EFFECT OF POLYGLYCOLS ON HYDRATE FORMATION DURING DRILLING OPERATIONS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ABBAS N.TAHİR

IN PARTIAL FULFILLMENT OF THE REQUIREMENT
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
PETROLEUM AND NATURAL GAS ENGINEERING

SEPTEMBER 2005

Approval of Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master Science

Prof. Dr. Birol Demiral
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science

Prof. Dr. Mahmut Parlaktuna	Prof. Dr. Tanju Mehmetoğlu
Co-Supervisor	Supervisor

Examining Committee Members

Prof. Dr. Birol Demiral	(METU-PETE)
Prof. Dr. Tanju Mehmetoğlu	(METU-PETE)
Prof. Dr. Mahmut Parlaktuna	(METU-PETE)
Assoc. Prof. Dr. Hakkı Gücüyener	(TPAO)
Asst. Prof. Dr. Evren Özbayoğlu	(METU-PETE)

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Name, Last name:
Abbas N. Tahir

Signature :

ABSTRACT

EFFECT OF POLYGLYCOLS ON HYDRATE FORMATION DURING DRILLING OPERATIONS

N. Tahir, Abbas
M.S., Department of Petroleum and Natural Gas Engineering
Supervisor : Prof. Dr. Tanju Mehmetoğlu
Co Supervisor : Prof. Dr. Mahmut Parlaktuna

September 2005, 55 pages

The aim of this experimental study is to investigate the inhibitive properties of polyglycol and polyglycol+KCl aqueous solutions on hydrate formation, which causes serious fluid flow problems, especially during deepwater drilling operations.

As the petroleum industry continues to search oil in deeper and deeper seas, the possibility of facing hydrate problems during drilling operations increases because of the suitable conditions for hydrate formation.

The main goal of this study is to investigate the hydrate inhibition capacity (thermodynamic and/or kinetic inhibition) of polyglycol and KCl which are mainly used in drilling fluids for shale inhibition and wellbore stability.

A high pressure hydrate forming reactor is used to form and dissociate methane hydrate from aqueous solutions of polyglycol and polyglycol+KCl. In total 10 experiments were carried out, 5 of them with 0%, 1%, 3%, 5% and 7 % by volume of polyglycol solutions (Group-A experiments). The remaining 5 experiments (Group-

B) had 8% by weight of KCl in solution in addition to the same polyglycol concentrations of Group-A experiments.

Among the two chemicals tested for their hydrate inhibiting potentials, polyglycol did not exhibit any thermodynamic inhibition capacity while KCl was observed to have the ability of hydrate inhibition thermodynamically. On the other hand, increase in polyglycol concentration at constant KCl concentration (Group-B) increases the hydrate formation depression capacity of KCl.

Polyglycol inhibits methane hydrate formation kinetically. The higher the polyglycol concentration in aqueous solution, the lower is the initial rate of methane hydrate formation (corresponding to first 15 minutes of hydrate formation).

On the other hand, there exists a slower change of methane hydrate formation rate as polyglycol concentration increases.

Key Words: *Hydrate inhibition, polyglycol, KCl, thermodynamic inhibition, kinetic inhibition.*

ÖZ

POLİGLİKOLLERİN SONDAJ OPERASYONLARI SIRASINDA HİDRAT OLUŞUMUNA ETKİLERİ

N. Tahir, Abbas
Y.Lisans., Petrol ve Doğal Gaz Mühendisliği
Tez Yöneticisi : Prof. Dr. Tanju Mehmetoğlu
Ortak Tez Yöneticisi: Prof. Dr. Mahmut Parlaktuna

Eylül 2005, 55 sayfa

Bu deneysel tez çalışmasının amacı poliglikol ile poliglikol+KCl sulu çözeltilerinin, özellikle derin deniz sondajlarında ciddi akış problemlerine yol açan hidrat oluşumunu engelleme özelliklerini araştırmaktır.

Her geçen gün petrol arama faaliyetlerini daha derin denizlere yönlendiren petrol endüstrisinin, sondaj operasyonları sırasında hidrat problemi ile karşılaşma olasılığı artmaktadır, çünkü çalışılan ortamların koşulları hidrat oluşumu için uygun şartlara sahiptir.

Bu çalışmanın temel amacı, sondaj operasyonları sırasında sondaj sıvısı içinde kil inhibisyonu ve kuyu kararlılığını sağlamak amacıyla kullanılan poliglikol ve KCl nin hidrat engelleme kapasitelerinin (termodinamik ve kinetik) araştırılmasıdır.

Çalışma kapsamında yüksek basınçlı bir hidrat oluşturma reaktörü vasıtasıyla poliglikol ve poliglikol+KCl sulu çözeltileri kullanılarak metan hidratı oluşum ve çözünme deneyleri yapılmıştır. Yapılan toplam 10 adet deneyin 5 tanesi hacimce %0, %1, %3, %5 ve %7 derişimli poliglikol sulu çözeltileri iledir (Grup-A deneyleri).

Diğer 5 deney ise Grup-A deneyleri ile aynı poliglikol derişimlerine sahip fakat ağırlıkça %8 derişimli KCl içeren sulu çözeltilerle yapılmıştır (Grup-B).

Hidrate engelleme potansiyelleri için test edilen iki kimyasal içinde poliglikol termodinamik engelleyici özelliği göstermemiş, KCl nin ise termodinamik engelleyici olduğu görülmüştür. Öte yandan, KCl sulu çözeltisi içinde artan poliglikol derişimi ile (Grup-B) KCl nin hidrat engelleme kapasitesinin arttığı gözlemlenmiştir.

Poliglikolün metan hidrat oluşumunu kinetik olarak engellediği sonucuna varılmıştır. İlk 15 dakikalık hidrat oluşum verileri karşılaştırıldığında sulu çözelti içinde artan poliglikol miktarının hidrat oluşum hızını düşürdüğü görülmüştür.

Öte yandan, metan hidrat oluşum hızındaki değişimin poliglikol derişiminin artmasıyla azaldığı saptanmıştır.

Anahtar kelimeler: *Hidrat inhibisyonu, poliglikol, KCl, termodinamik engelleyici, kinetik engelleyici.*

ACKNOWLEDGMENTS

The author is grateful and expresses his sincere thanks to Prof. Dr. Mahmut Parlaktuna and Prof. Dr. Tanju Mehmetoğlu for their guidance, patience, advice and assistance in supervising the project, without their support he could not have come this far. His appreciation is extended to for their valuable contribution through constructive suggestions that they made.

The author is deeply grateful to his family; his mother Almas Abbas and two brothers; Firnas and Yılmaz Tahir for providing all means of the help for him to study and especially his mother Almas Abbas for her unconditional support and care, patience and understanding, fostering and always being there to listen.

The author extends his appreciation to Turkish Petroleum Corporation (TPAO) Research Center for providing the chemicals used in the experiments.

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CHAPTER 1

INTRODUCTION

Hydrates are crystalline solid substances which are formed by water and gas molecules under suitable temperature and pressure conditions. Water forms a solid skeleton through hydrogen bonding and gas molecules are entrapped in the cavities of this skeleton with the help of weak van der Waals forces. Prevention of the formation of hydrates during deepwater drilling operations is one of the tasks of drilling engineer because it causes congestions, plugs, blockages and fluid flow problems both in the wellbore and in the platform components.

Hydrates were firstly discovered by Davy (1810). One century later, Hammerschmidt (1934) introduced hydrates to oil industry after recognizing that the solid structure seen in the trans-continental gas pipelines is not the ice but hydrate. After this discovery oil industry focused on various hydrate related research topics. Among those topics, hydrate prevention and inhibition studies cover a relatively high percentage.

On the other hand, the discovery of in-situ hydrate reservoirs under deep oceans and permafrost regions brought a new research area on hydrates, recovery of gas from hydrate reservoirs. It can be speculated that hydrates are one of the most promising unconventional resources of supplying future’s energy. This speculation is based on the fact that 1 m^3 of hydrate can contain as much as 170 Sm^3 of gas.

This study, however, will be focused on hydrates as a nuisance during deep water drilling operations. The two aspects of hydrates are the main causes of the problems:

- Tendency to be adhesive to metal surfaces resulting in plugs.
- High gas content of hydrates which results with very high pressures after dissociation.

Since hydrate formation during deepwater drilling operations results in highly expensive remediation operations, prevention of gas hydrate formation becomes very crucial for the operator of the well.

In the use of water base drilling muds, hydrates may cause problems in two different means: i) the hydrates may form a “plug” or solid mass within the wellbore, ii) water required for the formation of hydrates may come from the water based drilling mud itself, which in turn causes fluid flow problems.

Thus, hydrate formation during drilling operations causes formation fluid flow problems, blockages in blow out preventer (BOP) stack or parts of it, plugs in choke or kill lines which will result problematic well control operations, even differential sticking.

One of the commonly used hydrate preventing methods in oil and gas fields all over the world is injection of chemical inhibitors. New hydrate formation inhibition methods are developed and new inhibitor types are introduced by ongoing researches as long as hydrates’ popularity and oil and gas production costs keep increasing.

There are two kinds of hydrate inhibitors; thermodynamic and kinetic inhibitors. While kinetic inhibitors delay formation of hydrates for hours, may be days, thermodynamic ones act as antifreeze and lowers the hydrate formation temperature by lowering the activation of water molecules that enclathrates gas molecules.

The use of synthetic oil based drilling fluids with very low toxicity and good bioremediation qualities have inherent advantage to control the hydrate formation in deep water drilling. However, strict environmental regulations make limit the use of fluids in deep water drilling. Furthermore, these fluids contain sufficient water to form hydrate. Therefore, instead of synthetic using oil based drilling fluids, the water based drilling fluids are used in deepwater drilling operations with the use of salts to inhibit hydrate formation.

Glycols are used in water based drilling fluids and are an alternative to oil based and synthetic fluids for stabilizing troublesome clays and shale, drilling environmentally- sensitive areas, drilling high-angle and extended reach wells. Polyglycols are most effective when used in conjunction with an inhibitive salt, such as KCl, in non-dispersed polymer systems; they can be used as additives in most water-base systems.

It is already known from the literature that KCl can be used as a thermodyanamic hydrate inhibitor. On the other hand, other type of glycols (ethylene glycol) are used for dehydration and hydrate inhibiton applications in oil industry.

It is aimed in this study to examine the hydrate inhibiting capacity (thermodynamic and kinetic) of aqueous solutions of polyglycols and polyglycol+KCl.

CHAPTER 2

EFFECTS OF HYDRATES DURING DRILLING

When natural gas and free water are in contact under low temperature and high pressure conditions, an ice-like solid structure is formed, called gas hydrates (Englezos, 1990). In this structure, "hydrogen bonded water molecules form a cage-like structure that surrounding gas molecules forming a solid substance with a high gas density – 1 m^3 of hydrate can contain 170 Sm^3 of gas" (Halliday, 1998). There are three types of gas hydrate structures, sI, sII, sH structures. The properties of hydrate structures were extensively described in the previous M.Sc. and Ph.D thesis completed in Petroleum and Natural Gas Engineering Department of METU (Karaaslan, 2001; Serdar, 2001; Doğan, 2002; Alp, 2005); therefore those subject will not be covered here, but the effects of them during drilling and their prevention methods will be the subject of the following sections.

2.1. Effects of hydrate on the drilling:

More than 1.2 million tons of methanol is currently used annually for prevention of hydrate formation in the world at a total cost of 400 million dollars. It is claimed that removal of large hydrate plugs from wells and pipelines is 30-50 times more expensive than their prevention. Therefore, it is momentously easier and cheaper to prevent hydrate formation than to remove them (Makogon, 1997). Today, the urgent gas hydrate problems are;

- creation of new methods of preventing the formation of large hydrate plugs in the wells, especially in conditions of deep sea zones including kinetic inhibitors,
- providing the stability of constructed and operated engineering objects in the hydrate formation zone,

- creation of new technologies based on hydrates,
- development of effective methods for discovery of gas hydrate deposits and for gas production from them,
- revealing the role of natural gas hydrates in global changes.

Hydrates are serious danger for safety (Figures 2.1 and 2.2) since 1m^3 of hydrate can contain 170 Sm^3 of gas which will be unstable and difficult to control even by BOP. As showing in the figures, thick wall crushed in a well by hydrate and solid hydrate plug in the gas condensate well.

Although, deepwater rigs have insulation on the riser; riser, BOP, choke and kill lines are exposed to hydrate formation all the time because of the cold environment under high pressure. One of serious effects of hydrate on well control operations is the plugging of choke and kill lines which do not allow circulation. Formation of hydrate in BOP or under BOP prevents monitoring of well. In some cases, it becomes impossible to close or fully open the BOP because of the existence of hydrate.

Formation of hydrate requires the existence of water and gas in addition to high pressure and low temperature. During drilling the water comes from two sources, drilling fluid (mud) and formation water containing salt.

The cost of hydrate prevention during drilling is high (approximately 1 million dollars or more per well as hydrate formation cost) due to the cost of insulation and also due to the remediation operations, which includes the cost of hydrate inhibitors and the cost of heating.

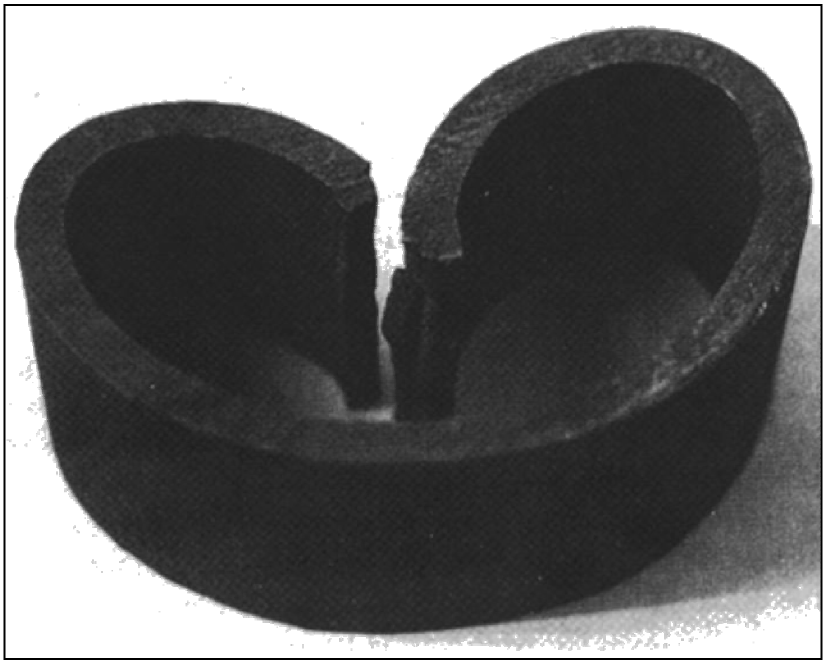

Figure 2.1 Cut of a 64 mm diameter thick wall crushed in a well by hydrate at depth 1245 m, temperature 7 ºC (Makogon, 1997)

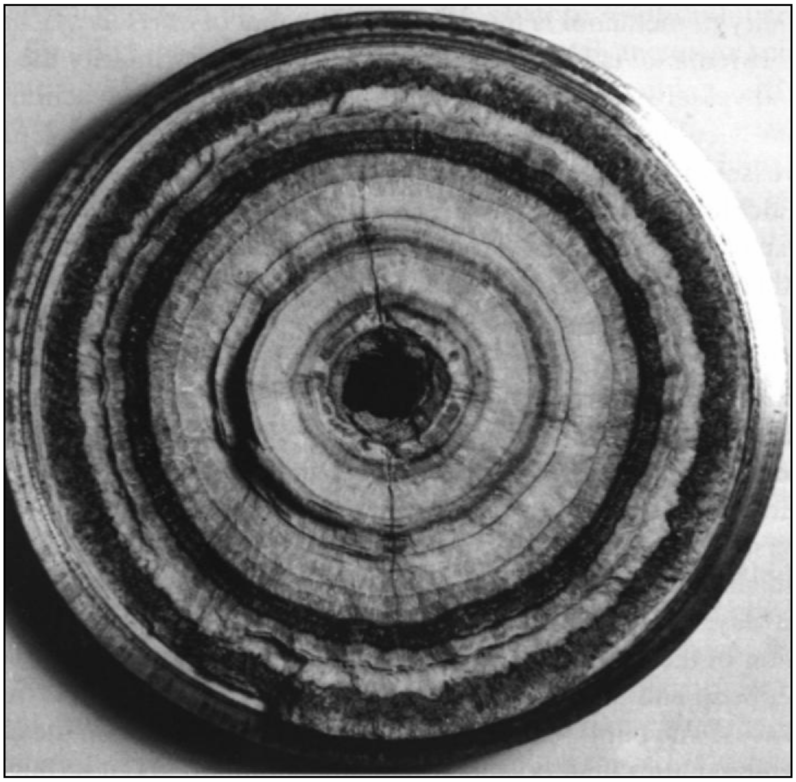

Figure 2.2 Solid hydrate plug in the gas condensate well, 4” diameter (Orenburg field well no: 197 (Makogon, 1997)

2.2. Formation of Hydrates in Wells

One of the most important problems that must be solved during oil and gas drilling and production is hydrate formation in wells. Hydrates can form in any place; in a layer (in sediments); in the well bottom zone; in the fountain pipes and in the annular space; in the well head equipment before, inside, and after the orifices; and in separators and pipelines i.e. hydrates form where water and gas are present at the appropriate temperature and pressure. They may form in the drilled well if drilling utilizes the fresh water solutions in the low temperature and high pressure intervals, during the drilling while entering the pay-zone, during mastering and testing of a well, and during the well shut-in period. When the well operating pressure is lower than the gas saturation pressure and temperature is below hydrate equilibrium, hydrates also form not only in the gas and gas condensate wells, but also in the oil wells. Presence of the low-temperature wax promotes the formation of hydrate plugs and sharply complicates the formation of solid phase in the flow.

