**CHAPTER ONE**

**1.0 INTRODUCTION**

Formation of natural gas hydrates is a major concern and poses a serious threat to economics of the operations as well as personnel safety for the offshore production of oil and gas. Gas Hydrates are crystalline compounds, ice like solids that form when gas molecules are trapped in hydrogen bonded water cages under high pressure and low temperature conditions. Figure 1 below present a hydrate formation diagram in the pressure – temperature phase. The white region covers pressures and temperatures at which hydrates are thermodynamically unstable and is therefore hydrate free as indicated. The region labelled “hydrate risk” is where stable hydrates can exist, although in practice they may not form due to a failure to nucleate or slow formation kinetics. In the “hydrate zone“, the degree of sub cooling is sufficient such that hydrates form spontaneously (klomp et al 1993)23.



**Figure 1:** Typical hydrate formation diagram26

**1.1 IMPORTANCE OF HYDRATES PREVENTION IN OIL AND GAS OPERATIONS**

Gas hydrates generates considerable operational, safety and flow assurance concerns with hydrates deposit in subsea pipelines and process equipment which agglomerate to block tubing, flow lines and facilities, other than blockage the other problem that hydrate poses is the movement of hydrate plugs in the pipeline at high velocity which can cause rupture in the pipeline. With the petroleum industry endeavouring to develop promising oil and gas prospects in deeper water, the interest in gas hydrates control has increased in the Gulf of Mexico, Brazil, the North Sea, Persian Gulf, West Africa and other parts of the world.

Hydrate blockages in the gas and gas-condensate transportation lines can be a consequence of the failure of the chemical injection system, unscheduled shutdowns at the host platforms, or inadequate inhibitor treatment during well start up.

1. The hydrates can form in the wellbore, while the fluids go through pressures and temperature induced phase changes near the mud line.
2. Unprocessed fluids produced from subsea completed wells may be transported through subsea pipelines over a long distance to a main platform. Such flow lines are susceptible to hydrate formation and possibly plugging.
3. They also form during planned and unplanned shut-ins during hurricanes, the area subjected to hydrate formation during extended shut downs and cold restarts for a dry tree well is inside the production tubing above the mud line (Riser), because the riser is not usually insulted, thus it quickly enters hydrate conditions once the well is shut-in.
4. Failure of the chemical injection system or inadequate inhibitor treatment during early start up.

The formation of hydrate blockages have been experienced in the Gulf of Mexico.



**Figure 2:** Some new horizons for upstream gas operations

**1.2 DEEP WATER OIL AND GAS OPERATION USING GULF OF MEXICO AS A CASE STUDY**

Deep water oil and gas exploration in the Gulf of Mexico has been a great success since the oil industry took the first step in the middle of 1990s. By the end of 2004, production from the deep water fields in the Gulf of Mexico grew to an estimated 3.9 billion Cubic feet of natural gas per day and 953,000 barrels of oil per day, which accounted for approximately 65% of the Gulf of Mexico oil production in 2004. The exploration and development within the deep water Gulf of Mexico shows no sign of diminishment as evidence by the 118 deep water projects on production as of 2006 (US Department of the interior 2006). It has been forecast that the deep water fields in the Gulf of Mexico would be producing nearly 2.0 million B/D in 2008.

The temperature in deep water is usually near 400F, hydrate inhibition and control is often the design basis for deep water field development. As more multiphase hydrocarbons are produced from deep water fields and transported over long distances, flow assurance becomes a more critical factor in the design stages of any oil and gas production system. The flow assurance covers all issues related to the maintenance of the flow of oil and gas from reservoir to reception facilities.

Extra ordinary care is usually taken in design and operation of deep water systems to ensure that they remain hydrate free during normal steady state operation, short and long term production shut down to prevent hydrate blockage, because the cost of hydrate blockage in deep water pipeline can be extremely high since it takes days or months for plugs to dissociate, the cost of hydrates plug remediation in subsea flow line is very high with significant loss in revenue and also very challenging.

**CHAPTER TWO**

**2.0 LITERATURE REVIEW**

The challenges of hydrate control in deep water operations emerge from harsh environment and the inaccessibility. Deep water wells must produce large volumes of oil and gas to justify their development cost, even a short term interruption in production can cost the operator millions of dollars. In other to keep the operating condition of a well or a hydrocarbon production system free from hydrate and risks, several techniques can be applied to prevent or remove the hydrate and move wellbore fluids out of the region. These techniques are

**2.1 TECHNIQUES FOR HYDRATE PREVENTION OR REMOVAL**

**2.1.1 DEPRESSURIZATION**

It requires reduction of pressure that results in temperature decrease at hydrate interface, resulting in heat exchange when external temperature becomes higher than hydrate equilibrium temperature (evaporation process) however this evaporation process can take a long time due to the high latent heat of evaporation. Bleeding off the tubing pressure needs to be performed in a controlled manner since a hydrate plug can become a projectile during the disassociation process and could cause damage to downstream equipment. This approach is often impractical for normal operations, since the pressure required for transportation of production fluids would usually exceed the hydrate formation pressure at the ambient temperature. This also leads to reduced production rate; however this option incurs cost in the form of deferred production.

**2.1.2 PRESSURIZATION**

This process needs a high pressure source greater than the bottom hole pressure, in an attempt to move the hydrate plug downward. This is rarely effective since an increased pressure tends to solidify the plug in the hydrate forming region.

**2.1.3 MECHANICAL REMOVAL**

These require utilization of coil tubing to drill, circulate heated fluids or run a heated wire line brooch. It is usually successful in reaching, eliminating the plug, and usually applicable when equipment is readily available and cost effective. However use of these tools in the hydrate formation region could cause tools to become stuck, if hydrates reform, one should be aware of the potential for trapped pressure.

**2.1.4 REMOVE SUPPLY OF WATER (DEHYDRATION)**

Prevent the formation of hydrates by removing the supply of water using separation and dehydration. This approach has proved popular for the export of sales gas but is impractical for subsea applications.

**2.1.5 HEAT MANAGEMENT**

This practice is applied when plug location is known and disassociation can be controlled. Applying heat to the outside could melt a plug from the outside. Heat applied to the middle of a hydrate plug could cause over pressurization, a plug could dislodge and become a projectile. However it may not be cost effective for longer flow lines to carry high GOR fluids.

**2.1.6 REMOVE SUPPLY OF HYDRATE FORMERS**

Prevent the formation of hydrates by removing the supply of hydrate forming molecules perhaps by gas-liquid separation. This approach has been proposed for subsea operation where gas and liquids are separated subsea and are transported to the process facilities in separate pipelines. The gas pipelines still requires hydrate inhibitors but the liquid line (containing oil and water) is able to operate satisfactorily without forming hydrates due to the absence of hydrates formers. There is still no practical use of this method.

**2.2 CHEMICAL INJECTION**

**2.2.1 CONVENTIONAL THERMODYNAMIC INHIBITORS**

The most popularly used solution in the industry to prevent operational problems from hydrate formation is continuous injection of conventional thermodynamic inhibitors such as (methanol or mono ethylene glycol). In addition, the naturally occurring inorganic salt which exist in both sea water and formation water also acts as thermodynamic inhibitors that shift the hydrate equilibrium curve to the left, thus when the flow conduit cools down to the ambient temperature during shut down or restart, it stays on the right side of the hydrate curve, However shifting the hydrate curve to the left until the operating conditions during any production scenario is saved from hydrate risks, with the proliferation of deep water operations and a subsequent rise in the use of conventional hydrate inhibitors with proven technology, but due to an increase in water cut and other factors might require an excessive amount of inhibitor that would be injected, which raises the issues of the logistics of transportation and storage systems for large volumes of inhibitor on the hub facility, which has a significant impact on the operating and capital expenses of the field development. In recent years, there is also a significant push back from the downstream side of the business, with refineries limiting the allowable methanol concentrations in exported oil or condensate, which can cause problems in desalting operations and effluent streams water management, similarly the allowable methanol content in the gas streams is constantly being decreased with severe penalties incurred for deviations from gas plant specifications.

