4. From the plot of glycol circulation rate against water content of the gas it is seen that higher glycol circulation rates are needed in the dehydrator column if the gas sent into the dehydrator column has larger water content and thus the amount of water to be removed from the gas to meet specification.
5. According to Fig 4.14, hydrate formation reduces the amount of gas flow through the orifice. The flow rate through the orifice conducting natural gas stream E before hydrate formation was 2465829.4scf/hr but after hydrate of about 2.25'' thickness was formed the flow rate reduced to 668146.4scf/hr.

5.2 CONTRIBUTIONS TO KNOWLEDGE

The work has contributed the following to knowledge:

1. Computer programs in Microsoft Visual Basic Language were written which could be applied to predict the possibility of hydrate formation in a gas stream and prescribe the appropriate inhibition technique for hydrate formation in a gas stream. This saves the time for the rigorous tests, reading of graphs and charts and manual computations in order to achieve the same purpose.

2. It is very much easier for the engineer to know the best approach he needs to take in order to eliminate the possibility of hydrate formation in gas the company is handling.

5.3 RECOMMENDATION

As this work has successfully confirmed the predictability of hydrate formation in gas streams and determinability of the best inhibition technique to hydrate formation, the following areas are also recommended for further studies;

1. Extraction of methane gas from hydrates.
2. Experiments and engineering analysis on the effect of hydrate formation on piping equipment and tanks.
3. Comparative analysis of the different hydrate chemical inhibitors in use, viz Sodium Chloride, Ethylene Glycol, Methanol, Zinc Chloride, Acetone, Calcium Chloride etc.

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NOMENCLATURE

BOP = Blowout preventer

Btu/lb-R = British thermal unit per pound per rankine

CH_4 = Methane

Cl = Chlorine

C_2H_6 = Ethane

CO_2 = Carbon dioxide

C_{wi} = Water content of inlet gas

C_{wo} = Water content of outlet gas to meet specification

C^i = Orifice Flow Constant

D = Pipe diameter

d = Orifice diameter

Deg F = Degree Fahrenheit

ft/s^2 = Foot per square second

F_b = Base Orifice Factor read

F_r = Reynold’s Number Factor

F_{pb} = Pressure Base Factor

F_{tb} = Temperature Base Factor

F_{tf} = Flowing Temperature Factor

F_g = Specific Gravity Factor

F_{pv} = Supercompressibility Factor

F_m = Manometer Factor

F_l = Gauge Location Factor

F_a = Orifice Thermal Expansion Factor

g = Gravitational acceleration

gal/hr = Gallon per hour

gal.TEG/lb_mH_2O = Gallon of TEG per pound of water

GWR = Glycol to Water ratio

h_w, = Differential pressure at 60^0F

H_2S = Hydrogen sulphide

in = Inch

K = Kelvin

KI = Kinetic Inhibitors

Kvsi = Vapor-solid distribution coefficient

lb_mH_2O/MMscf = Pound of water per million standard cubic foot

lb_m/hr = Pound per hour

lb/MMscf = Pound per million standard cubic foot

m = metre

M = Molar weight

MMscf/d = Million standard cubic foot per day

mol% = mole percent

m^3 = Million cubic metre

NGH = Natural Gas Hydrate

N_2= Nitrogen

psia = Pound per square inch (atmosphere)

psig = Pound per square inch (gauge)

q = Gas flow rate

q_G = Glycol circulation rate

scf/hr = Standard cubic foot per hour

SG = Specific gravity

TEG = Tri-ethylene glycol

TI = Thermodynamic Inhibitors

T_m = Temperature During Orifice Boring

US = United States of America

USGS = United States Geological Survey

wt % = Weight percent

Xi = mole fraction of component i in the water-free solid hydrate.

Y = Expansion Factor

Yi = mole fraction of component i in the water-free vapor

Z = Compressibility factor

^{0}C = Degree celsius

^{0}F = Degree Fahrenheit

% = Percent