The operation regime, design and geothermal gradient in a well, fluid composition, and other factors play essential role on defining the locations and intensity of hydrate accumulations in a well. The interval of the hydrate formation in a well is determined by drawing a diagram of the hydrate equilibrium curve dependent on the well operating parameters and the actual temperature in a well. The lower boundary of hydrate formation is determined by the intersection of two temperature curves. The equilibrium curve is constructed from the hydrate equilibrium pressure values for a known gas composition, the actual temperature curve from the results of the well thermometer measurements.

Under certain conditions, when the well is operated only in the annular space, the hydrate formation may bear the localised character in the gas throttling locations during its flow through loose junctions. Cases more often encountered are hydrate formation in the stems of wells which were inoperative for a long time or formed during well conservation.

Usually, temperature stabilization in a shut well filled with gas results in the cold zones of the rock to the temperature lowering below the hydrate equilibrium. Nuclei form from the films of water on the tube walls. The following crystallization, as usual, results in a total plugging of the well bore. The length of the hydrate plugs may reach tens or hundreds of meters. In some cases of hydrate formation and accumulation of plugs in sections of the pipe, crushing and breaking well columns, which results from great stresses developed in the pipe, will present.

2.3. Complications during the Drilling of Wells

Although in-situ hydrates are considered as unconventional resources for natural gas and mankind may benefit from them in the future by dissociation processes, there is always a risk of dissociating hydrates while drilling permafrost regions and especially hydrate bearing formations. Therefore, operator of the drilling operation will face extremely high pressures due to release of gas from hydrates which can be controlled by cooling drilling fluid during drilling. Another way of the prevention of hydrate dissociation is the insulation during ongoing drilling operation.

Barker and Gomez (1987) pointed out the negative effects of hydrates for petroleum industry. Two geologically separated wells, in which hydrate formation occurred and plug occurred during drilling, have been investigated. One of these wells had 350 m and the other had 950 m thick hydrate bodies, both deepwater wells. Hydrate formation in wells can cause human injury, time loss and uncontrolled flow or pollution. These hydrate formation cause plugs in choke lines and kill lines and BOP in drilling operations. Hydrate types are determined by gas composition, liquid composition, temperature and pressure conditions. Pre-well analysis should be done by the possibility of hydrate formation during drilling operations of deepwater wells. This pre-analysis of the well should contain long term shut-in prevention of hydrates. In both cases time that passes to plug the wellbores are several hours. High salinity is a function of depression for hydrate formation.

Hydrate formation tendency of water based muds was first recognized in the Gulf of Mexico. Water based muds have higher tendency than pure water to form hydrate, because their water content have many sites for crystal nucleation. After this property of water based muds was recognized, inhibitive drilling fluids development researches begun.

The hydrate saturated layers are characterized by an extremely low permeability, which prevents the filtration of drilling mud into the layer and the formation of a protective layer of dry mud on the well walls. The absence of a protective layer on the walls of the well opens the gas hydrate deposit during the drilling at temperature above hydrate equilibrium. In that case, existence of chemically active solutions results in hydrate decomposition. Decomposition in hydrate in a well bottom zone of the layer is accompanied in a number of cases with a sharp weakening of the bonds between the grains, fluidizing of a part of the rock, and ejection into a well. This process accompanied by an intensive formation of caverns, and shearing rock may cause seizing of tools. A gas evolving from hydrates at a high pressure results in an intensive saturation and ejection of drilling mud from a well.

Intensity of hydrate decomposition and gassing of a drilling fluid are determined mainly by the excess temperature of drilling mud above the equilibrium temperature of hydrate in a layer. Released gas then flows in a well, dissolves in the drilling mud, decreases its density, and results in an emergency ejection of the mud from a well. The pressure of the released gas is determined, not by a hydrostatic pressure, but by the temperature of hydrate decomposition. However, the ejection of drilling mud is accompanied by a sharp intensifying of hydrate decomposition, which, in turn, results in a significant cooling of the rock in the zone of hydrate decomposition and decay of the process of hydrate decomposition.

To prevent an intensive formation of cavities, seizing of the drilling tools, and gassing and ejection of a drilling mud due to hydrate decomposition, it is necessary to increase the density of a drilling mud, decrease the mud temperature below hydrate equilibrium, or a combination of these two methods.

2.4 Using Inhibitor in Deep Water Drilling

The use of synthetic oil based drilling fluids which have very low toxicity and good bioremediation qualities (these properties allow disposal of cutting offshore) have inherent advantage to control the hydrate formation in deep water drilling. However, stringent environmental regulations make limit the use of fluids in deep water drilling. Furthermore, these fluids contain sufficient water to form hydrate. Therefore, instead of synthetic using oil based drilling fluids, the water based drilling fluids are used in deepwater drilling operations with the use of salts (mainly NaCl) to inhibit hydrate formation (Sloan, 2000).

Barker (1998) pointed out the rules-of-thumb for the formation of hydrates during deepwater drilling operations:

- Hydrate problems are common in drilling operations, especially deepwater drilling operations.
- Hydrates not only form solids but they remove the water content of the mud causing mud's solid particles as plugs.
- In drilling hydrate formation risky formations, waiting and stoppage times of an ordinary drilling operation is enough to plug inside of the wellbore.
- Congestion may take only several hours, in case of no fluid flow in the wellbore.
- Hydrate plugs could be removed by thawing from both ends, not only thawing at mid-plug.
- The most practical and economic way of preventing hydrate formation is to use salts as hydrate depressants.

There are several ways of preventing or inhibiting the formation of hydrate. Three of the prevention methods are lowering the system pressure, increasing the system temperature by heating, and drying the system to get rid of water by dehydration. All of these methods are theoretically possible but not practical, and, therefore are not commonly used. For example, dehydration is not possible for sub sea wells or small platforms with limited space. Heating and insulation can be used independently or jointly, however it may not be cost effective for longer flow lines carrying high gas-oil ratio fluids.

The fourth and the most widely used hydrate prevention method is the chemical inhibition. There are three kinds of chemical inhibition: thermodynamic inhibitors, kinetic inhibitors and anti-agglomerants. The essence of thermodynamic inhibition is that the third active component is added to two-component system (water + gas) which changes the energy of intermolecular interaction and changes thermodynamic equilibrium between molecules of water and gas. These kinds of inhibitors work by lowering hydrate formation temperature like antifreeze and changing the thermodynamics of the system. This method is not economical because of the usage of methanol and glycol in huge amounts and in high dosages. There exists certain dependence between the concentration of an inhibitor in water and temperature of hydrate formation.

Despite the fact that the use of thermodynamic inhibitors is very effective, the concentrations required can be considerably high. The effective dosage is dependent upon the severity of the condition. This is also related to the degree of sub cooling, that is defined as the temperature difference between the hydrate dissociation temperature and the operating temperature at a given pressure. Most of the new developments in deepwater environments are challenged with a high degree of sub cooling. Controlling hydrates in these operations would mandate a large volume of thermodynamic inhibitors to be shipped offshore. The huge volume requirement complicates the logistics and raises a safety concern. In some cases it is impossible to pump such a high volume of inhibitors due to constraints of pressure rating and delivery capacity. Therefore, an alternative inhibitor with a much lower effective concentration is very desirable for deepwater operations.

Kinetic inhibition means affecting the nucleation and growth rate of the hydrate crystals. Kinetic inhibitors keep away the hydrate crystals from critical size to reach growth season of the hydrate crystals. Crystal modifiers slow the rate of hydrate formation and prevent agglomeration. These kinds of hydrate inhibitors do not disrupt thermodynamic equilibrium. They do not prevent nucleation, they just control the rate of nucleation.

Kinetic inhibitors are polymers and their effective concentration for preventing hydrate formation is about 10-100 times lower than that of methanol and ethylene glycol so that it becomes economically appropriate. They prevent hydrate nuclei to form larger crystal, and thus delays hydrate formation. Some examples of kinetic hydrate inhibitors (KHI) are PVP (polyvinylpyrrolidone), VC-713 (Ndimethylaminoethylmathacrylate), PVCap (polyvinylcapralactam), VP/VC (poly Nvinylpyrrolidone/Nvinylcaprolactam polymers) (Kelland, 1995).

Anti-agglomerants are polymers and surfactants that only work in the presence of both water and hydrocarbon phases to prevent hydrates from agglomeration or deposing in pipeline (Frostman, 2000). They are added in low concentrations of less than 1 % by weight and prevent the agglomeration (Kelland, 1995).

2.5 Previous Studies on the Chemical Inhibition of Hydrate Formation

Makogon et.al. (1999) have investigated thermodynamic and kinetic inhibitors with methane hydrates. Induction time of hydrate formation depends on the gas composition and water structure, pressure and super cooling and cooling rate. They have tested four different types of kinetic inhibitors with fresh water and seawater with different composition. The amount of super cooling depends on gas and water composition and pressure. According to authors of this paper, there are three morphological types of hydrates; massive, whiskery and gelly.

Lai and Dzialowski (1989) have published experimental results of tests done using a hydrate generator setup. In this research, different types of drilling fluids have been tested. These fluids were lime, sea water gyp, polymer and dispersed muds with varying salt amounts. It is obvious that there is a need for developing new hydrate inhibitive fluids. While lignosulphanate muds have contributive effects on hydrate formation, salt, glycerine, and propylene glycol have negative effects on hydrate formation. But caustic, gel, diesel and calcium have minor effects on hydrate formation. While certain polymers slow down the hydrate formation rate, the equilibrium data of the most of the polymer-salt systems were near or very close to salt aqeous solutions.

2.5.1 Thermodynamic inhibitors

Salts are one of the thermodynamic inhibitors which ionize in solution and interact with water molecules by bonds resulting with a cluster. Those bonds are stronger than van der Waals forces. Therefore, bonds form clustering around the polar solute molecule and the potential hydrate guest molecules diminish in water. This phenomenon is known as salting out. Thus the temperature of the hydrate formation will decrease. In other words, when salts or formate salts like potassium formate are dissolved in water, the salts dissociate into ions. This means that for each mole of formate salt dissolved two moles of ions are formed. After that the crystal lattice is formed between water and salts and appears as precipitation. It is noticed at high concentration that the relationship between the salt concentration and its effect on the water phase is not linear (Fadnes, 1998).

Ebeltoft et.al. (1997) have focused on the salt / polymer systems which were used successfully in Gulf of Mexico (GOM) even at 2287 m. water depth. They also tested twenty five drilling fluids in terms of hydrate inhibiting effects. Among these tests NaCl is the best thermodynamic hydrate inhibitor. KCl, NaBr and $CaCl_2$ then follows NaCl as thermodynamic hydrate inhibitors. They have also tested glycol as a thermodynamic hydrate inhibitor. According to results obtained the best performance comes from ethylene glycol. Maximum hydrate suppression was from the solution of 5 wt % KCl + 15 wt % NaCl + 10 wt % Ethylene Glycol (17.8 ^{o}C suppression).

Howard (1995) indicated how to calculate the effect of salts on the hydrate formation temperature by freezing point depression data for the salts. The rule of the thumb, which is based on the theory described by Sloan (1990), to predict the effect on the hydrate formation temperature for any natural gas:

$$T_{eq,s} = T_{eq} - 0.8 \times \Delta T_{freezing} \tag{2.1}$$

where:

$T_{eq,s}$ = hydrate equilibrium temperature in brine, ºC

T_{eq} = hydrate equilibrium temperature in water, ºC

$\Delta T_{freezing}$ = freezing point depression by brine, ºC

Kotkoskle et. al. (1992) have tested 16 drilling muds in order to understand the thermodynamic equilibrium of hydrates. According to the results of tests glycerol and salty muds are more effective than bentonite, barite and polymers in terms of hydrate inhibition. The authors agreed that the hydrate formation in fresh water based muds depend on the concentration of salt. Only salt will behave as antifreeze for hydrate formation among the other constituents of fresh water based mud. After testing various salt types, they came to a conclusion that the most effective salts in terms of effectivity and degree of sub cooling are; $CaCl_2$, NaBr and NaCl.

Halliday et.al. (1998) described and underlined the importance of developing new hydrate inhibitors. These new inhibitors use low molecular weight organic compounds and their densities are low. Their suppressive capability is bigger than conventional thermodynamic hydrate inhibitors. In this paper a new generation thermodynamic, water soluble, low density, low viscosity, low molecular weight hydrate inhibitor was introduced. These new inhibitors are easily combined with salts and increase their suppression. They all meet all the conditions in terms of environment and compatible for all drilling fluid additives.

2.5.2 Kinetic inhibitors:

In the early stage of nucleation and growth, the inhibitor binds to the surface of hydrate particles. So, one can prevent them to reach critical size at which the particle growth become thermodynamically stable or delay the growth of these particles. It is observed that there are two delays due to the effect of the kinetic inhibitor, one of them is a delay time before hydrate is visibly detected; the second one is a period of slow growth. The true induction time as critical nuclei which may have formed much earlier, but they prevented it from growing to visible size by using the kinetic inhibitor; however, the time to when hydrate is first detected is not necessarily be the same (Kelland, 1995). Some examples of kinetic hydrate inhibitors (KHI) are PVP (polyvinylpyrrolidone), VC-713 (Ndimethylaminoethylmathacrylate), PVCap (polyvinylcapralactam), VP/VC (poly Nvinylpyrrolidone / Nvinylcaprolactam polymers).

Thus, kinetic inhibitors do not preclude the process of hydrate formation, but only shift in time and in space the formation of large hydrate plugs. Kinetic inhibition is a temporary inhibition. It is effective in dynamics and dangerous in statics and forces the shutdown of systems of production and transportation of hydrocarbons. Nevertheless, kinetic inhibition is appropriate in conditions when the condensed water cannot be removed from the flow before the moment of hydrate formation.

Kinetic inhibitors must be very soluble in water, not hydrolyse to insoluble compounds, and adsorb well on a polar surface of hydrate microcrystals forming an external surface preventing the association of hydrate crystals. They also must have a low toxicity, be of moderate cost, and be available and environmentally friendly.

Fu et.al. (2001) described the Low Dosage Hydrate Inhibitor (LDHI) especially on the KHI as second generation of hydrate inhibitors. These inhibitor types were developed for deepwater oil and gas fields. One of the crucial advantages of the (KHI) is the independence on the water cut in the system. They examined some properties and advantages besides disadvantages of KHI. According to them one advantage of KHI was being environmental friendly and non-toxic. And they also investigated on the compatibility of other drilling fluids and performance drop by interference with other chemicals both water soluble and oil soluble. The negative effect of high pressure due to deeper water wells (higher than 2000 psi) has been addressed. These new KHI have increased the sub cooling degree from 8 ^{o}C to 13 ^{o}C and corresponding shut-in time extended from 24 hours to 48 hours. LDHI are nontoxic chemicals independent of water cuts in deepwater wells of gas fields.

Kelland et.al. (1995) described the kinetic hydrate inhibitors, and their working mechanism in micro scale. They tested several chemicals and effects on hydrate formation in a sapphire cell with temperature and pressure as variables. According to them these chemicals can be grouped in three classes. First class delays the hydrate formation process for a particular time period. Second class prevents agglomeration and makes hydrate crystals transportable. Third class of kinetic inhibitors showed combined characteristics of class I and class II types.