 The problem becomes even more acute during events such as a production shut in caused by a hurricane, when several barrels of methanol are bull headed into the tubing of oil wells, upon restart resulting in the need for large umbilical to deliver high inhibitor volumes, specialised pumping facilities, their topside weight, space consideration which causes a significant fraction of the methanol to be carried over into the oil export resulting in downstream problems. Thus this led to concerted effort in the past decade to getting an alternative to conventional inhibitors. The possible solution for this problem is by injecting a Low Dosage Hydrate inhibitor (LDHI) or Hybrid Hydrate Inhibitor (HHI). This should be able to manage hydrate risks with a lower amount of inhibitor as compared to the conventional inhibitor such as methanol or glycol.

**2.2.2 LOW DOSAGE HYDRATE INHIBITOR**

Generally there are 2 types of Low Dosage Hydrate Inhibitor (LDHI) that have been used in the industry. The Kinetic Hydrate Inhibitor (KHI) usually consists of water soluble polymers and acts by delaying hydrate crystal nucleation and initial crystal growth processes (klomp et at 1997), its effectiveness depends on the sub cooling of the system. Clark et al (2005) reported that sub cooling in the range 19.80F and 23.40F can keep KHI very effective for days to weeks. Once this period has elapsed, there is often a rapid conversion of the remaining water into large hydrate accumulations, usually resulting into a blockage.

The other type of Low Dosage Hydrate Inhibitor (LDHI) is Anti agglomerants (AA), which acts as hydrate dispersant that will allow hydrate crystals to disperse into liquid hydrocarbon phase, instead of allowing the formation and accumulation of hydrate crystals into a blockage. The anti agglomerants properties of the LDHI are believed to be caused by a hydrate philic head that is incorporated within the hydrate crystals and a hydrate phobic tail that disperse the hydrates into a liquid hydrocarbon phase (Mehtal et al 2002)7. AA LDHI known till date requires the presence of a liquid hydrocarbon phase to suspend the hydrate crystals in a slurry form and its effectiveness is dependent on the type of oil/condensate, the salinity of the formation water and the water cut. At higher water cut, the dispersed hydrate crystals may increase the viscosity of the liquid hydrocarbon phase that could prevent the slurry from flowing. (Mehtal et al 2002)7, quoted less than 50% water cut as the value where significant increase in viscosity would be expected. (Clark et al 2005)17 quoted water cut limitation between 50 to 75% and a gas oil ratio less than 100,000scf/stb for the effectiveness of Anti agglomerant LDHI. Anti Agglomerant LDHI have also been successfully applied in the field and are rapidly gaining recognition and acceptance in the industry. The applicability window of some of the AA type LDHI’s is independent of sub cooling and can be effective even at sub cooling of greater than 400F. They have also been used during the start up of some direct vertical access wells in the Gulf of Mexico.

**2.2.3 HYBRID HYDRATE INHIBITOR**

Ideally operators producing from deep water wells want total hydrate control without the problems associated with thermodynamic (THI) or Low Dosage hydrate inhibitors (LDHI). Laboratory Studies and previous onshore field experience indicted that hydrate inhibition synergy is gained through the combination of thermodynamic inhibitors and the low dosage hydrate inhibitors (Budd et al 2004)19. This is termed Hybrid Hydrate Inhibitor (HHI) by combining chemistries of thermodynamic, kinetic, and AA inhibitor properties the hybrid product provides the benefits of all the new technologies with much lower rates of usage (Pakulski, Szymczak,and Sanders 2005)2, because of its performance, logistical and cost drivers presented by the use of methanol which the cost is far less than the speciality LDHI chemistry. The logistics have to do with pump sizing, since the conventional LDHI requires new pumps and configurations.

**2.2.4 POLY ETHER AMINE GAS HYDRATE INHIBITORS**

The use of polyether amine (PEA) is their ability to form multiple hydrogen bonds through oxygen, nitrogen, and active hydrogen atoms. Thus they can associate with several molecules of water to attach themselves to ices and hydrate crystals. An interesting property of PEA’s is their synergistic effects on hydrate inhibition, when applied concurrently with polymeric kinetic hydrate inhibitors (KHI) or thermodynamic hydrate inhibitors (THI). The hydrophobic polypropylene glycol functionality of THI gives PEA’s properties of multi headed surfactants having hydrophilic amines groups3. The combination inhibitors are better inhibitors than a single component one. The PEA’s have an excellent record in protecting gas producing wells from plugging with hydrates and found applications for hydrate inhibition in oil and gas fields, onshore and offshore production flow lines and completions.

Quarternized polyether diamines as been described from literature to be formed by reacting PEA with alkyl halides to form Anti Agglomerant (AA)20, which are efficient AA Hydrate inhibitors, while different derivatives can produce dual functionality compounds such as corrosion inhibitors and gas hydrate inhibitors (Dahl mann et al). The other additional PEA’s properties making them more attractive hydrate inhibitors is the chemical structure of PEA’s indicating they must scavenge oxygen and be capable to adhere to metal surfaces. The PEA’s anti corrosion properties has been published by (Hope et al), they also counter react the corrosiveness of methanol.

**2.3 HYDRATE MONITORING SYSTEM**

The key to the overall success of hydrate inhibitor is a full integration of a good front end-design, comprehensive deployment plan and an effective monitoring program6. The amount of inhibitor depends on various parameters including water cut, inhibitor loss to hydrocarbon phases, aqueous and non aqueous fluid compositions, operating conditions. Generally for hydrate monitoring system, a safety factor is considered and the resulting inhibitor is injected without much downstream measurements. Despite the usual safety margins, gas hydrates are formed, which could result in serious operational and safety concerns. This is mainly caused by changes in the system conditions such as rates of production, water cut or malfunctions of the equipment affecting both capital and operating expenditure.

For an effective monitoring system, techniques based on downstream and online measurements have been developed. These techniques are used for hydrate monitoring and early warning system, to reduce the risk of gas hydrates in subsea pipeline6.

1. Monitoring hydrate safety margin to optimize injection rates. The degree of hydrate inhibition measured by means of this technique could provide the necessary technical information for the field operators to know how far the thermodynamic conditions of the system is adequately inhibited against hydrate formation.
2. Detecting initial hydrate formation, as an early warning system against hydrate blockage. This system detects the changes in the system caused by hydrate formation with the aim of giving the operator enough time to prevent a blockage.

Benefit of reliable hydrate monitoring system, is that the field operator would be able to cope with changes in the amount of water in a system coming from the reservoir or condensation from vapour phase within a pipeline and in the system conditions caused by seasonal changes in seabed temperatures, or pipeline pressures, These therefore reacts and adjust appropriately to the inhibition injection rate. It would also be possible to determine if too much inhibitor is being used, thus allowing for the inhibitor dosage to be reduced, reducing the associated cost and environmental impact.

The main advantages of these techniques include minimising the amount of inhibitor required and preventing pipeline blockages caused by hydrates, hence the cost of inhibition, impact on the environment, cost of remedial actions, and deferred production.

**CHAPTER THREE**

**3.0 METHODOLOGY**

In other to apply the right strategy on preventing or managing the formation of hydrates, it is necessary to have a good hydrate monitoring system, to gain an understanding of the water, gas, temperature, produced water cut and pressure for a particular system. The previous methods used for prevention of hydrates must also be considered for already existing wells, in other to justify the economics of right strategy to use.

**3.1 CASE HISTORIES GULF OF MEXICO**

Relevant case histories on the application of hydrate inhibitors in an offshore environment. These breaks down into four types of application

**3.1.1 DOWN HOLE APPLICATIONS**

For offshore down hole treatment, operators install capillary lines in the annular space between the tubing and casing, this because of the surface controlled sub safety valve that precludes any insertion of a capillary line. These capillary lines are run below the hydrate zone and then enter the production tubing through a specialty entry port. If the well was not constructed with a chemical line below the hydrate zone or if the line is damaged, the operator must consider a work over.

**3.3.2 WELL HEAD APPLICATIONS**

The most common applications of hydrates inhibitions at the well head in the Gulf of Mexico, is for the control of hydrates in fuel gas systems. This fuel gas that is produced from the platforms is used as source of energy to run the platform equipment. The use of hydrate inhibitors for this applications controls hydrate formation and allows smooth operations of the platforms.

**3.1.3 FLOW LINE APPLICATIONS**

Hydrate inhibitors are used to control hydrate formation in a subsea flow line, for deep water operations where hydrates can form in the flow line between the producing well and the platform due to the heat loss to the sea temperature, because the riser is not usually insulted combined with the producing high pressure, which makes it enter into the hydrate conditions. Szymczak et al 2006 reported the use of a THI/PEA inhibitor in the Gulf of Mexico to control hydrate formation for a water depth of 1000 ft, to prevent hydrates formed in the flow line between the producing well and the platform. Also it was found that during extended shut down, the wellbore fluid can be pushed down below the mud line using dry gas from glycol contact tower followed by methanol, this also eliminates the hydrate risk during extended shut downs.

 **3.1.4 PIPELINE APPLICATION**

The most critical application of hydrates inhibitor is pipeline application; this is usually applied during winter time only. Gulf of Mexico pipelines carry million standard cubic feet of gas per day, plugs by hydrates carries a high financial consequences

**2.2 STRATEGIES OF DEPLOYMENT OF HYDRATE INHIBITORS**

Over the period of development and deployment of hydrate inhibitor, a series of key requirements as been stated which collates the most appropriate information enabling the cost effective solution to be proposed.

1, Information about the produced gas and liquids, the production rate, water chemistry, gas composition, condensate composition, Gas Oil Ratio, Water Cut

* Gas Composition: This has significant consequence, if in the initial stages of planning, because for new development gas composition could change, which could result in the use of an inappropriate inhibitor or wrong dose regime and in extreme cases the inhibitor failing to function at all when deployed, but for more mature fields the gas composition will remain constant
* Produced Water Chemistry: The composition of produced water should be determined. This allows identifying the presence of salt which is widely recognised as reducing the temperature at which hydrates will form. This will eventually allow accurate optimisation of treatment rates.
* Condensate/ Crude Composition: The presence of hydrocarbon liquid phase is essential to be present for Anti Agglomerant hydrate inhibitor to be effective. Such inhibitors are not preferred in a gas stream mixed with various volumes of water and little condensate.
* Water Production Rate/ Water Cut: Knowledge of the average water production rate is necessary in other to determine the effective dosage rate of the inhibitor to be injected and also to make comparison between different inhibitors.

2, Determination of hydrate formation conditions for the well fluid: soft ware’s are used to perform the calculations to estimate the hydrate formation conditions and hydrate dissociation curve by inputting the composition for the total well fluid stream. Also a complete system description is necessary to identify where hydrates form in the transport and production system.

3, Determine which hydrate inhibitor option is best for the field: In evaluating the different hydrate inhibition method, different factors are considered

* Degree of sub cooling: a higher degree of sub cooling requires greater hydrate inhibition methods. For example, with sub cooling temperatures greater than 140C, Kinetic Hydrate Inhibitors are in capable of preventing hydrates formation
* Water Cut: An increase in water cut, causes an increase in the amount of methanol required to prevent hydrates from forming, which might be greater than the maximum injection rate for the system, which poses safety hazards and environmental issues
* Determine the length of time required for hydrate protection: At a particular sub cooling temperature, the kinetic hydrate inhibitor as a maximum time for preventing hydrates formation. The kinetic hydrate inhibition treatment should be designed so that the KHI induction time is greater than the produced fluids residence time in the hydrate forming region of the production process. This will enable the produced fluids to pass through the production system without forming hydrate blockages even though the system is operating in the hydrate forming region.
* Health, Safety and Environmental Constraints: Each producing region has legislation governing HS&E issues. These must be taken into consideration at each step in the evaluation process. Products that does not meet regulatory requirements cannot be deployed

4, Determine proportion of hydrate inhibitor required per produced water volume: The calculation of the hydrate inhibitor volume per well is based on the shut in pressure, predicted water rate, umbilical size and injection pressure

5, Reliable Hydrate Monitoring System with techniques based on downstream and online measurements: This system gives an early warning by detecting the changes in the system caused by hydrate formation with the aim of giving the operator enough time to prevent a blockage, by installing a multi phase flow meter (MPFM) for both reservoir monitoring purposes and also provide an opportunity for subsea facilities operations optimization in real time. This technique minimizes the amount of inhibitor required and preventing pipeline blockages caused by hydrates, hence reducing the cost of inhibition, impact on the environment, cost of remedial actions, and deferred production.

6, Switching from a Thermodynamic Inhibitor to a Low Dosage Hydrate Inhibitor: for a mature asset, what is the current hydrate prevention strategy, that is the existing procedures or for new development such as unplanned shutdown for preventing formation of hydrates

7, what are the other existing or potential chemical treatments: When identifying an inhibitor formulation, the interaction between other specialty additives must be evaluated. Where synergy and anti synergy between the hydrate inhibitors, wax, corrosion and scale inhibitors must be observed. It is critical to have addressed these possibilities before moving to field development

8, Proper logistics and product transfers: A standard procedure which covers the entire handling and transportation process such as dedicated transfer hoses, transfer pumps and delivery/storage tanks should be in place to aid in the prevention of cross- contaminating chemical products, also to maintain the quality of the manufactured inhibitor.

9, Injection system maintenance: The proper assembly and care of a chemical injection system is extremely important because improper maintenance can ruin the most carefully laid plans. Replacement or repair of a continuous injection or components, particularly down hole capillary lines can be very costly, not to mention cost of lost production. It is essential to ensure the integrity of the chemical injection system is not compromised from the start of the production till the end.