Pakulski (1997) has focused for new high efficiency non-polymeric gas hydrate inhibitors and its way of work and structure. Both oilfield practical and research laboratory data gave the same result that the kinetic gas hydrate inhibitors are more effective in terms of performance of preventing hydrate formation than classical thermodynamic hydrate inhibitors. Kinetic inhibitors are high molecular weighted water soluble polymers that need polar carrier solvents. This non-polymeric newly designed product do not need any polar carrier solvent. This is a big advantage over polymeric KHI. This new product, tetrahydrofuran/salt water system were tested in both laboratory and field conditions and the results were in a supportive manner in terms of hydrate inhibition technology. This new product as hydrate inhibitor will have commercial potential over the classical ones.

Kelland et al. (1995) discussed and introduced the scope of work of kinetic inhibitors and antiagglomerants to develop new cost effective hydrate inhibitors in terms of injection dosages and pump requirements. Conventional methods of inhibition by injecting methanol and glycol are expensive if the dosage of injection of methanol or glycol is thought today. There is need for development of a new environmentally friendly and cheaper method of preventing hydrate. They have also compared the hydrate types.

Schofield et.al. (1997) have performed a work on the effects of lecithin from food and beer industries to control pressure and fluid flow in the Alaskan region. Using lecithin as chemical hydrate inhibitor has the advantage of being environmentally friendly. In Alaskan region, weighted drilling fluids are ineffective to control gas dissociated from hydrates. As an additive in food sector Lecithin served as a hydrate inhibitor and kept hydrates stable under current conditions and made gas release into well.

Becke et. al. (1992) have introduced hydrate equilibrium in research laboratory. They searched for the effect of hydrocarbons on hydrate inhibition and the influence with methanol as hydrate inhibitor. Presence of liquid hydrocarbon in the system decreases the temperature of decomposition of hydrate. The higher the volume of hydrocarbon and higher the molecular weight of the liquid hydrocarbon the higher drop in equilibrium temperature. The authors investigated whether while preventing hydrate formation the methanol reduction can be established or not. The results of this research showed that oil phase used in inhibition will definitely reduce the amount of methanol to be used and thus the cost.

A kinetic inhibitor poly-N-vinylpyrrolidone $(\text{-}C_6H_9NO\text{-})_x$ (PVP) has undergone sufficient and successful testing in industry. PVP is injected as an alcohol or aqueous alcohol based solution into an oil and gas flow to create a 0.5% concentration. PVP is supplied as granules or as a liquid concentrate (Makogon, 1997).

2.5.3 Anti-agglomerants

The anti- agglomerant inhibitors are particularly effective in preventing hydrate plugs or flow stoppage, such as shut in, with subsequent cooling and restarting. The anti agglomerants have one water attractive end and the other end attracts oil. Therefore, when oil increases the water hydrate droplets suspended as emulsified droplets. Otherwise, the water phase increase the oil droplets suspend as emulsified droplets (Sloan, 2000).

Frostman (2000) pointed out antiagglomerants (Low Dosage Hydrate Inhibitor ,LDHI) work different than thermodynamic hydrate inhibitors and kinetic inhibitors. Unlike Thermodynamic Hydrate Inhibitor (THI) and Kinetic Hydrate Inhibitor (KHI), Anti – Agglomerants (AA) allow hydrates to be formed but keep the particles small not to agglomerate. They show high performance in preventing hydrate formation up to 2 weeks shut-in and 7000 psi. AA hydrate inhibitor have been tested for its compatibility to other drilling fluids, chemicals, metals, etc. and based on these test results this AA was tried in Gulf of Mexico for 1.5 month. This 1.5 month trial showed the ease of applicability of LDHI to deepwater wells.

2.6. Polyglycol

A product of M-I *L.L.C* (A Smith/Schlumberger Company) is tested throughout this study for its effectiveness on thermodynamic and kinetic hydrate inhibition. The following section will give some information on the properties of this product.

As chemical description is related to alcohols, glycols have many of the properties of diesel and mineral oils, but contribute virtually no toxicity to the fluid. Glycols are used in water based drilling fluids and are an alternative to oil based and synthetic fluids for stabilizing troublesome clays and shale, drilling environmentally-sensitive areas, drilling high-angle and extended reach wells. Above the cloud point, they form Micro-Emulsions which block pore spaces in the formation preventing fluid invasion providing stability to water sensitive formation. The emulsions form a hydrophobic membrane on the well bore and cuttings and block pore space in filter cake to reduce fluid loss. Glycol enhances shale and clay inhibition. In addition to that, the glycol reduces dilution rates and improves filter cake, thus reduces fluid loss. Another advantage is improved lubricity. They also do not harm the environment.

2.6.1. Glydril MC polyglycol

Glydril MC polyglycol of M-I *L.L.C* is a medium cloud point (the temperature, where polyglycol additives change from being soluble which is at lower temperature to being insoluble at higher temperature) additive designed for medium to high salinity polyglcol systems.

The physical appearance is straw yellow to opaque, brown liquid. It has 1.012 Specific Gravity and solubility in water is variable. Cloud point of this liquid is above 150°F in situation of 3% of Glydril MC polyglycol and 10% concentration by volume of NaCl.

The advantage of the use of Glydril MC polyglycol is the improving wellbore stability, shale inhibition, lubricity, and high temperature filtration control. Also it has benefit in reducing dilution rates, mud consumption, and bit balling potential. Another advantage is low toxicity. However, the limit in its use is the increase in plastic viscosity as an insoluble liquid.

The effectiveness of polyglycol is increased when used in conjunction with an inhibitive salt, such as KCl.

A performance report “Nigeria: Glydril Prometes Trouble- Free Drilling” (Nigeria Performance Report, 1998) includes information about deepwater well offshore Nigeria was successfully completed by using a potassium chloride, Glydril MC system. They used 4 to 5% Glydril MC to achieve chemical well bore stability. The KCl+Glydril MC fluid provided a cost effective system for drilling all hole sections. The overall mud cost for the drilling phase was approximately 27% less than the programmed cost.

Another performance report “Denmark: Glydril System Successfully Drills 7,827-ft Section” (Denmark Performance Report, 1998) contains information about how the drilling fluid performed exceptionally throughout the well, giving high levels of lubricity and well bore stability. The system, utilizing a high potassium content, was designed to stabilize the long section of reactive and lubricity. Also this system had lower fluid costs by completely recycling which affected in reducing overall fluid costs. Also it was environmentally acceptable. The Glydril water-base system was approved for discharge, thus lowering the overall mud costs by eliminating the expense of slurrification and injection equipment. This system did not affect on the cementing operation and also the cement contamination did not affect of performance of the system. The combination of Glydril MC and glids HD provided low coefficients of friction resulting in minimum torque and drag throughout the system. The addition of Glydril MC and 1.5% Glide HS provided chemical well bore stability

CHAPTER 3

STATEMENT OF THE PROBLEM

As the petroleum industry continues to search for oil in deeper and deeper seas, the possibility of facing hydrate problems during drilling operations increases, because of the suitable conditions for hydrate formation.

Use of methanol and glycol became quite popular for the inhibition of hydrate, but the costs of using those chemical in huge quantities forced petroleum industry to develop new technologies of chemical inhibitors to prevent hydrate formation during drilling. Chemical hydrate inhibitors are classified into thermodynamic inhibitors and kinetic inhibitors. While thermodynamic ones shift thermodynamic equilibrium of the system composed of water and methane gas molecules, in other words behaves like antifreeze and reduces the activity of water of the system to inhibit hydrate formation during drilling, kinetic inhibitors reduce the hydrate formation rate to prevent hydrate formation for long periods during the drilling operations' periods.

This experimental study is aimed to investigate the hydrate inhibition capacity (thermodynamic and/or kinetic inhibition) of polyglycol and KCl which are mainly used in drilling fluids for shale inhibition and wellbore stability.

CHAPTER 4

EXPERIMENTAL SET-UP AND PROCEDURE

4.1. Experimental Set-Up

The schematic diagram of the experimental set-up which was used to carry out the hydrate formation tests is shown in Figure 4.1. The main piece of the set-up is a cylindrical high-pressure reactor with dimensions of 3.4 cm in diameter; 15 cm in length. It has the volume of 143 ml where hydrate crystals were formed and dissociated. It is made of brass and tested up to 1200 psi. The high-pressure reactor is placed into a constant temperature water bath with volume of 125 liters. The temperature of the bath is controlled by means of a temperature controller/circulator and a refrigerated chiller both are immersed into the water bath. The high pressure reactor is equipped with a thermocouple (with an accuracy of ±0.2 °C) and a pressure transducer (with an accuracy of ± 0.01 bar) to measure cell temperature and pressure. Those measuring devices are connected to a data-logger and a personal computer to record the temperature and pressure as functions of time. A motor with a constant rate of 30 rpm is used during the experiments to provide the rocking of the reactor. This motor is set outside of the bath and is attached to the reactor with an arm which transfers the turning motion of the motor to a rocking motion of the reactor. Two glass marbles are placed into the cell to provide the agitation of the fluid content of the reactor. Temperature and pressure are recorded every 5 seconds throughout the experiments.

Other pieces of the set-up are a vacuum pump to evacuate the cell before filling it with the reagents used to form hydrate and a high pressure methane bottle to supply the methane to form hydrate.

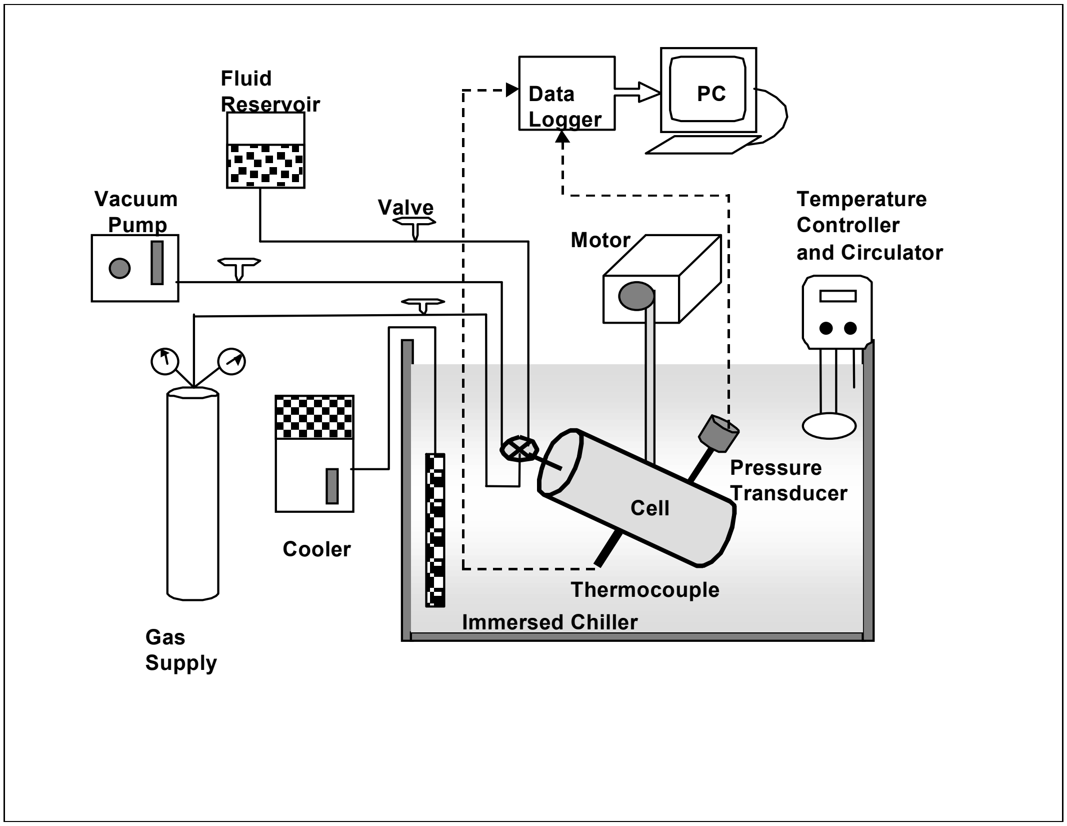

Figure 4.1 Schematic diagram of the experimental set-up

4.2 Reagents

The effectiveness of two chemicals, namely polyglycol and potassium chloride, on their hydrate inhibition capacities were tested throughout this study. Pure methane was used as the hydrate forming gas.

Ten tests were carried out with different concentrations of polyglycol and potassium chloride. Those tests are grouped with respect to their chemical contents:

- **Group A**: Polyglycol was the only additive for those tests. The normal concentrations of polyglycol range from 3 to 5 % by volume of the liquid phase. In this study, experiments were carried out with 0, 1, 3, 5 and 7% by volume of polyglycol.
- **Group B**: Within this group of experiments potassium chloride was added to the liquid by a constant concentration of 8% by weight in addition to polyglycol. Table 4.1 lists the concentrations of chemicals for all tests.

Table 4.1 Concentration of reagents used in the experiments

Test No	Polyglycol Concentration (Volume %)	KCl concentration (Weight %)
GROUP A		
A-1	0	0
A-2	1	0
A-3	3	0
A-4	5	0
A-5	7	0
GROUP B		
B-1	0	8
B-2	1	8
B-3	3	8
B-4	5	8
B-5	7	8

4.3 Experimental Procedure

The following steps were followed while running a hydrate formation - dissociation test:

1. At the beginning of each experiment, a leak control from high pressure reactor is conducted by using air under high pressure after finalizing all connections of the reactor.
2. After ensuring that there is no leak in the cell, the cell is evacuated by using the vacuum pump to minimize the contamination of the reactor content by air.
3. 60 cm^3 of aqueous solution (water, brine and/or polyglycol solution) is injected into the reactor. This is achieved by means of a syringe connected to the valve at the top of reactor. Since the reactor was under vacuum conditions, the atmospheric pressure activates the syringe to inject the aqueous solution into the cell.
4. The temperature of the cell is adjusted to 12 °C and the high-pressure cell is pressurized to the pressure of 62 bar by methane.
5. The cell is rocked for a while at constant temperature to dissolve the methane in water. After having a constant-stabilized pressure condition in the cell, cooling is started.

6. Cooling of the system causes a slight but continuous drop of cell pressure. This gradual pressure drop in the cell is due to the increase in solubility of gas in water as well as pressure-temperature relationship through gas law. On the other hand, a sharp change in the pressure drop trend indicates the start of hydrate formation.
7. The cooling and the rocking of the cell continue for a certain period of time after the start of hydrate formation.
8. At the end of hydrate formation process, rocking and cooling of the cell is stopped and the system is allowed to heat with the aid of ambient temperature.
9. Increase in temperature results with dissociation of hydrate.

CHAPTER 5

RESULTS AND DISCUSSION

There are two main aqueous solution groups in this study. Group A contains aqueous solutions of polyglycol in different concentrations and Group B contains aqueous solutions of potassium chloride and polyglycol in different concentrations (Table 4.1). All the tests were carried out by applying the experimental procedure given in Section 4.3. The typical experimental data of a hydrate formation-dissociation test is given in Figure 5.1 as the plot of pressure and temperature versus time for Test A-1.

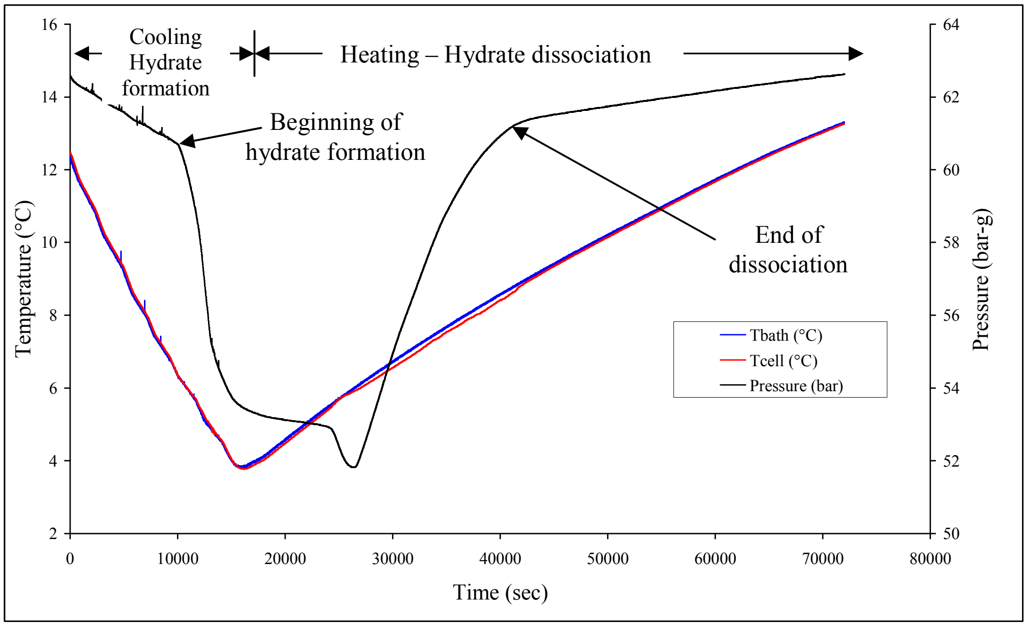

Figure 5.1 Typical temperature and pressure versus time plot (Test A-1)

Analysis of Figure 5.1 indicates the following periods and specific points during the experiment:

- At the initial stage of experiment while the system is cooled down by means of refrigerated chiller there exists a drop in pressure owing to the increase in solubility of gas in water as well as the dependency of pressure and temperature through the real gas law.
- But, there is a certain point in the cooling period that there is a sudden change and increase in the slope of pressure decline curve. This is the point where hydrate formation starts and the loss of free gas into the solid hydrate structure is observed as an additional pressure drop.
- During heating period, pressure starts to increase because of the dissociation of hydrate. A change in the slope of pressure curve indicates the point at which all of the existing hydrate disappeared. This point is taken as *Hydrate equilibrium Point* of the system under investigation and the temperature and pressure corresponding to this point are reported as *Hydrate Equilibrium Temperature and Pressure*.