**3.3 POTENTIAL COST IMPACT OF SWITCHING FROM AN EXISTING HYDRATE PREVENTION STRATEGY TO AN LDHI / HHI HYDRATE INHIBITOR.**

The majority of HHI/LDHI trials and applications are taking place in systems originally designed for either methanol or mono ethylene glycol use. The reasons operator choose to expand many of these trials into permanent application vary from the capacity of the system to inject methanol, cost comparison of injecting HHI/LDHI, convenience of HHI/LDHI including the logistics of transportation and storing. The following case histories gave the illustrations of the successful control of gas hydrates formation in real systems and the favourable uses of hybrid/LDHI hydrate inhibitor at real assets to enable hydrocarbon production

**3.4 HYBRID HYDRATE INHIBITOR/ AA LDHI APPLICATIONS**

**3.4.1 FIELD A**

The field A is 100% Company X owned fields, which is located in the Gulf of Mexico. The fields consist of 3 subsea wells D5, D6 and D3, the wells are located in a water depth of 5400 ft. They are tied back by a 17 mile long, 8 by 12 inches dual active heating flow lines to the marlin tension leg platform located in a 3,200 ft water depth. D5 and D6 are producing from the same reservoir, while well D3 is producing from another reservoir. For reservoir management and water onset purposes, a subsea multiphase flow meter (MPFM) was installed in the jumper between well D3 and flow line crude shows non-plugging characteristics with water cut up to 10% from experimental work done earlier on the field. Field A hydrate management was described based on this type of self inhibition characteristics9, but the recent reservoir studies have predicted the maximum water cut of 25% for the non plugging characteristics of the oil, with the increase in water production it raises the need for a new hydrate management strategy.

**3.4.1.1 Wells and Reservoir Properties**

As at when this study was performed, the well D3 was on an average producing 14,200 B/D of oil and 18.6 MM Scf/day of gas, while wells D5 and D6 were on the average producing at 12,200 B/D and 5000 B/D of oil and also producing 23.3 MM scf/D and 9.8 MM scf/D of gas respectively. These 3 wells flow to a common 3 phase separator. The separator yields a water cut of less than 1%. But recent reservoir studies predict the maximum water cut up to 27%, which raises the concern if the present self non-plugging hydrate characteristic of the crude is capable of preventing the formation of hydrates.

**3.4.1.2 EXISTING HYDRATE MANAGEMENT STRATEGY**

The experimental work performed in 2002 using the analogue crude with sufficient amounts of hydrate forming components (methane, ethane, propane, iso butane, nitrogen, carbon dioxide) to the crude to obtain the same composition of oil phase as its real system at experimental conditions and 3.5% water salinity shows an operating condition of Field A flow line during normal production is outside the hydrate risk region with water cut up to 25%. It is believed that the crude contains natural surfactants that disperse hydrate into slurry form, thus continuous injection of hydrate inhibitor is not required to prevent hydrate blockages up to 25% water cut. But prior to an extended shut down, methanol is injected at the tree to flush the well jumper with methanol to displace the live fluid in the flow line and also during cold restart methanol is injected at the tree until the tubing head temperature stays above the hydrate free temperature.

Field A, hydrate management throughout the life of the field relies on its non-plugging hydrate characteristics. But due to the increase in the water cut above the self non plugging characteristics of the crude, the existing strategy needs to be revisited, which poses some challenges because the existing subsea infrastructure may not have an extra umbilical available to deliver additional chemical or the platform may not have the capacity to accommodate new facilities.

Based on the subsea architecture and operating condition, new preventive strategies procedure prior to an extended shut down and during cold restart such as the one given below were considered.

**3.4.1.3 FAST RESTART AFTER EXHAUSTING THE NON-PLUGGING CHARACTERISTICS OF THE OIL FOR A COLD RESTART**

If well D3 can be ramped up as quickly as possible during cold restart the well could warm up quicker, thus reducing the inhibitor amount to dose the water coming out of the well and also reduce the volume of deferred production, knowing the maximum inhibitor injection rate based on the existing facilities, the dosage requirement and ramp up time. It can be determined if the water coming out of the well during cold restart will be properly dosed. To capture the worst scenario, the simulation was based on the time when well D3 produces at maximum water cut9. Different inhibitors injected through different paths had been evaluated as follows:

1, **Methanol injection through methanol line:** Based on the existing methanol pumps at the topsides, the maximum methanol injection rate that can be delivered to each of the wells is 6 gal /min. Which makes the cumulative methanol amount at the end of 2 hours injection will only be 17 barrels. The required methanol dosage determined by other flow assurance studies is 0.575 barrels of methanol per barrel of water. Thus 41 barrels (1722 gal) of methanol is required to dose 71 barrels of water, since the maximum injection rate for 2 hours is just 17 barrels (714 gal), the water is still under dosed and the well would not come on production. So therefore methanol injection with a fast restart of 2 hours is not appropriate for the cold restart.

**2, Kinetic Hydrate Inhibitor (LDHI) injection through chemical injection line:** Baseon 6000 Psi maximum pump discharge pressure available at the topsides and 0.5 –in ID chemical line, the maximum injection rate into the chemical injection lines that can be delivered to each of the wells is 0.18 gal/min. based on vendors recommendation the dosage is 0.0171 barrel (0.72 gal) of KHI per barrel of water. To dose 71 barrels of water, 51 gals of KHI is required, since the maximum volume of KHI at the end of 2 hours injection is only 22 gals, the water is also still under dosed. So therefore KHI injection through chemical injection line with a fast restart of 2 hours is not also appropriate for the cold restart.

**3, Anti Agglomerants Hydrate Inhibitors (LDHI) injection through chemical injection line:** Also based on the 6000 Psi maximum pump discharge pressure and 0.5 in ID chemical line, the maximum injection rate is 0.37 gal/min. The injection rate is higher than KHI, since AA is less viscous. Based on vendor’s recommendation the dosage is 0.01 barrel (0.42 gal) of AA per barrel of water. To dose 71 barrels of water, 30 gals of AA is required. To deliver 30 gals of AA LDHI in 2 hours injection period, only 0.25 gal/min injection rate is required. Thus this inhibitor can be delivered via the chemical injection line to dose the water during cold restart.

**4, Hybrid Hydrate Inhibitor through a methanol line:** The new breed of hydrate inhibitor, which is a synergy or a combination of methanol, Kinetic hydrate inhibitor, and anti agglomerants inhibitors called the Hybrid hydrate inhibitor, would be injected through the existing methanol injection line, which can deliver 6 gal/min. The required HHI dosage based on vendor’s recommendation is 0.05 barrel (2.1 gal) of HHI per barrel of water. To dose 71 barrels of water, 149 gals of HHI is required. To deliver 149 gals of HHI in 2 hours injection period, only 1.24 gal/ min injection rate is required. Therefore methanol line can deliver the required HHI amount to dose water during the cold restart.

**3.4.1.4 VOLUME AND COST OF INHIBITOR REQUIRED AFTER EXHAUSTING THE NON-PLUGGING CHARACTERISTICS OF THE OIL**

**1,** **Methanol injection through methanol line:** To dose 71 barrels of water, 1,722 gals of methanol is required and based on the maximum injection rate that can be delivered to each of the wells which is 6 gals/min. This means the well has to be ramped for 5 hours. The total cost of prevention can then be calculated

Cost of hydrate prevention =

(Unit cost of Methanol ($/gal) \* 1,722 gals required)+ (Transportation cost ($/gal)\*1722 gals) + Pump Maintenance cost.

The average annual price of methanol is $0.4 - $0.8/ gal. The current price used is $0.64/ gal\*\*, also the average transportation cost of methanol offshore to the Gulf of Mexico is $5/gal. Therefore the treatment cost with use of methanol is

Treatment cost = ($0.64\*1,722 gal) + ($5\*1,722 gal) = **$9,712.08**

The well D3 that is been dosed was producing an average of 14,200 B/D of Oil and 18.6 MMscf/Day of gas. If the well is been ramped for 5 hours to bring the well on production, this means the well would have lost an average of **2,958.35 barrels of Oil and 3.875 MMscf of gas**.