Closer look to pressure-temperature-time graph during hydrate formation and dissociation clearly show some other aspects of hydrates. Figure 5.2 is the change in cell pressure, bath and cell temperatures during hydrate formation process. With the initiation of hydrate formation (indicated by green vertical line in the figure), cell temperatures start to deviate from bath temperature. Since hydrate formation is an exothermic process (giving heat to the surroundings) the cell temperature becomes higher than bath temperature.

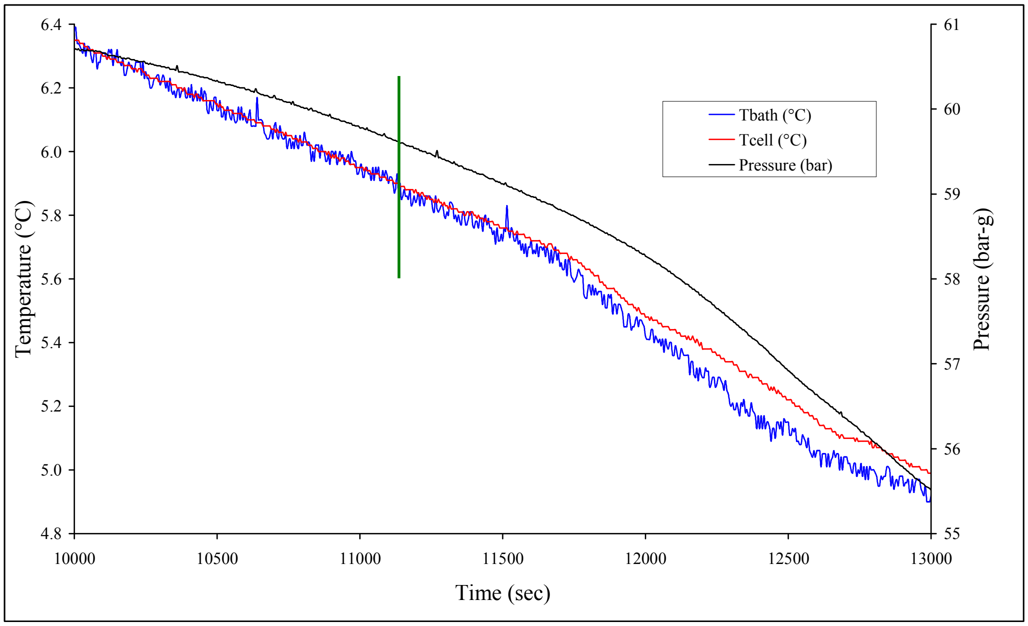

Figure 5.2 Pressure-temperature-time graph during hydrate formation (Test A-1)

Figure 5.3 is again the pressure-temperature-time plot of Test A-1, but this time only for dissociation period. It is also known that hydrate dissociation is an endothermic process (taking heat from surrounding) cell temperature should be lower than bath temperature. This is the case after the time of 26000 sec. One important observation from Figure 5.3 is that there is a second hydrate formation period which takes place during heating. It occurs just before considerable hydrate dissociation begins which is determined with the deviation of cell temperature from bath temperature and becomes lower than it.

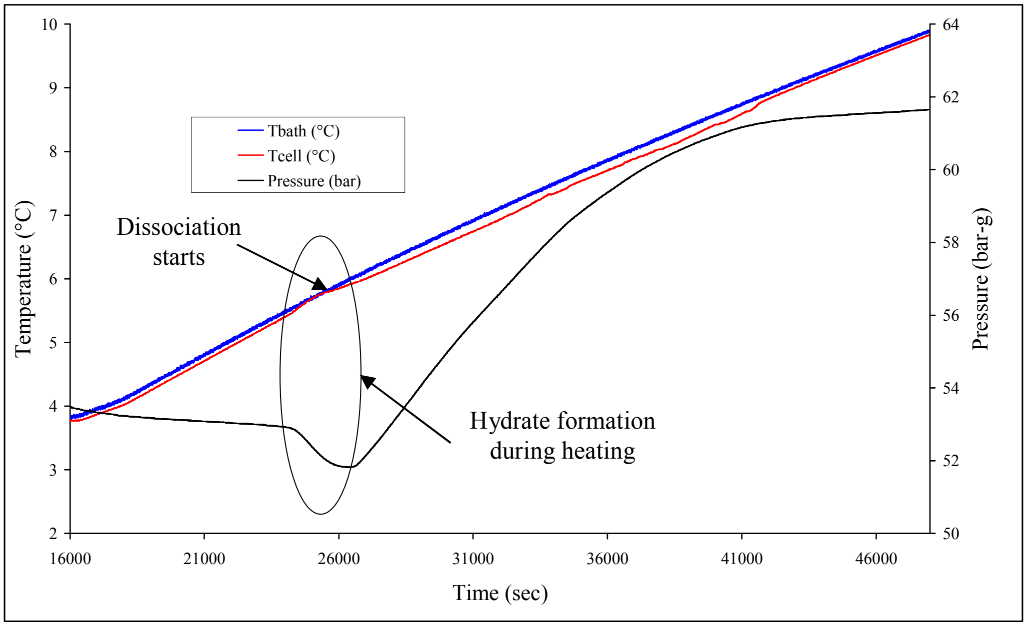

Figure 5.3 Pressure-temperature-time graph during hydrate dissociation (Test A-1)

Another way of representing hydrate formation-dissociation data is the plot of pressure versus temperature. Figure 5.4 shows this type of plot for Test A-1. This graph is also known as hydrate hysteresis curve since the path during hydrate formation is not followed during hydrate dissociation. Although the hydrate equilibrium point is reached during cooling, the formation of hydrate does not start at this point. The difference between the hydrate equilibrium temperature and the temperature at which hydrate formation starts is known *degree of sub-cooling*.

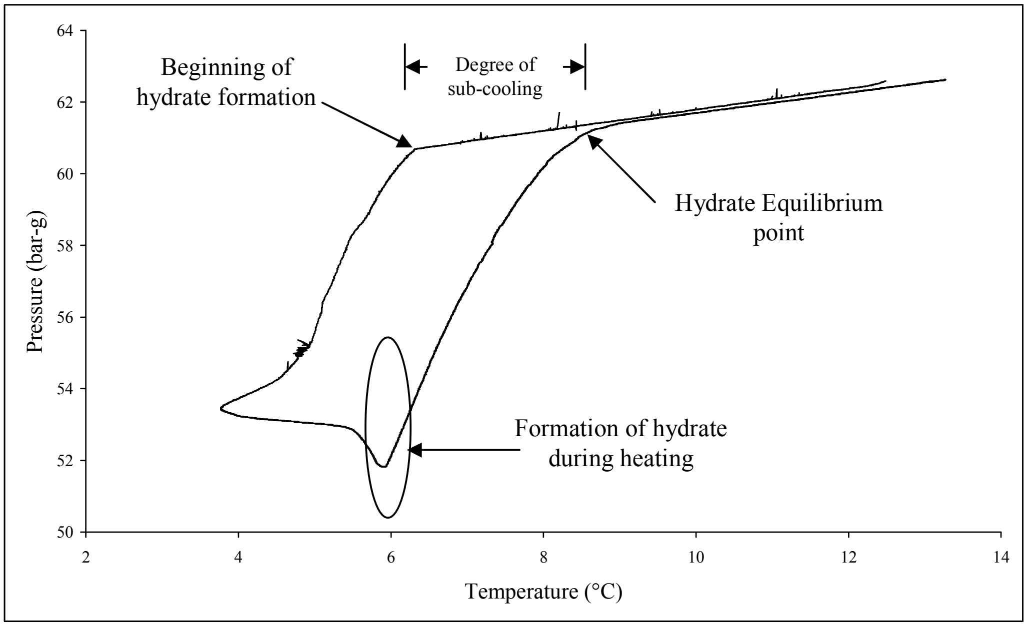

Figure 5.4 Hydrate hysteresis curve (Test A-1)

The last type of figure that will be used to interpret the experimental results is the number of moles of free gas in the cell versus temperature. The data for this graph is derived from the raw data with the use of real gas law:

$$P\,V = z\,n\,R\,T \qquad (5.1)$$

Where;

P = pressure in the cell (psig),

V = volume of free gas in the cell (cuft).

z = compressibility factor of gas, which is the function of pressure, temperature and gas composition,

n = number of moles of free gas in the cell (lb-mole)

R = universal gas constant, (=10.73 cuft psi/lb-mole °R)

T = cell temperature (°R).

Two variables of Equation 5.1, P and T are the recorded data. Although there exists an expansion from liquid water to solid hydrate during hydrate formation (in other words, decrease in free gas volume), the gas volume is assumed to be constant at 83 cm^3, since the amount of hydrate formed is relatively small. The maximum error introduced with this assumption is only 1.5% (Karaaslan, 2001). Gas compressibility factor for methane (z) is calculated by using Lee and Kesler's (1975) compressibility factor expression. Figure 5.5 is the number of moles of free gas versus time plot for Test A-1.

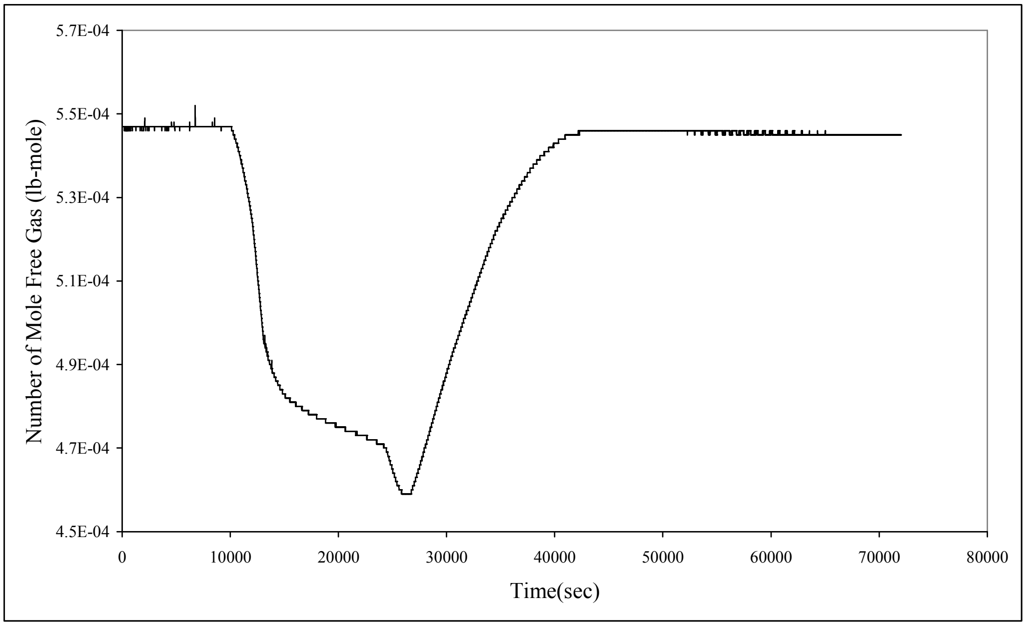

Figure 5.5 Change of number of moles of free gas with time (Test A-1)

Figures 5.1, 5.4 and 5.5 are used to determine the following parameters for hydrate formation-dissociation:

- Hydrate equilibrium conditions,
- Change in hydrate formation temperature as function of chemical concentration,
- Hydrate formation rate.

The first two items will be analyzed under the heading of Thermodynamic Analysis (Section 5.1) while hydrate formation rate will be discussed in the section of Kinetic Analysis (Section 5.2).

5.1 Thermodynamic Analysis

Hydrate hysteresis curves (pressure-temperature diagrams) for Group A and Group B experiments are given in Figures 5.6 and 5.7. The effect of chemicals on hydrate formation and hydrate equilibrium points are deduced from these figures.

Analysis of Figure 5.6 gives the effect of polyglycol on beginning of hydrate formation as well as on hydrate equilibrium point. It is clear from hydrate hysteresis curves that increase in polyglycol concentration affects the beginning of hydrate formation, but not the hydrate equilibrium point. On the other hand, beginning of hydrate formation is not generally reported in the literature, since it depends on some other factors, such as history of water that is forming hydrate, rocking of the cell (mass transfer). Therefore, beginning of hydrate formation will be discussed qualitatively but hydrate equilibrium points will be reported quantitatively (Table 5.1).

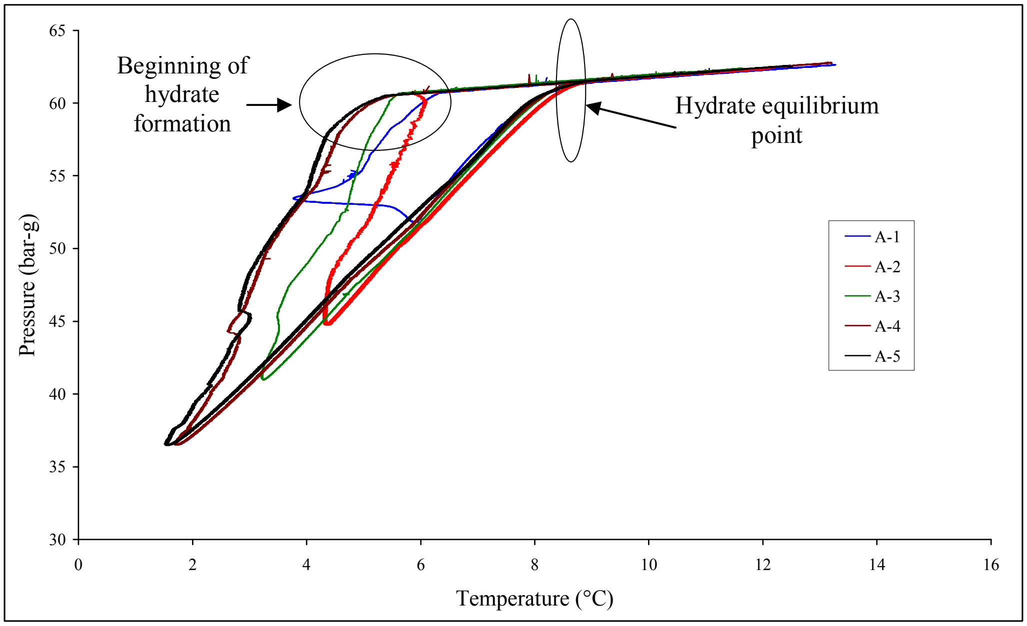

Figure 5.6 Hydrate hysteresis curves for Group A experiments

Figure 5.7 gives the effect of joint effect of polyglycol and KCl on hydrate formation. Although the KCl concentration is the same for all Group B experiments (8 % by weight), the existence of KCl promotes the effect of polyglycol on both beginning of hydrate formation and hydrate equilibrium point. The hydrate equilibrium points of all experiments are listed in Table 5.1. The difference between the hydrate equilibrium points of the experiments with chemicals from the hydrate equilibrium point with pure water is reported as *hydrate formation depression*.