**2, Kinetic Hydrate Inhibitor (LDHI) injection through chemical injection line:** To dose 71 barrels of water, 51 gals of KHI is required and based on the 0.5in ID, the maximum KHI injection rate that can be delivered to each of the wells which is 0.18gals/min. This means the well has to be ramped for 5 hours. The total cost of prevention can then be calculated

The total cost of hydrate prevention =

(Unit cost of KHI ($/gal) \* 51 gals required)+ (Transportation cost ($/gal)\*51 gals) + Cost of new pumps + Cost of pump maintenance.

Assuming the current cost of KHI is $25/ gal, the treatment cost for preventing hydrates from forming is therefore

Cost of treatment = ($25/gal\* 51 gal) + ($5/gal\* 51 gals) = **$1,530**

The well D3 that is been dosed was producing an average of 14,200 B/D of Oil and 18.6 MMscf/Day of gas. If the well is been ramped for 5 hours to bring the well on production, this means the well would have lost an average of **2,958.35 barrels of Oil and 3.875 MMscf of gas**.

**3, Anti Agglomerants Hydrate Inhibitors (LDHI) injection through chemical injection line:** In other to inhibit a system containing 71 barrels of water, 30 gals of AA hydrate inhibitor is required, the total cost of prevention can then be calculated

The total cost of hydrate prevention =

(Unit cost of AA ($/gal) \* 30 gals required)+ (Transportation cost ($/gal)\*30 gals) + Cost of new pumps + Cost of pump maintenance.

Assuming the current cost of AA hydrate inhibitor is $18/gal, the treatment cost for prevention of gas hydrates is therefore

Cost of treatment = ($18/gal \* 71 gal) + ($5/gal \* 71 gals) = **$1,633**

The well D3 that is been dosed was producing an average of 14,200 B/D of Oil and 18.6 MMscf/day of gas. If the well is been ramped for 2 hours to bring the well on production, this means the well would have lost an average of **1,183.33 barrels of Oil and 1.55 MMscf of gas.**

**4, Hybrid Hydrate Inhibitor through a methanol line:** In other to inhibit the system containing 71 barrels of water, 149 gals of HHI is required to effectively inhibit the system from hydrates. The total cost of prevention can then be calculated as

Cost of hydrate prevention =

(Unit cost of HHI ($/gal) \* 149 gals required)+ (Transportation cost ($/gal)\*149 gals) + Reduced cost of maintenance of pumps.

Assuming the current cost of Hybrid hydrate inhibitor is $8/gal, the treatment cost for prevention of gas hydrates is therefore

Cost of treatment = ($8/gal \* 149 gal) + ($5/gal \* 149 gals) = **$1,937**

The well D3 that is been dosed was producing an average of 14,200 B/D of Oil and 18.6 MMscf/Day of gas. If the well is been ramped for 5 hours to bring the well on production, this means the well would have lost an average of **1,183.33 barrels of Oil and 1.55 MMscf of gas.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| % Increase or decrease in price of inhibitor | Cost of Treatment using Methanol to Inhibit Hydrates $ | Cost of Treatment using KHI to inhibit Hydrates $ | Cost of Treatment using AA to inhibit hydrates $ | Cost Of Treatment using HHI to inhibit Hydrates $ |
|  -20% | 9,491.66 | 1,275 | 1,377.4 | 1,698.6 |
|  -10% | 9,601.87 | 1,402.50 | 1,505.2 | 1,817.8 |
|  0% | 9,712.08 | 1,530 | 1,633 | 1,937 |
|  10% | 9,822.29 | 1,657.5 | 1,760.8 | 2,056.2 |
|  20% | 9,932.50 | 1,785 | 1,888.6 | 2,175.4 |
|  30% | 10,042.70 | 1,912.5 | 2,016.4 | 2,294.6 |

**Table 1:** Cost of treatment of Field A using different inhibitors with percentage change in price

**3.4.2 FIELD B**

A deep water Gulf of Mexico system with platform located in 1980 ft of water depth, was chosen for the first field test of a new anti-agglomerant LDHI. The platforms supported 10 Dry tree wells and 2 subsea wells. The subsea wells were located in 1722 ft of water approximately 4 miles from the platforms, paraffin inhibitor is injected down hole and the line is pigged every 5-8 days. The subsea equipment consisted of a subsea header and dual 4 inch flow lines which are round trip pig gable and uninsulated25.

**3.4.2.1 WELL AND RESERVOIR PROPERTIES**

At the time of field test, only one subsea well was flowing and the subsea well was producing 3,600 BOPD, 0-10 BWPD, and 2.3 MMSCF/D. Fluids from the subsea well was commingled with production from several dry trees in a header, prior to bring on the second subsea well. The total platform produced 27,000BOPD, 1150 BWPD, and 28MMSCF/D of associated gas, subsequent analysis showed that the sample of reservoir fluid contains 29,000 ppm Cl-, which translates to a salt content of approximately 4.8 wt%25. The complete reservoir fluid composition and brine composition based on the subsea well was used in the multiphase program to predict the hydrate stability curve.

**3.4.2.2 EXISTING HYDRATE MANAGEMENT STRATEGY**

As the flow line was uninsulted, the temperature of the produced fluid was expected to drop rapidly from the well head temperature at the subsea to 420 F, the system was producing at very low water cut (<1%). Theoretical thermodynamic predictions suggested hydrates could form during normal operations of the subsea well. Pigging the flow line increases the hydrate formation tendency due to the increase in pressure, as the water cut increases the plugging tendency also increases. The worst case conditions were expected to occur during shut in and subsequent start up. Methanol injection was the existing hydrate management strategy at approximately 350 gals/ Day to control hydrates at 2,500 psi and 450 F25.

**3.4.2.3 IMPROVED HYDRATE MANAGEMENT STRATEGY**

Injection of new Anti agglomerant low dosage hydrate inhibitors. The low viscosity of the LDHI is 23 cp at 400 F and 11 cp at 770 F, under normal operating conditions facilitated filling the umbilical and sufficient LDHI was easily applied through the 4 mile umbilical with a small injection pump. Chemical compatibility, Fluid compatibility and Material Compatibility test was done on the LDHI, which shows good compatibility apart from the material compatibility, where AA LDHI is more detrimental to viton than methanol. Since viton is only found in the platform methanol pump and the LDHI would only be in contact with viton while the methanol was being displaced from the umbilical, meaning mild incompatibility over a short time was not a major concern.

AA LDHI was injected via the existing methanol injection at a pump rate of 50 gals/ hr to displace methanol from the umbilical, until 330 gallons of AA LDHI had been pumped after 6.6 hours. The AA LDHI was switched to a smaller pump and the rate decreased to 0.104 gal/ hr, which is required to inhibit 2 barrels of water per day. The AA LDHI field test was done for 1.5 months, two brief shut in about 24 hours were experienced throughout the field test period.