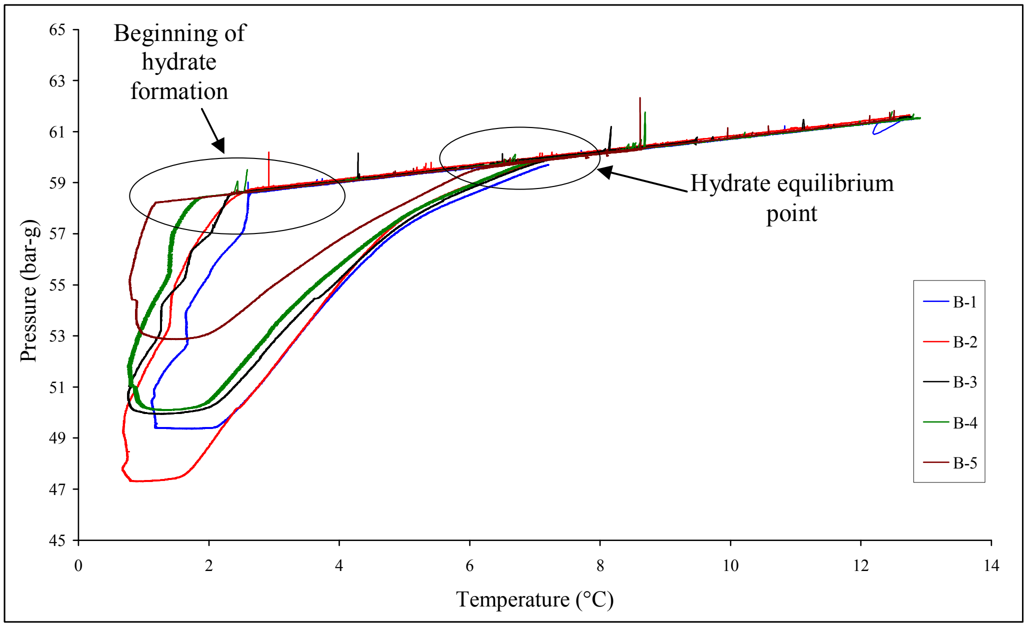

Figure 5.7 Hydrate hysteresis curves for Group B experiment

According to the results of hydrate formation depression results from Table 5.1:

- Although there is a slight decrease in hydrate equilibrium temperature with the existence of polyglycol in aqueous solution compared to pure water experiment (Test A-1), this decrease in not significant. It can be concluded that polyglycol can not be considered as thermodynamic inhibitor for methane hydrate formation.

- On the other hand, the hydrate formation depressions obtained from Group B experiments are higher compared to Group A experiments owing to the existence of 8% by weight of KCl. Experiment B-1 with no polyglycol in solution but only KCl resulted with a hydrate formation depression of 1.54 °C compared to experiment A-1 (pure water). Hydrate formation depression slightly increases with concentration of polyglycol in solution (Figure 5.8).

Table 5.1 the dissociation and depression hydrate temperatures

	Hydrate Equilibrium Temperature (°C)	**Hydrate Formation Depression (°C)**
Group A		
A-1	8.96	0
A-2	8.82	0.14
A-3	8.73	0.23
A-4	8.78	0.18
A-5	8.94	0.02
Group B		
B-1	7.42	1.54
B-2	7.55	1.41
B-3	7.15	1.81
B-4	6.91	2.05
B-5	6.33	2.63

Table 5.2 compares the hydrate formation hydrate equilibrium temperatures of two groups' experiments having the same concentration of polyglycol concentration. The difference of the hydrate equilibrium temperatures show that KCl can be treated as a thermodynamic methane hydrate inhibitor and its effectiveness slightly increase with the increase in polyglycol concentration (Figure 5.9).

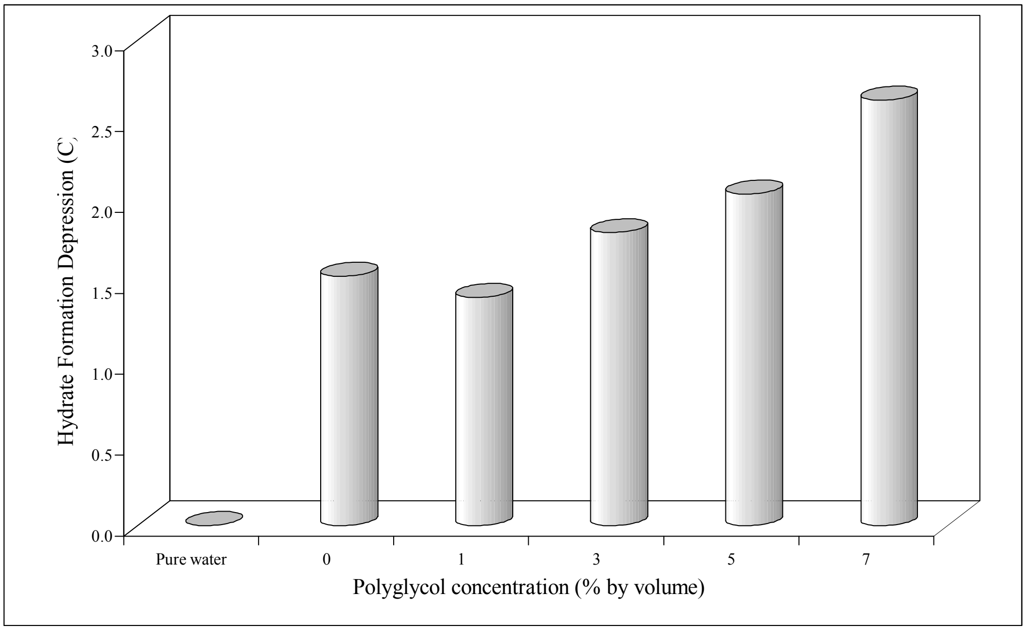

Figure 5.8 Hydrate formation depressions for Group B

Table 5.2 Differences between two groups of experiments

Polyglycol Concentration (% by volume)	**Hydrate Equilibrium Temperature (°C)**		**Difference (°C)**
	GROUP A	**GROUP B**	
0	8.96	7.42	1.54
1	8.82	7.55	1.27
3	8.73	7.15	1.58
5	8.78	6.91	1.87
7	8.94	6.33	2.61

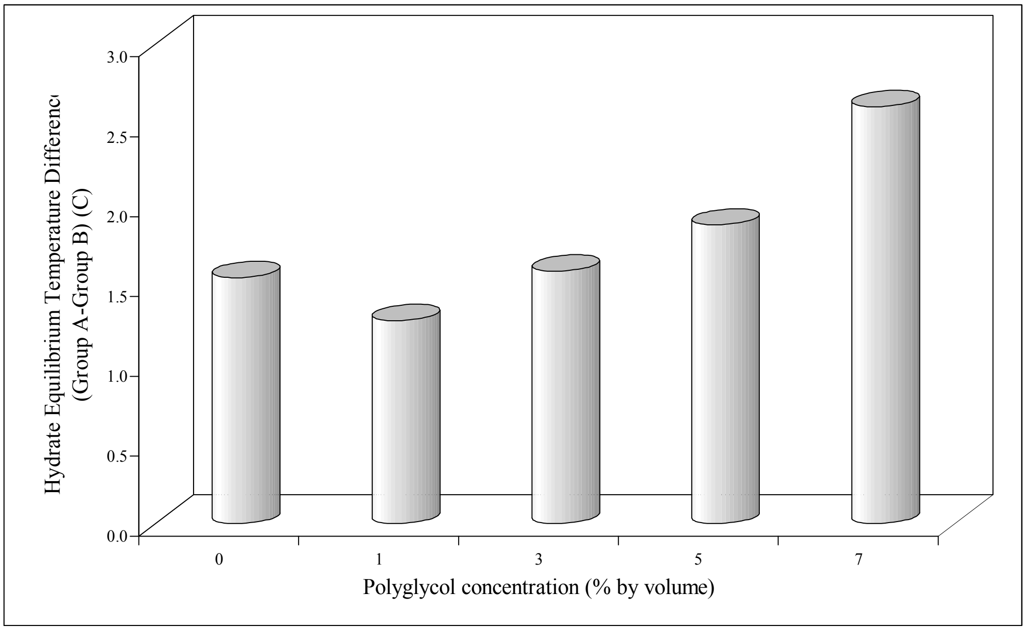

Figure 5.9 Hydrate equilibrium temperature differences of two group experiments

5.2 Kinetic Analysis

Kinetic analyses were made using the plots of number of moles of free gas versus time in the first 15 minutes after beginning of hydrate formation. Figure 5.10 is an example derived from experiment A-1.

After plotting the number of moles of free gas versus time in the first 15 minutes of hydrate formation (Figure 5.11), the linear behavior of the change of free gas moles with time gives the rate of change of number of free gas moles during hydrate formation, in other words, it can be taken as hydrate formation rate. Methane hydrate formation rates of two different experiment groups are listed in Table 5.3 and plotted in Figures 5.12 and 5.13.

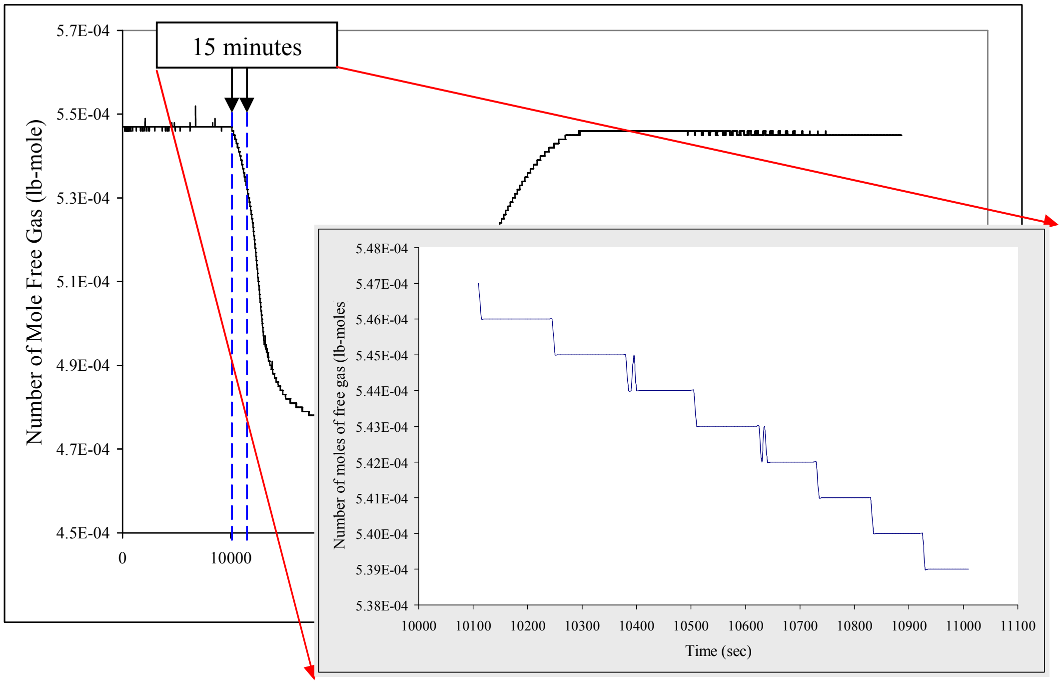

Figure 5.10 Procedure for estimation of hydrate formation rate

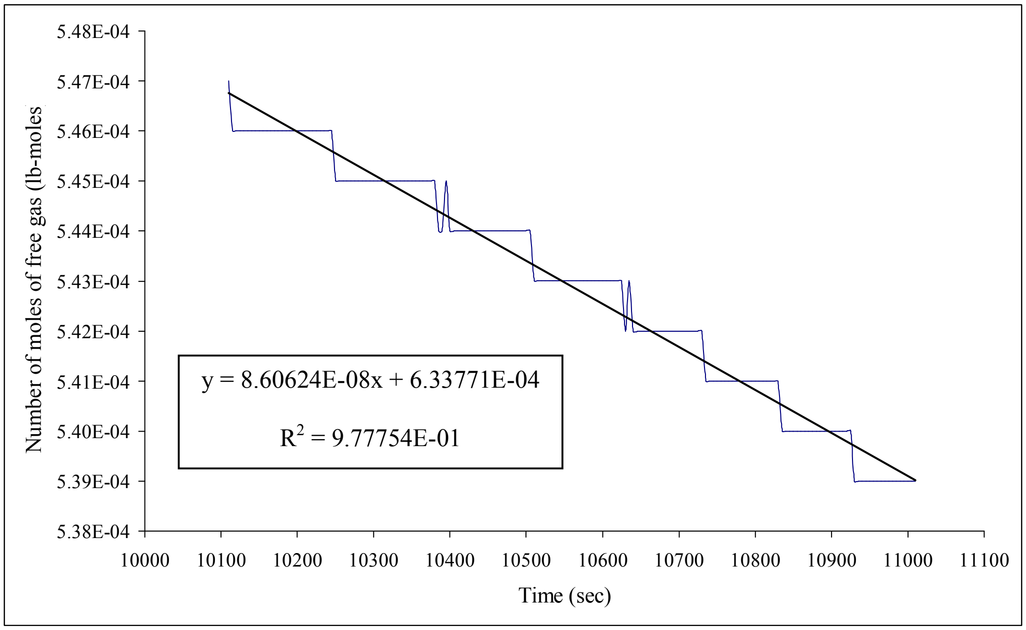

Figure 5.11 Methane hydrate formation rate for Test A-1

Table 5.3 Rates of hydrate formation for the first 15 minutes

Experiment	**Rate (lb-moles/s)**
A-1	8.61E-08
A-2	3.88E-08
A-3	3.08E-08
A-4	1.65E-08
A-5	1.35E-08
B-1	1.34E-08
B-2	1.11E-08
B-3	6.12E-09
B-4	6.63E-09
B-5	9.52E-09

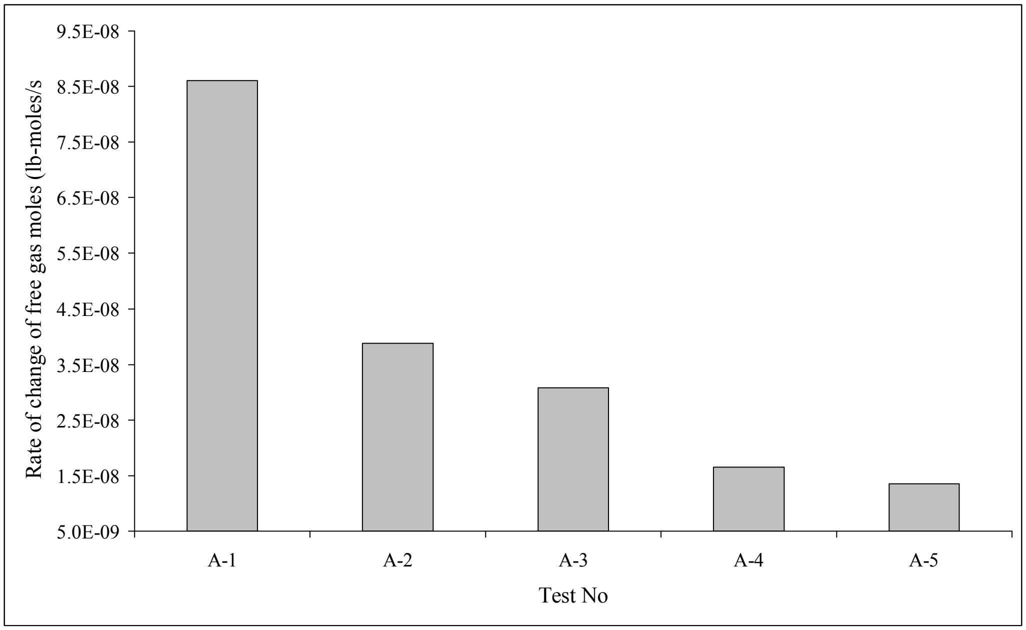

Figure 5.12 Methane hydrate formation rates for Group-A experiments

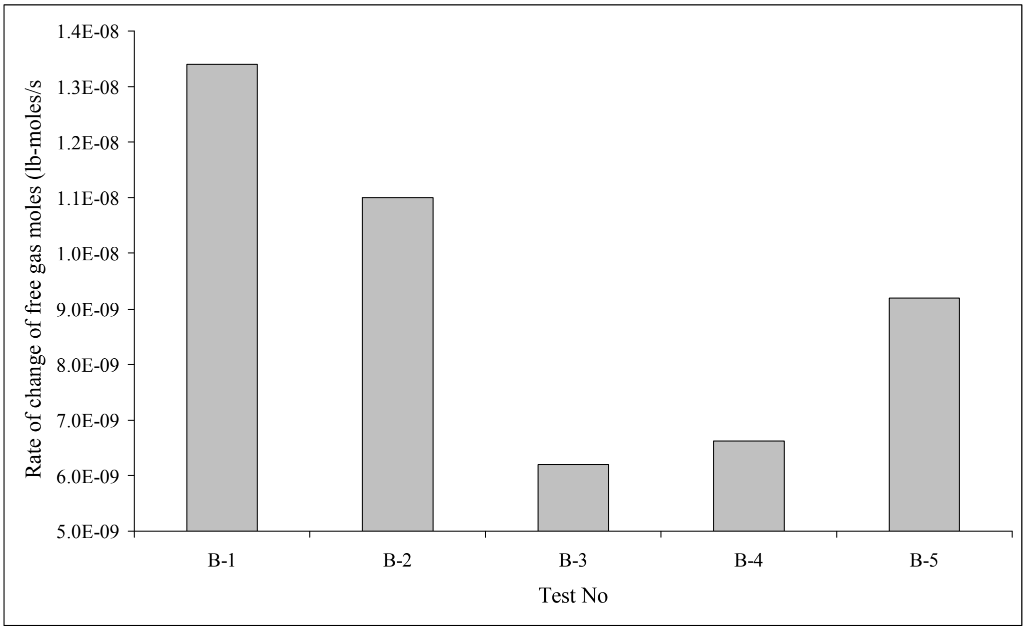

Figure 5.13 Methane hydrate formation rates for Group-B experiments

Analysis of Figure 5.12 and 5.13 show that:

- The rate of methane hydrate formation decreases with the concentration of polyglycol (Figure 5.12, Group-A experiments) concentration suggesting that polyglycol has a potential of being a kinetic hydrate inhibitor, although it does not affect the thermodynamically the hydrate formation.
- Use of polyglycol and KCl together (Figure 5.13, Group B experiments) also has a potential of being kinetic hydrate inhibitor. After having the maximum inhibiting capacity at 3% by volume of polyglycol concentration (Test B-3) it shows an increasing trend but still lower than the rate obtained without polyglycol in solution (Test B-1).