The total number of days for field trial = (1.5 months\*30 days /month)–(2 days of Shut in) = 43 days

**3.4.2.4 ECONOMICS OF AA LDHI HYDRATE INHIBITOR COMPARED TO METHANOL**

Total Volume of AA LDHI inhibitor = (0.104 gal/hr\* 24hrs/day \* 43 days) + (330 gals required to displace the methanol from the umbilical) = **437 gallons of AA LDHI**

**Cost Of treatment of field B using AA LDHI for 43 days** = ($18/gal \* 437 gallons) + ($5/gal \* 437 gallons) = **$10,051**

 The required volume of methanol required to inhibit 2 barrels of water produced from the subsea well per day is 350 gals

Total Volume of Methanol required = (350 gal/day\*43 days) = **15,050 gallons of methanol**

**Cost of treatment of Field B using methanol for 43 days** = ($0.64/gal \* 15,050 gallons) + ($5/gal \* 15,050 gallons) = **$84,882**

**3.4.2.5 DISCUSSION OF FIELD A AND FIELD B RESULTS**

**A, Lower Chemical Costs**

With the large difference in the selling prices of specialty chemicals, The prices of LDHI’s are significantly higher than the commodity methanol or mono ethylene glycol ($AA LDHI >> $HHI > $MeOH), but the volume of the specialty chemicals is much lower than the volume of methanol that is required.

**B, Lower Transportation Costs**

The treatment cost is only a small portion of the cost to control hydrates. Another contributing cost is the transportation charge to supply hydrate inhibitor to the platform or field. Methanol is usually transported by dedicated supply boats, often necessitating special licences and permits. Since transportation costs is fixed $/gal, HHI transportation cost for field A was 91.35% lower than methanol transportation cost.

In addition to the cost of treatment which is inclusive of the cost of inhibitor and cost of transport, there are other costs that need considerations to ensure that the total cost of operation is measured and monitored. A program that carries excessive secondary cost can result in loss of the initial value supplied by the product itself. Based on the case study which is an offshore application of a hydrate inhibition program, the other costs include

**C, Lower Pump Maintenance**

 Pumping high volumes of methanol or MEG takes its toll on pump equipment because it increases the wear and tear on the pumps. Thus causing a high cost for maintenance and replacement of pneumatic pumps, with the hybrid application the pump maintenance costs are reduced significantly. This reduction brings up a critical point regarding pumps. If an operator is pumping methanol, the same pump can be used to pump the hybrid \inhibitor because the hybrid is in the lower range of the pump accuracy range. If the operator decides to use an AA LDHI, then the smaller pumps need to be installed. This is a hidden and frequently overlooked cost that arises when the operator switches from high volume solvent to a LDHI program.

**D, Storage on the Platform**

For offshore operations, every square foot of platform space is precious. A smaller foot print with the same outcome defines a better application. In the case of methanol the operator stores large volumes on the platforms at all times in the event of bad weather or other problems that resulted in delayed shipment. The field needs to have enough methanol available to assure continuous treatment in other to avoid production shut-in and loss of revenue during the shut in. The AA LDHI and the hybrid product require a significantly smaller foot prints and less risks of running out of products.

**E, Corrosion Inhibition of the Flow Line**

Methanol contains appreciable amount of dissolved oxygen, oxygen in the presence of water is a corrosion agent. If methanol is deployed for hydrate prevention, corrosion inhibitor must be added to treat methanol in other to mitigate the corrosive properties of the methanol. The hybrid hydrate inhibitor contains products that serve as mild corrosion inhibitor.21

**F, Labour and Safety Costs related to Crane Lifts**

One cost often not accounted for is the manpower time required to handle large quantities of methanol with increased activities of the crane lift which poses a safety hazard. The switch from methanol to AA LDHI/ hybrid reduces the manpower time required and crane lifts activities by the same proportion as the usage rate.

**G, No Intervention during Shut In**

Based on size of the chemical injection line the methanol injection rates can reach its maximum injection rate with an increase in water production, this raise a problem of potential hydrate formation which necessitate unplanned shutdown to inhibit the well.

In systems which have reached their limit of thermodynamic hydrate inhibitor injection, shut In often necessitate some type of intervention to mitigate the hydrate risk posed by higher sub cooling. This intervention is typically displacement of fluids or blow down, because of the synergy of methanol, KHI and AA which makes up the HHI, the KHI present would first provide a finite amount of “no touch time” but when the shut in time is exceeded the presence of methanol would dissolve any hydrates formed, and the presence of AA-type LDHI, which disperses the hydrates formed, tend to show good performance even during extended shut in. The HHI can treat higher water volumes for a given line size and such intervention is often avoided for systems treated continuously or for planned shut-ins of intermittently treated systems.

**H, Accelerate and Maximise Production**

In systems which are limited in their thermodynamic inhibition injection capabilities, HHI allow higher water production rates. This translates to simplified planned shut in procedures and enables faster restarts for systems requiring intermittent hydrate control. These applications afford accelerated production.

**I, Increase Ultimate Recovery**

In systems requiring continuous hydrate inhibitor treatment, the HHI in some cases can extend the life of the well. This is particularly true of gas condensate wells that load up when not produced at sufficiently high rates.

**J, Improve Operational Flexibility**

Having operational flexibility in terms of chemical injection for flow assurance helps protect against the unexpected reliance on methanol for hydrate control. The LDHI’s are in general more flexible than either methanol or MEG. When it comes to formulating multi functional products in turn allow adaptation to changing or unexpected conditions. A single chemical injection line can be adapted to handle 2 or more flow assurance issues.

**3.4.3 FIELD C**

**3.4.3.1 STRATEGY OF PREVENTING HYDRATES IN A DRY TREE OIL WELL IN FIELD C PRODUCING AT WATER CUT ABOVE 50%**

A dry tree well A-4, which is located in the Gulf of Mexico with a tension leg platform at water depth of 3,200 ft. It has a single 10-3/4 in. Production riser extended from the platform to the sea floor and 5-1/2 in. Production tubing, the chemical control injection mandrel and surface controlled sub safety valve are located at 5900 and 6,000 ft respectively. The well is equipped with distributed temperature system (DTS) which is a fibre optic system inserted through the chemical injection line down to 6,800 ft, this is used to monitor the temperature build up, by calculating the temperature every 3 ft on the time delay light pulse. As reservoir deplete, a 2 3/8 in. Coiled tubing was inserted down to 5,500 ft to allow gas lift injection. The well bore fluid is produced through the annulus between the coiled tubing and the production25.

In a dry tree the most critical area that is subjected to hydrate formation particularly during extended shut-in and cold restart is along the well bore above the mud line, since the production riser is in direct contact with the sea ambient temperature without any insulation.

**3.4.3.2 WELL AND RESERVOIR PROPERTIES**

Well A-4 is producing is at 2,700BOPD, 3,200BWPD (60%WC) and 1.22MMscf/day of Associated gas. The bottom hole temperature of the well is 2300F and estimated reservoir pressure is 4,350 psia25.

An experiment was performed on the appropriate hydrocarbon water mixture to determine the conditions of temperatures and pressures which hydrates can form. But the hydrate disassociation curves for well A-4 fluid shift by about 150Fdue to the 13.3% salinity of the produced water25. This shows the importance of having accurate water chemistry analysis in generating the curves. Based on the saline hydrate curve and maximum shut in well head pressure of 3000 psia, the temperature in the entire tubing must be above 600F to stay outside the hydrate formation region.

**3.4.3.3 EXISTING HYDRATE MANAGEMENT STRATEGY**

 The cool down time is 3 hours, which means if the well shut in is anticipated to be more than 3 hours; the well has to be treated with hydrate inhibitor to minimize hydrate risks. Well A-4 was inhibited with an Anti Agglomerant LDHI prior to an extended shut down and cold restart, if the well’s cumulative water cut during warm up time is lower than 50% WC, the AA LDHI should still be able to inhibit hydrates particles from agglomeration.