Methane hydrate formation rates of all tests were also estimated not only for the first 15 minutes but during the whole formation period by dividing the whole period into 15 minutes. The results are presented in Tables 5.4 and 5.5.

Table 5.4 Rate of methane hydrate formation for Group-A experiments

Time interval (min)	**Hydrate Formation Rate (lb-moles/s)**				
	A-1	**A-2**	**A-3**	**A-4**	**A-5**
0-15	8.61E-08	3.88E-08	3.08E-08	1.65E-08	1.35E-08
15-30	1.37E-08	3.73E-08	3.59E-08	2.20E-08	1.99E-08
30-45	2.65E-08	3.00E-08	3.18E-08	2.20E-08	2.15E-08
45-60	1.34E-08	2.77E-08	2.88E-08	2.36E-08	2.11E-08
60-75	5.88E-09	1.68E-08	2.35E-08	2.41E-08	2.23E-08
75-90	2.91E-09	1.18E-08	2.29E-08	2.15E-08	2.12E-08
90-105	1.66E-09	5.88E-09	1.99E-08	1.79E-08	1.89E-08
105-120		5.88E-09	1.21E-08	1.70E-08	1.81E-08
120-135			3.53E-09	2.32E-08	2.02E-08
135-150				2.19E-08	2.12E-08
150-165				1.58E-08	1.72E-08
165-180				9.35E-09	1.28E-08
180-195				9.35E-09	7.90E-09
195-210				4.42E-09	6.20E-09
210-225				2.91E-09	5.09E-09
225-240					3.67E-09
240-255					1.15E-09

Table 5.5 Rate of methane hydrate formation for Group-B experiments

Time interval (min)	**Hydrate Formation Rate (lb-moles/s)**				
	B-1	**B-2**	**B-3**	**B-4**	**B-5**
0-15	1.34E-08	1.11E-08	6.12E-09	6.63E-09	9.52E-09
15-30	9.53E-09	1.51E-08	8.03E-09	7.77E-09	1.03E-08
30-45	1.03E-08	1.41E-08	9.05E-09	7.25E-09	1.04E-08
45-60	9.86E-09	1.24E-08	9.10E-09	7.11E-09	9.31E-09
60-75	8.95E-09	1.11E-08	9.17E-09	7.07E-09	4.71E-09
75-90	7.63E-09	1.06E-08	9.26E-09	6.82E-09	3.47E-09
90-105	6.42E-09	1.01E-08	8.46E-09	6.22E-09	2.89E-09
105-120	6.11E-09	9.13E-09	8.06E-09	4.71E-09	2.12E-09
120-135	5.87E-09	7.95E-09	7.86E-09	1.92E-09	
135-150	5.39E-09	6.44E-09	6.40E-09		
150-165	5.12E-09	5.24E-09	2.78E-09		
165-180	4.72E-09	4.16E-09			
180-195	3.64E-09	1.92E-09			

The data given in Table 5.4 and 5.5 were plotted as function of time and the slope of best fit of each line are presented in Table 5.6. Those are the change of the rate of hydrate formation with time as function of polyglycol concentration. The results are also given in Figures 5.14 and 5.15.

Analysis of Figure 5.14 and 5.15 indicate that:

- Change of rate of methane hydrate formation for Group-A experiments (Figure 5.14) decreases with polyglycol concentration. This shows that methane hydrate formation can continue at a rate closer to the initial rate as polyglycol concentration increases. Although the rate of methane hydrate formation decreases with polyglycol concentration (Figure 5.12), the elongated time interval with initial hydrate formation rate may result with a severe hydrate formation condition at higher polyglycol concentration.
- The observation made for Group-A experiments is also valid for Tests B-3 and B-4 (Figure 5.15).

Table 5.6 Change of methane hydrate formation rate

Polyglycol Concentration (% by volume)	**Change of Hydrate Formation Rate (lb-moles/s/s)**	
	Group A	**Group B**
0	7.03E-10	4.55E-11
1	3.59E-10	5.76E-11
3	2.34E-10	1.79E-11
5	8.09E-11	3.37E-11
7	7.64E-11	9.04E-11

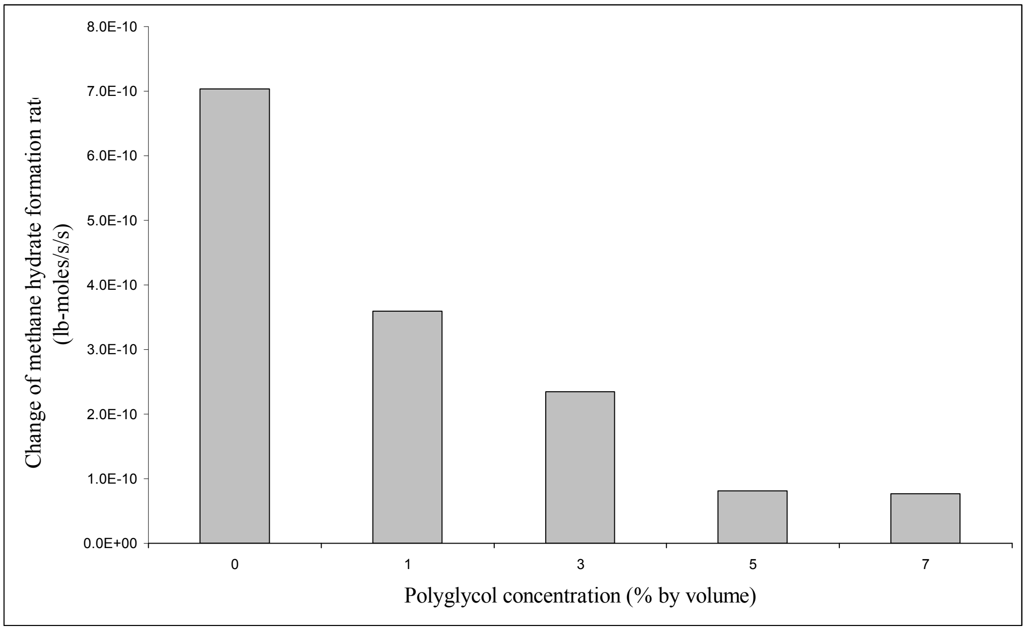

Figure 5.14 Change of hydrate formation rate for Group-A experiments

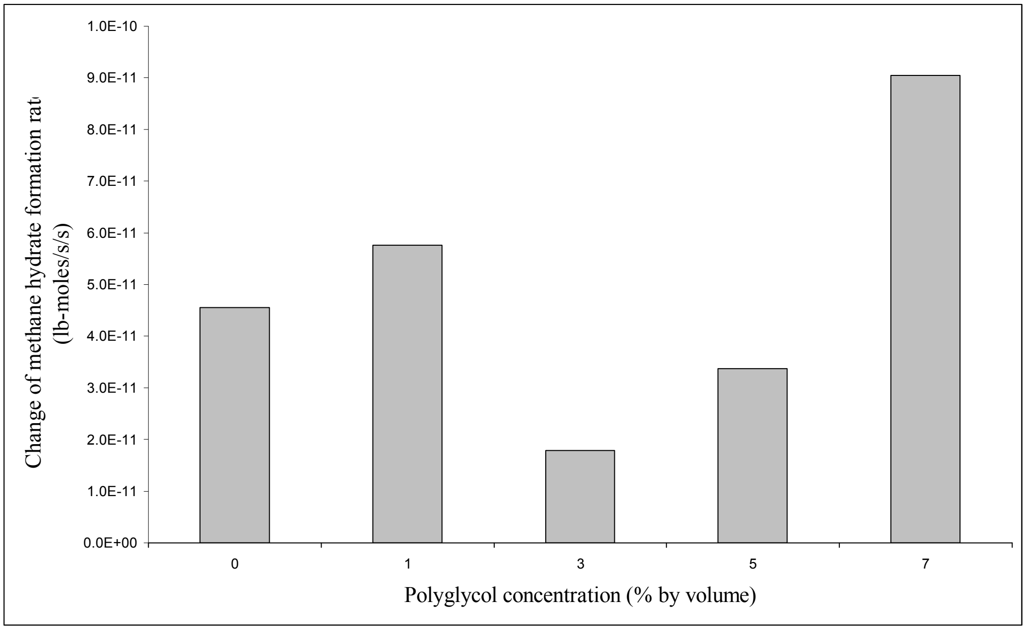

Figure 5.15 Change of hydrate formation rate for Group-B experiments

CHAPTER 6

CONCLUSIONS

The following conclusions can be drawn from the experimental results of this study:

- Among the two chemicals tested for their hydrate inhibiting potentials, polyglycol do not exhibit any thermodynamic inhibition capacity while KCl has an ability of hydrate inhibition thermodynamically.
- Increase in polyglycol concentration in the constant concentration KCl (8% by weight) aqueous solutions increase the hydrate formation depression capacity of KCl.
- Polyglycol inhibits methane hydrate formation kinetically. The higher the polyglycol concentration in aqueous solution the lower the initial rate of methane hydrate formation (corresponding to first 15 minutes of hydrate formation).
- On the other hand, there exists a slower change of methane hydrate formation rate as polyglycol concentration increases.

CHAPTER 7

RECOMMENDATIONS

Under the light of the results of current study, the followings are recommended for further studies:

- Performance of polyglycol with varying KCl concentration can be studied.
- To see the effect of other components of drilling fluids (bentonite, barite, other salts, different additives etc.), new experiments should be carried out.
- Methyl-ethyl glycol, a known hydrate inhibitor, can be tested to compare the effectiveness of polyglycol as hydrate inhibitor.