**3.4.3.4 IMPROVED STRATEGY FOR FIELD C PRODUCING ABOVE 50% WATERCUT**

The strategy to outrun the water during warm up time, is to minimize the water production during warm up, to push down the well bore fluid as far as possible at least below the mud line not only delays water production but also secures the well bore section above the mud line with non hydrates fluids. So during the extended shut down the well bore fluid can be pushed down below the mud line using the dry gas from the glycol contact tower (MEG) followed by diesel or methanol. This eliminates the hydrate risk during extended shut down.

As part of the cold restart procedure, opening the SCSSV requires dry gas injection followed by diesel until it is confirmed opened. The well is then opened as quickly as possible to minimize warm up time, to prevent hydrate formation during cold restart, a performance proven AA LDHI is then injected at the down hole chemical injection mandrel until the operating condition is safe from hydrate risk.

**3.4.3.5 RESULTS**

The transient simulation predicts that 1 hour after restart; the entire tubing is already outside the hydrate formation region, which confirms with the warm up time of the actual data to be 1 hour by measuring the temperature at the production manifold to be above 600F. Since the well never had hydrates issues during cold restart even with the recent steady state water cut of more than 90%, it proves that the concept of cumulative water cut along with the strategy to outrun the water, should be used to assess the applicability of AA LDHI during cold restart25.

**3.4.3.6 ECONOMICS OF FIELD C DURING AN EXTENDED SHUT DOWN**

At the well head tubing pressure of 500 psi, the well bore fluid is pushed down either by diesel (planned) or methanol (unplanned). The diesel injection volume in planned extended shut down is 1610 gallons, while the methanol injection volume in unplanned extended shut down is 1,605 gallons, based on 6 gallons per minute pump rate.

**Cost comparison for different strategies for unplanned extended shut down**

This can either be done with methanol or anti agglomerant inhibitor. Based on well tubing pressure of 500 psi and 6gallons per minute pump rate, 1605 gallons of methanol or 1,500 gallons of anti agglomerant inhibitor is required to push down the well bore liquid below the mud line.

**Based on the current price of Methanol taken as $0.64/gal and cost of transport taken as $5 per gallon**

Cost of using methanol for unplanned shut down= (1605 gals of methanol\* $0.64/gal) + (1605\*$5/gal) = **$9,052.2**

**Based on the current price of Anti Agglomerant taken as $18/gal and cost of transport taken as $5 per gallon**

Cost of using anti agglomerant for unplanned shut down= (1500 gals of methanol\* $25/gal) + (1500\*$5/gal) = **$45,000**

**3.4.3.7 DISCUSSION OF RESULTS OF FIELD C**

The actual data for the field shows that the cumulative water cut after 2 hours of restart was above 50% and the manifold temperature stayed above 650 F after the well had flowed for 1 hour, since the well never had hydrate issues during cold restart even with the recent steady state water cut of more than 90%. It proves that the concept of cumulative water cut along with the strategies to out run the water during warm up time by implementing the extended shut down and cold restart procedures using methanol to displace the wellbore fluid below the mud line, when water cut exceeds 50% was an effective strategy. Where the use of AA LDHI prior to shut in is ineffective and the use of AA LDHI for wellbore fluid displacement is not cost effective.

**CHAPTER FOUR**

**4.0 CONCLUSION**

Natural gas hydrates can completely plug production tubing in every system which produces some water and experiences cold temperatures with high pressures. The formation of this gas hydrate is a major concern and poses serious threat to the economics and personnel safety of the operators for the offshore production of oil and gas. Strategies of preventing or managing the formation of hydrates are considered for three different fields in the Gulf of Mexico as case studies in this project.

The strategy for hydrate prevention is by reviewing the fundamental of hydrate management, using the complete reservoir fluid composition, brine composition and well properties of the producing well to predict the operating conditions were hydrate form. This is also dependent on the operations of the platform, since a steady state operation requires continuous hydrate inhibition to inhibit the water hold up in the subsea flow lines in other to mitigate the possibility of hydrate blockages. While a transition operation such as start-ups and shut-in may require specific inhibitors for secondary hydrate control mechanism. The selection of hydrates strategies is based on technical and economic consideration. Different strategies are used at different stages of the field.

The continuous injection of conventional thermodynamic hydrate inhibitor such as methanol, mono ethylene glycol using a reliable downstream hydrate monitoring system was the existing strategy used to prevent hydrates for a steady state operation, but as the water cut increases, this increases the volume of methanol that would be required. This raises a lot of issues such as environmental and downstream allowable standard of dissolved methanol in the crude or gas that is been produced, since methanol also contains appreciable amount of dissolved oxygen which is a potential cause of corrosion, Because of the side effects of the use of thermodynamic hydrate inhibitors, a low dosage hydrate inhibitors such as the anti agglomerant or an hybrid hydrate inhibitor which is a synergy of methanol, kinetic hydrate inhibitor and anti agglomerant inhibitor as been formulated. The continuous injection of this newly formulated AA LDHI during steady state operations and injection of AA LDHI prior to shut in has proved effective for preventing formation of gas hydrates if the cumulative water cut is below 50%.

As the cumulative water cut increases above 50%, a new strategy is deployed during the transition operation, since the existing strategy of injecting AA LDHI prior to shut in would not be able to prevent the formation of gas hydrates because of the high water cut. Displacing the wellbore fluid with methanol below the mud line during extended shut down and out run the water during cold restart is the best strategy to manage hydrate risk during transition operations for a well producing at high water cut. After a short warm up time of about 1 to 2 hrs without any hydrate issue, the AA LDHI was then continuously injected during the steady state operations.

The economics of the project shows that the use of an HHI/AA LDHI is more economical, environmentally compliant, and efficient than the use of methanol or mono ethylene glycol during the steady state and transition operation of the platform when the well was producing at low water cut. But as the cumulative water produced goes above 50% water cut, the strategy of displacing the wellbore fluid below the mud line with methanol proves more efficient and cost effective compared to the use of injecting AA prior to shut in, while the use of AA LDHI to displace wellbore fluid proves not to be economical.

**REFERENCE**

1, Pakulski, M., Prukop, G., Mitchell, C,: “Field Testing and Commercial Application of High Efficiency Non-Polymeric Gas Hydrate Inhibitor in Offshore Platforms, SPE 49210, Presented at SPE Annual Technical Conference in New Orleans, Louisiana, USA, 27-30, September 1998.

2, Szymczak, S., Sanders, K., Pakulski, M.: “A Thermodynamic and low-Dosage Hydrate – Inhibitor Solution For Hydrate Control in the Gulf of Mexico”, SPE 96418, Presented at SPE Annual Technical Conference in Dallas, Texas, USA, 9-12 October 2005.

3, Szymczak, S., Pakulski, M.,: “Twelve Years of Laboratory and Field Experience For Polyether Polyamine Gas Hydrate Inhibitors”, ICGH 2008, Presented at the 6th International Conference on Gas hydrates in Vancouver, British Columbia, Canada, 6 – 10 July 2008.

4, Neff, S., FU, B., Mathur, A., and Bakeev, K.,: “Application of Low Dosage Hydrate Inhibitors in Deep Water Operations”, SPE 78823, Presented at SPE Annual Technical Conference in New Orleans, Lousiana, USA, 30 September – October 3, 2001.

5, Gounah, T., Renfro, K.D., Bolding, J., Embrey, M.,: Remediation of hydrate Plugs in Offshore Wells Via Capillary Tubing – A Cost Effective Alternative”, SPE 116148, Presented at SPE Annual Technical Conference in Denver, Colorado, USA, 21-24 September 2008.