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APPENDIX A

EXPERIMENTAL DATA FOR HYDRATE FORMATION/DISSOCIATION TESTS

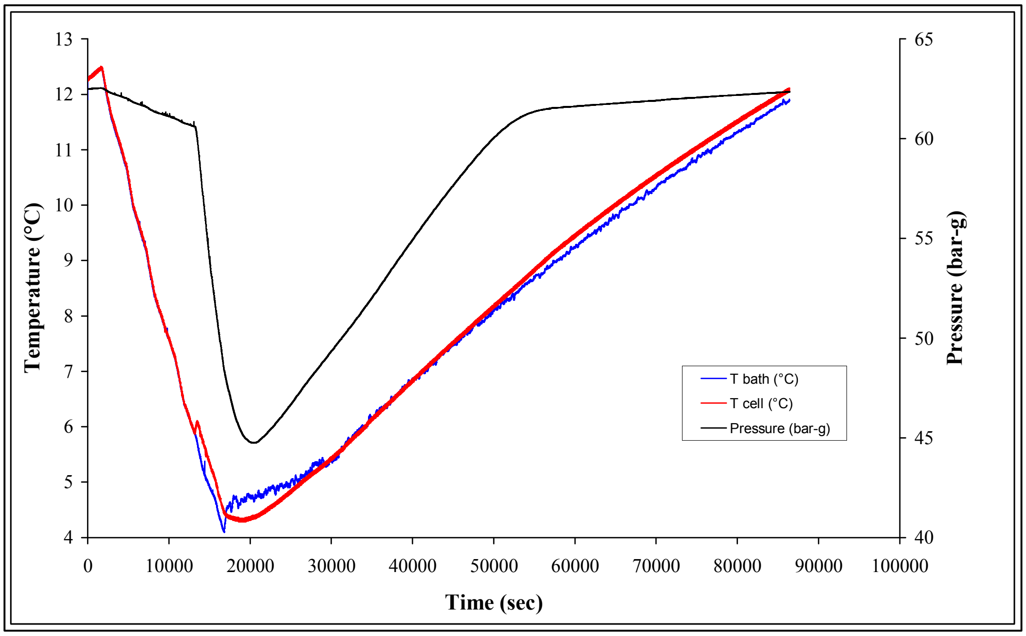


Figure A.1 Temperature and pressure versus time plot for Test A-2

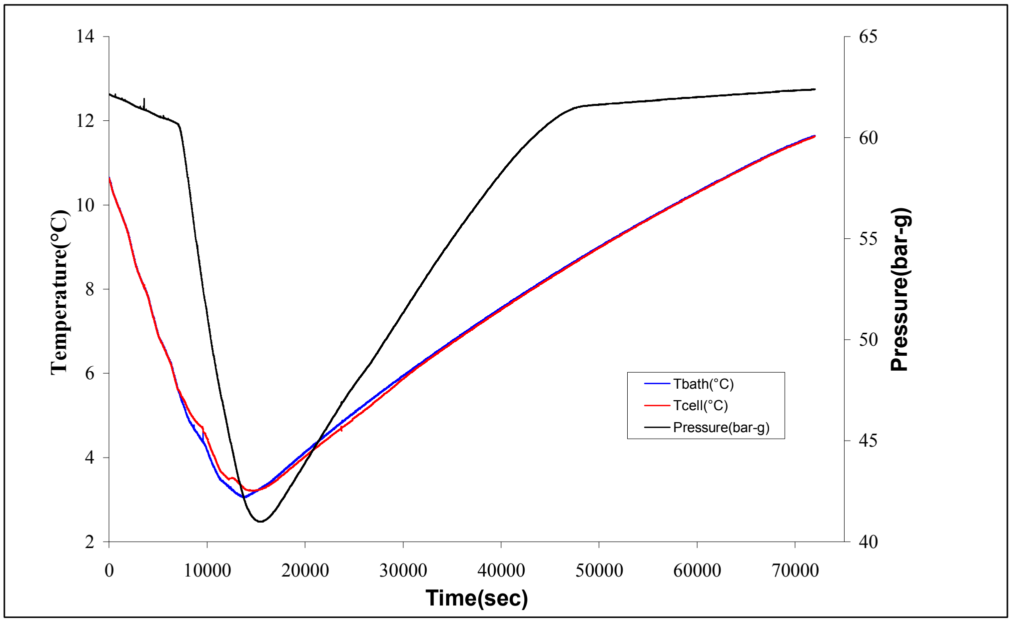


Figure A-2 Temperature and pressure versus time plot Test A-3

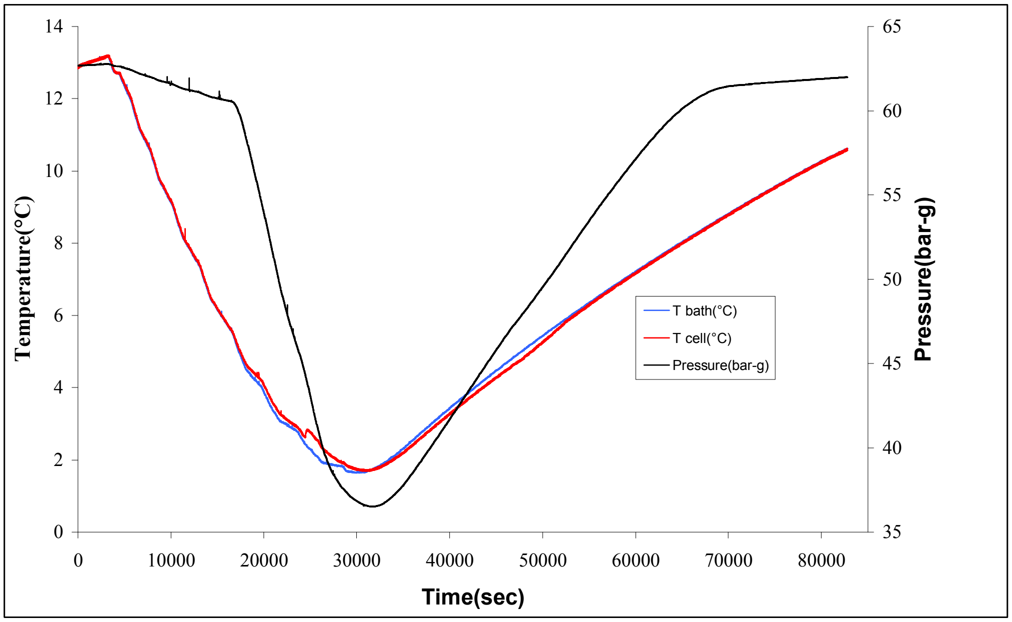


Figure A-3 Temperature and pressure versus time plot Test A-4

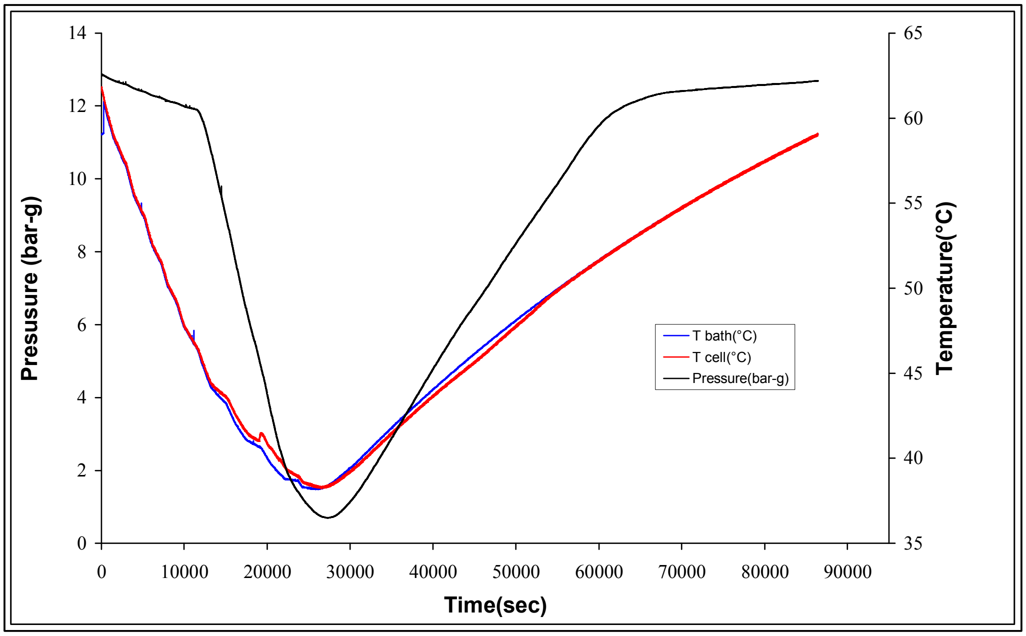


Figure A-4 Temperature and pressure versus time plot Test A-5,

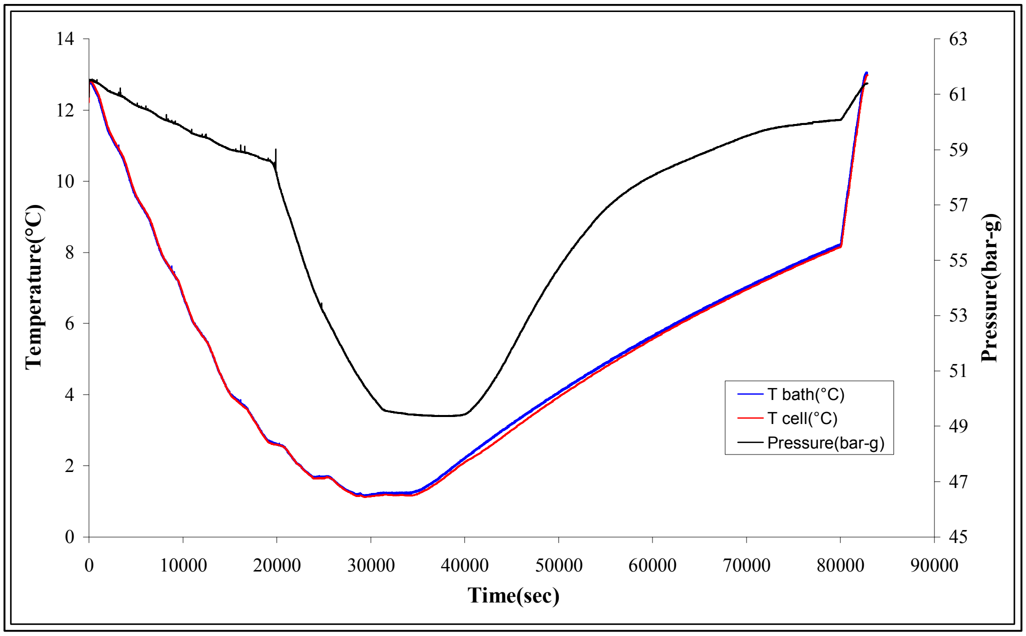


Figure A-5 Temperature and pressure versus time plot Test B-1

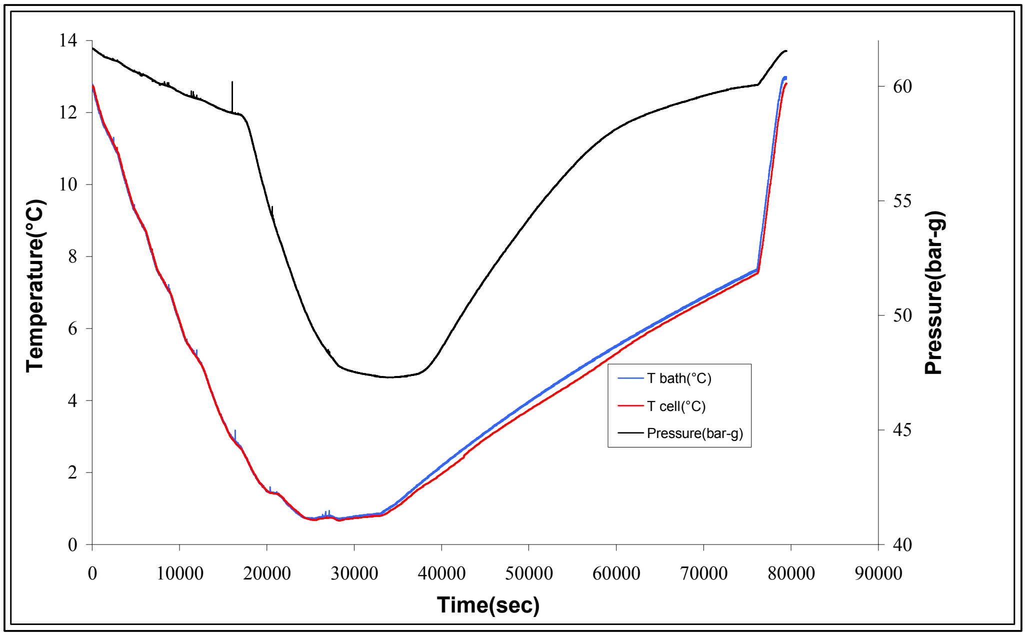


Figure A-6 Temperature and pressure versus time plot Test B-2

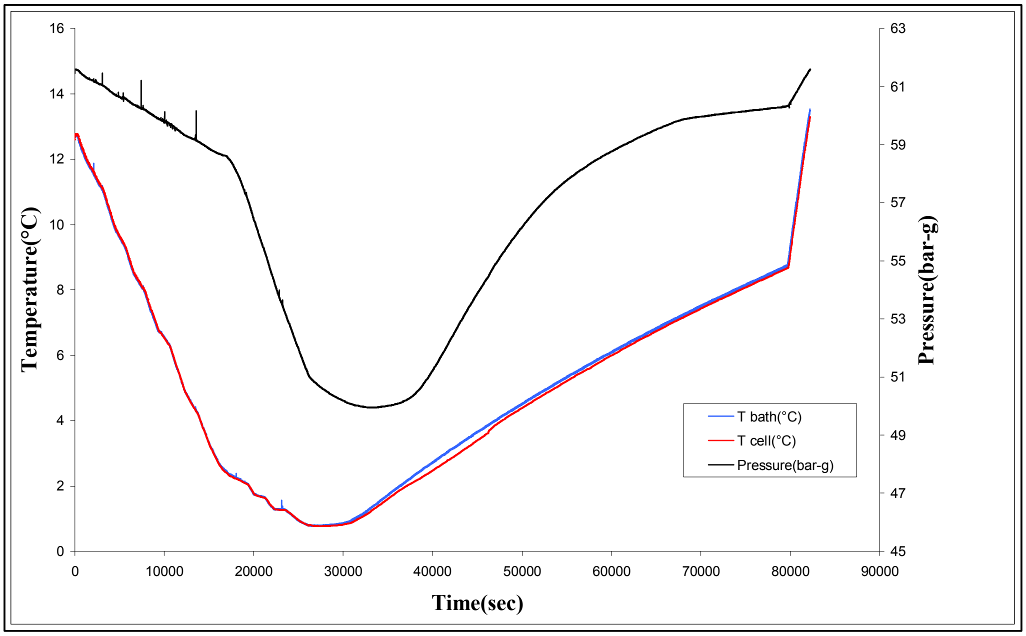


Figure A-7 Temperature and pressure versus time plot Test B-3

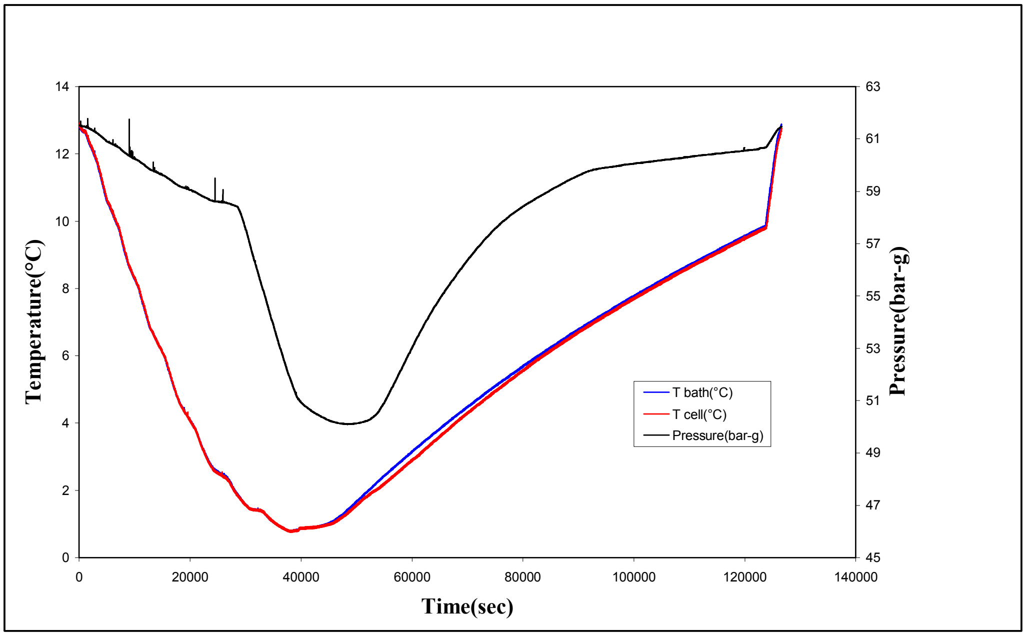


Figure A-8 Temperature and pressure versus time plot Test B-4

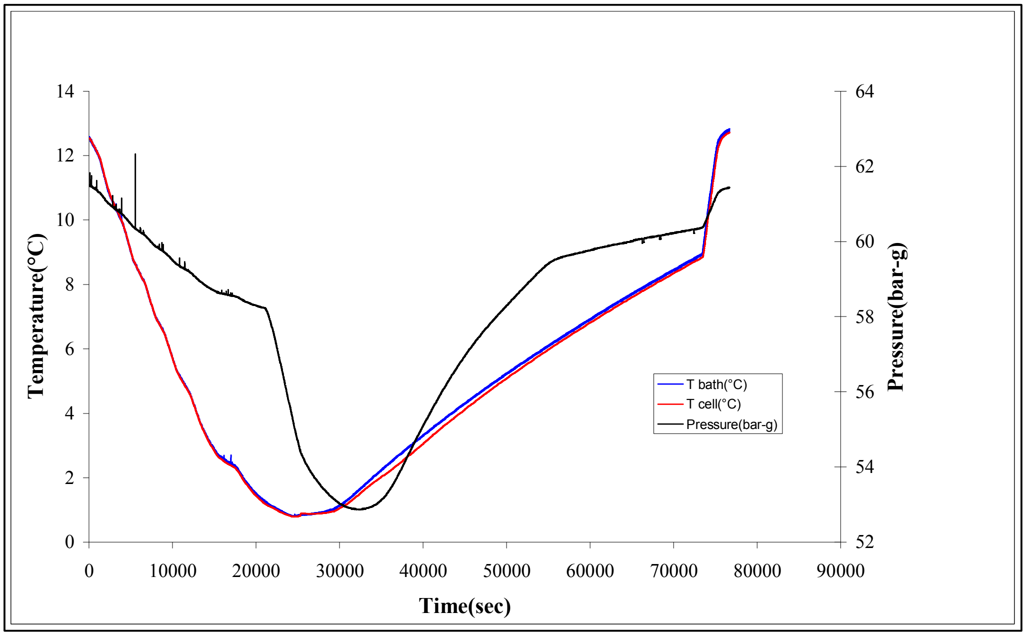


Figure A-9 Temperature and pressure versus time plot Test B-5

APPENDIX B

INITIAL HYDRATE FORMATION RATES

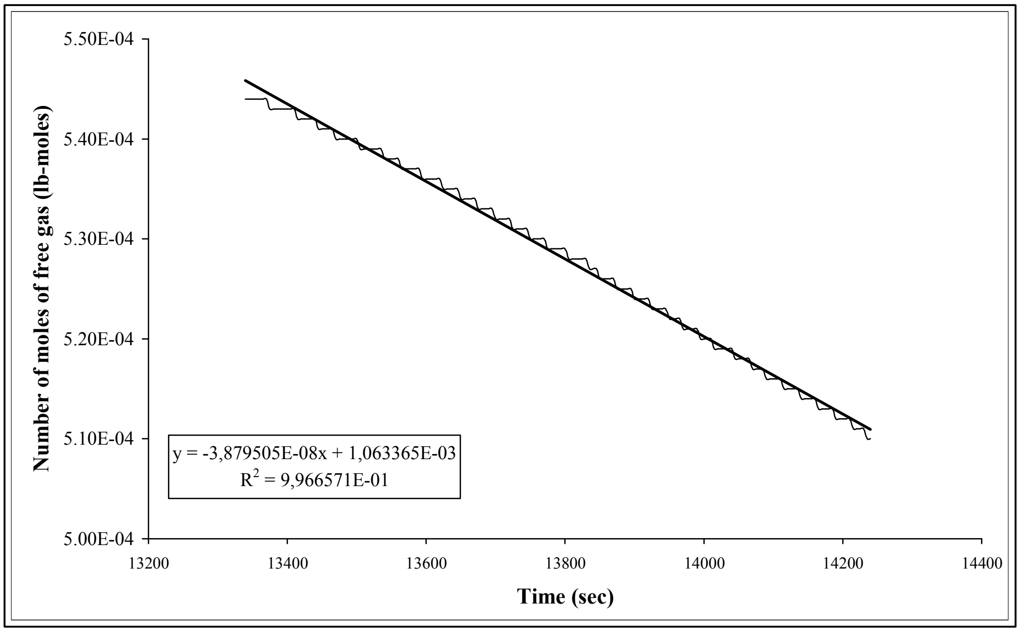


Figure B.1 Methane hydrate formation rate for Test A-2

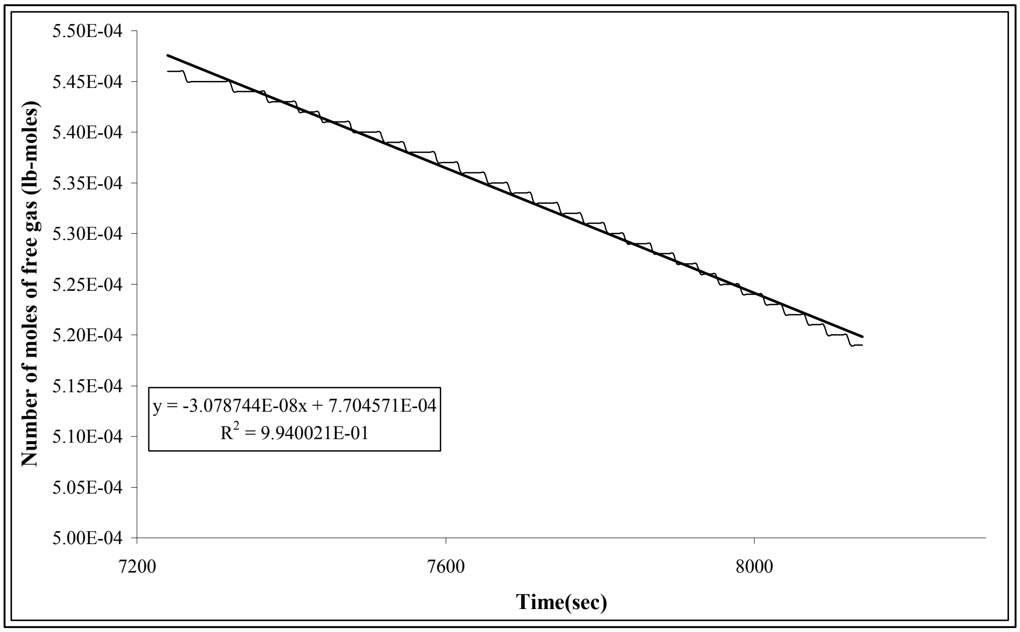


Figure B.2 Methane hydrate formation rate for Test A-3

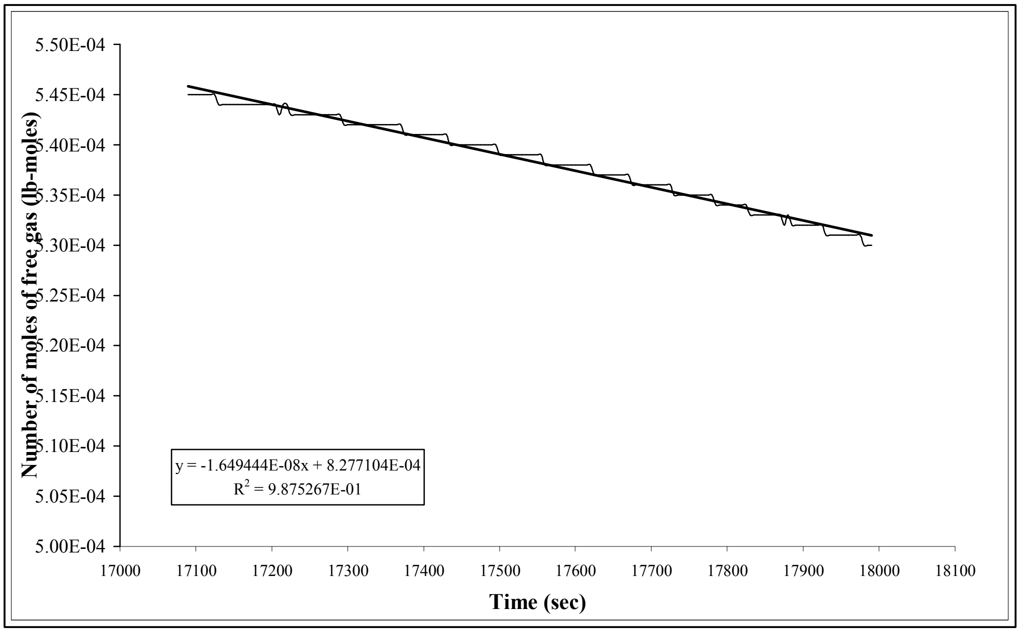


Figure B-3 Methane hydrate formation rate for Test A-4

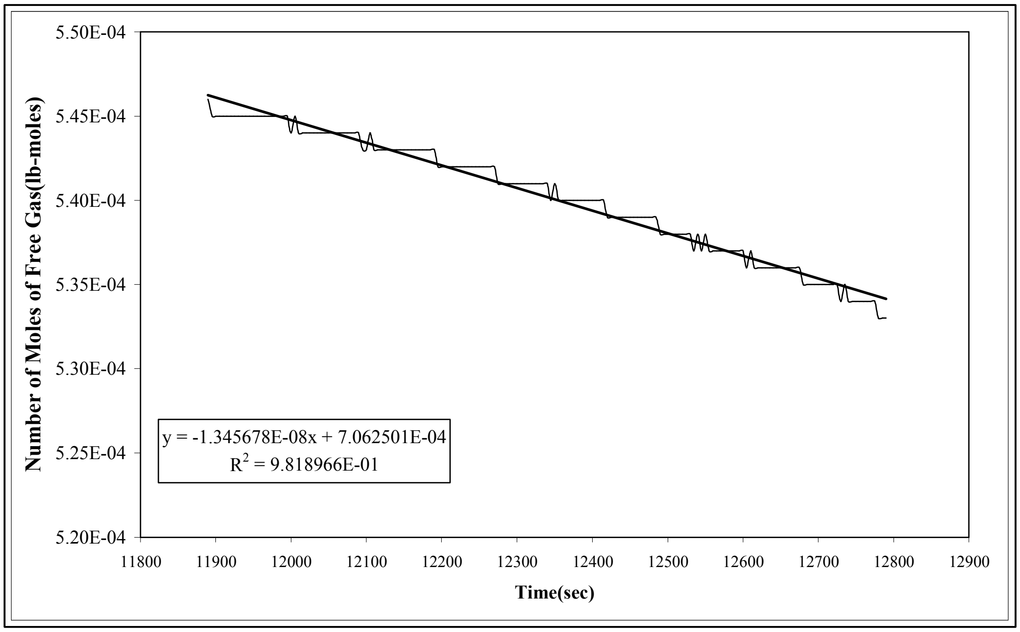


Figure B-4 Methane hydrate formation rate for Test A-5

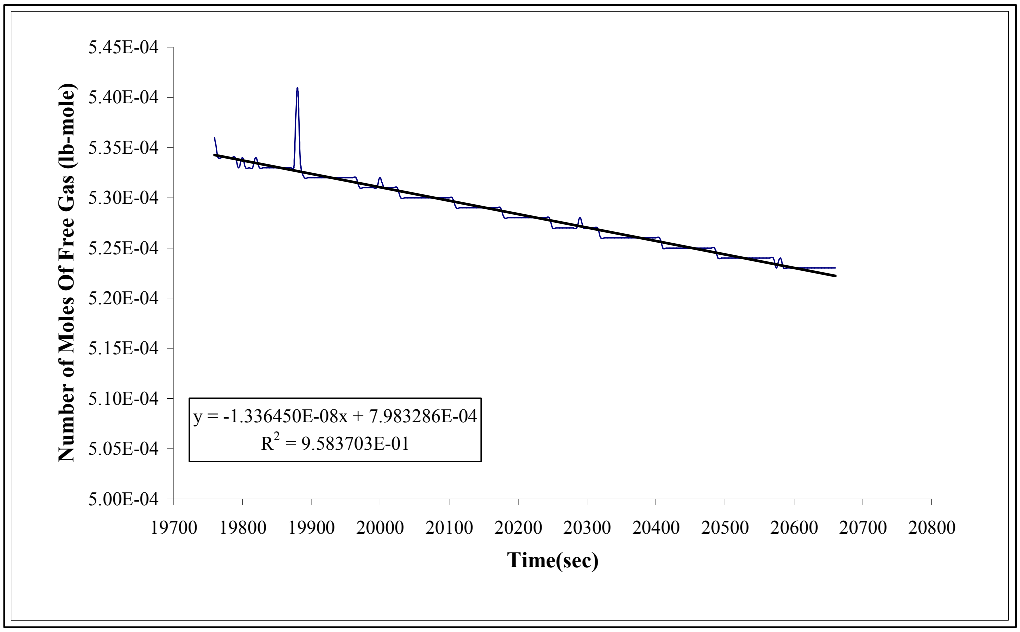


Figure B-5 Methane hydrate formation rate for Test B-1

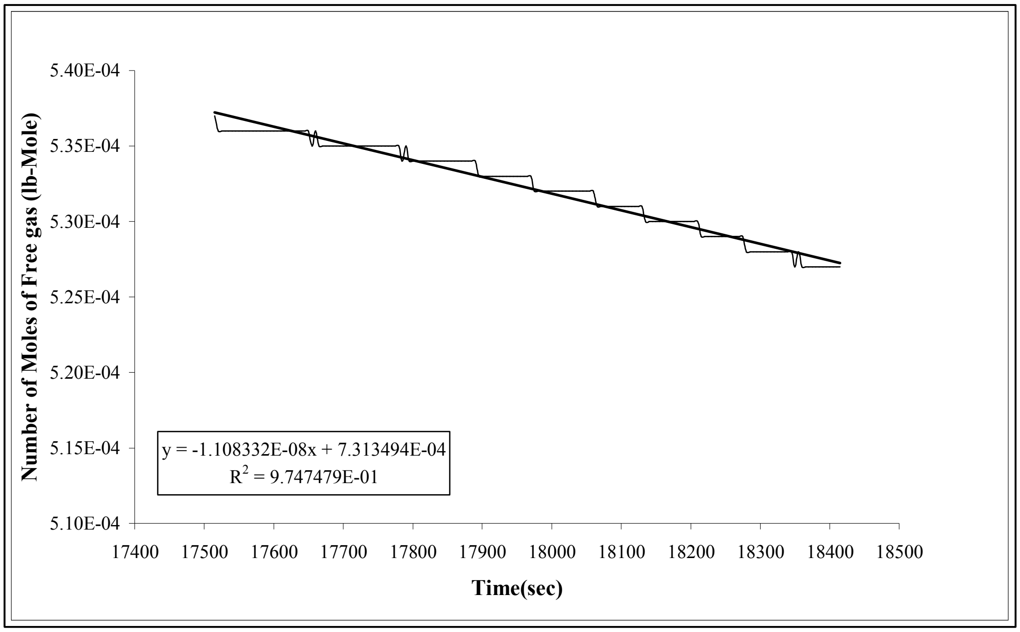


Figure B-6 Methane hydrate formation rate for Test B-2

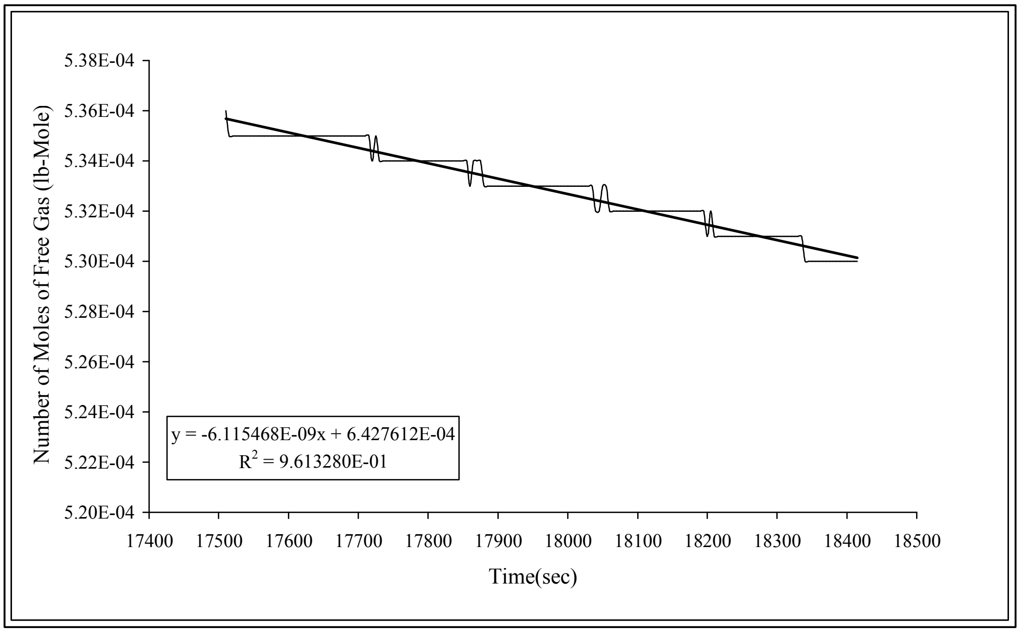


Figure B-7 Methane hydrate formation rate for Test B-3

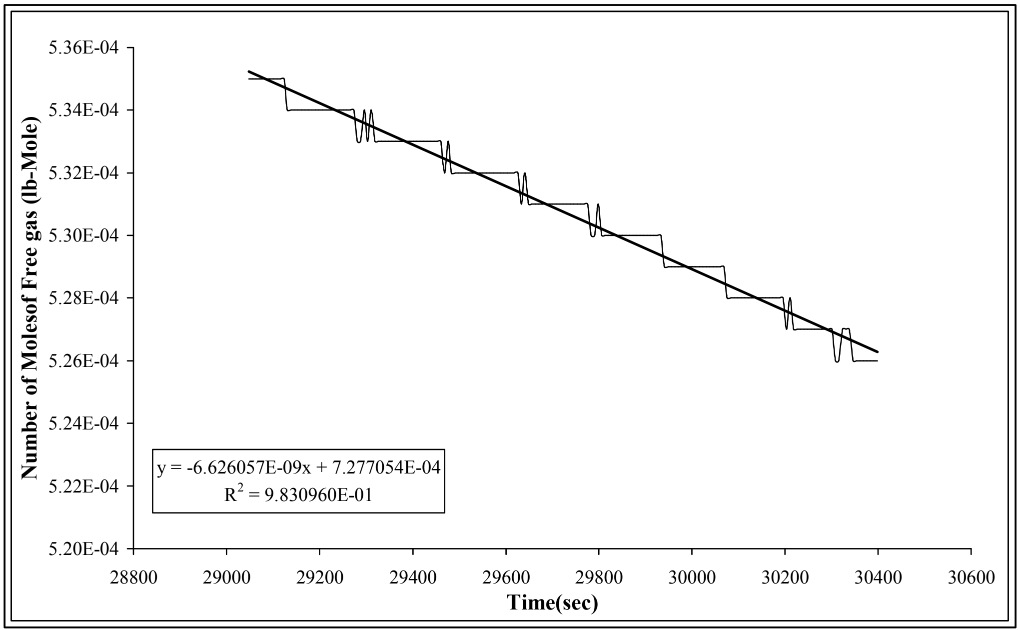
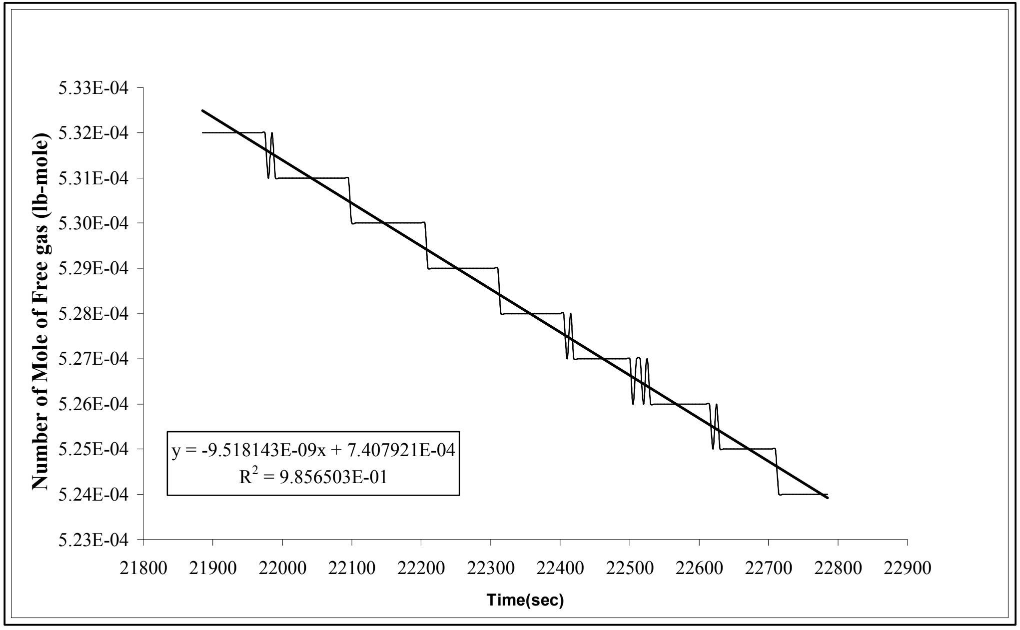


Figure B-8 Methane hydrate formation rate for Test B-4



Methane hydrate formation rate for Test (B-5)