6, Tohidi, B., Chapoy, A., Yang, J.,: “Developing a Hydrate Monitoring System, OTC 19247, Presented at The offshore Technology Conference in Houston, USA, 5-8 May, 2008.

7, Mehta, A.P., Herbert, P.B., Cadena, E.R., Weatherman, J.P.,: ”Fulfilling The Promise of low – Dosage Hydrate Inhibitors: Journey From Academic Curiosity to Successful Field Implementation”, SPE 81927 Revised for Publications from Paper OTC 14057, Presented at the Offshore Technology Conference in Houston, USA, 6-9 May, 2002. 36 8, Harun, A.F., Fung, G., Erdogmus, M.,: “Experience in AA-LDHI Usage for a Deepwater Gulf of Mexico Dry Tree Oil Well” SPE 100796, Presented at the Asia Pacific Oil and Gas Conference in Adelaide, Australia, 11-13 September, 2006.

9, Harun, A.F, Blanchard, T.J., Erdogmus, M.,: “Managing Hydrate Risks for a Black Oil Long Subsea Tie-Back When Water Cut Predictions Exceed Original Design”, SPE 111138, Presented at the North Africa Technical Conference in Marrakech, Morocco, 12-14 March, 2008.

10, Phillips, N.J., Grainger, M.,: “Development and Application of Kinetic hydrate Inhibitors in The North Sea”, SPE 40030, Presented at the Gas Technology Symposium in Calgary, Alberta, Canada, 15-18 March, 1998.

11, Commodity methanol prices are listed at www.methanex.com. Average annual prices are tabulated in the methane annual reports, also available on this website.

12, Frostman, L.M., and Przybylinski, J.L.,: “Successful Applications of Anti-Agglomerant Hydrate Inhibitors”, SPE 65007, presented at SPE International Symposium on Oil Field Chemistry in Houston, USA, 15 February 2001.

13, Frostman, L.M., Thiev, V., Crosby, D.L., Downs, H.H.,:”Low-Dosage hydrate inhibitors: Reducing Costs in Existing Systems and Designing for the future”, SPE 80269, Presented at SPE International Symposium on Oil Field Chemistry, in Houston USA, 15 February, 2003.

14, Leporcher, E., Kinnari, K., Labes-Carrier, C., Maurel, P., Vandersippe, W.,:”Multiphase Flow: Can we take Advantage of hydrodynamic Conditions to Avoid hydrate Plugging During Deepwater Restart operations”, SPE 77647, Presented at SPE Annual Technical Conference in San Antonio, Texas, USA, 29 September - 2 October, 2002

15, Cooley, C., Wallace, B.K, Gudimetla, R.,:”hydrate Prevention and Methanol Distribution on Canyon Express”, SPE 84350, Presented at SPE Annual Technical Conference in Denver, Colorado, USA, 5-8 October, 2003.

16, Clark, L.N., Anderson, J.,:”Low Dosage Hydrate Inhibitors: Further Advances and Development in Flow Assurance Technology and Applications Concerning Oil and Gas Production Systems”, IPTC 11538, Presented at the International Petroleum Technology Conference held in Dubai, UAE, 4-6 December, 2007.

17, Haghighi, H., Azarinezhad, R., Chapoy, R.A., Tohidi, B.,: “Hydra Flow: Avoiding Gas Hydrate Problems”, SPE 107335, Presented at the SPE Europec/EAGE Annual Conference and Exhibition held in London, United Kingdom, 11-14 June, 2007.

18, Jordan, M.M., Feasay, N.D.,:”Meeting the Flow Assurance Challenges of Deep Water Developments: From Capex Development to Field Start Up”, SPE 112472, Presented at SPE North Africa Technical Conference held in Marrakech, Morocco, 12-14 March, 2008.

19, Budd, D., Hurd, D., Pakulski, M.,: “Enhanced Hydrate Inhibition in Alberta Gas Field”, SPE 90422, Presented at SPE Annual Technical Conference Held in Houston, Texas, USA, 26-29 September, 2004.

20, Pakulski, M.,:”Quarternized Polyether Amines as Gas Hydrates Inhibitors, US Patent, 6025302

21, Hoppe, R., Martin, R.L., Pakulski, M.K., and Schaffer, T.D.,:”Corrosion Mitigation With Gas Hydrate Inhibitors”, SPE 100474, Presented at the SPE Gas Technology Symposium held in Calgary, Canada, 15-17 May, 2006.

22, Klomp, U.C. et al.:”Methods for Inhibiting the Plugging of Conduits by gas Hydrates”, US Patent 5,648,575 (1997).

23, Anseline, M.T., Reijnhout, M.J., Muijs, H.M., and Klomp, U.C.,:1993, World Patent, WO 93/25798.

24, Willmon, J.G., Edwards, .M.A.,: “From Pre-commissioning to Start up Getting Chemical Injection Right”, SPE 96144, presented at the SPE Annual Technical Conference, Dallas, Texas, USA, 9-12 October, 2005

25, Frostman, L.M.,:”Änti - Agglomerant Hydrate Inhibitors for Prevention of Hydrate Plugs in Deepwater Systems”, SPE 63122, Presented at the SPE Annual Technical Conference held in Dallas, Texas, USA, 1-4 October 2000.

26, Pickering, P.E., Edmonds, B., Moorwood, R.A.S., Szczepanski, R., and Watson, M.J.J.,:”Evaluating New Chemicals and Alternatives for Mitigating Hydrates in Oil and Gas Production”.

APPENDIX A

**Economics for Field A to inhibit 71 barrel of water**

The average annual price of methanol is $0.4 - $0.8/ gal, the current price of methanol is taken as $0.64/gal

If current price for KHI is $25/gal

Current Price for AA is $18/gal

Current Price for HHI is $8/gal

The Current Price of Crude Oil taken as $63.35/bbl, but if assume the price of Oil to be worst case as $25/bbl

The Current Price of natural gas as $3.55/Mscf, and also assumes the price of gas to be $1.55/Mscf

The Base Case to be methanol injection for 5 hours with a deferred or lost production of 2,958.35 Barrels of oil and 3.875 MMscf.

**Based on the current price of Methanol taken as $0.64/gal**

Treatment cost = ($0.64\*1,722 gal) + ($5\*1,722 gal) = $9,712.08.

**Based on the current price of KHI taken as $25/gal**

Cost of treatment = ($25/gal\* 51 gal) + ($5/gal\* 51 gals) = $1,530

**Based on the current price of AA hydrate inhibitor taken as $18/gal**

Cost of treatment = ($18/gal \* 71 gal) + ($5/gal \* 71 gals) = $1,633

But the well was ramped up in 2 hours with an increased production of 1,775.02 barrels of oil and 2.325 MMScf of gas.

Increased in revenue due to increased production = (1,775.02bbl \* $25/bbl) + (2.325MMscf\*1000 Mscf/MMscf\*$1.55/Mscf) = $47,979.25

**Based on the current price of HHI hydrate inhibitor taken as $8/gal**

Cost of treatment = ($8/gal \* 149 gal) + ($5/gal \* 149 gals) = $1,937

But the well was ramped up in 2 hours with an increased production of 1,775.02 barrels of oil and 2.325 MMScf of gas.

Increased in revenue due to increased production = (1,775.02bbl \* $25/bbl) + (2.325MMscf\*1000 Mscf/MMscf\*$1.55/Mscf) = $47,979.25



