EVALUATION OF GAS HYDRATE MITIGATION BY CHEMICAL INJECTION METHOD

A PROJECT REPORT

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EVALUATION OF GAS HYDRATE MITIGATION BY CHEMICAL INJECTION METHOD

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CERTIFICATE

This is to certify that the work contained in this thesis titled "EVALUATION OF GAS HYDRATE MITIGATION BY CHEMICAL INJECTION METHOD" has been carried out by RANGITH KUMAR RS under my supervision and has not been submitted elsewhere for a degree.

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ABSTRACT

Since from the early 1900s, transportation of gas from one place to another through pipelines have been very difficult due to the formation of the hydrate in gas pipelines. It has led to the issues with safety and properly sustained production. All the Oil and Gas industry spends hundreds of million dollars annually combating their effects. In order to overcome this issue chemical injection methods are used to mitigate the formation of the hydrate in the pipeline.

The chemical methods covered will include thermodynamic hydrate inhibitors, kinetic hydrate inhibitors, and anti-agglomerants. In this paper a problem is been designed and comparison of the different inhibitors are done. In this model, calculations were made on the injection rate of different inhibitors. The same model and calculation methods were used for finding the injection rate and the best economical inhibitor is been found out by comparing the inhibitors' properties to determine which one was best suited for use on the current fields.

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1.0 Introduction to flow assurance problems

Flow assurance deals with the risks and problems arising from the challenging properties and behavior of the produced hydrocarbons, associated fluids, and solids. It is an evaluation process that ensures that produced fluids from the wells are delivered safe to its desired location. It is a structured engineering analysis process that utilizes the in-depth knowledge of fluid properties and thermal-hydraulic analysis of the system to develop strategies for control of solids such as hydrates, wax, asphaltenes, and scale formations.

Deep-water production environment and transportation through longer tiebacks, pipelines, and flowlines provides conditions that brought about flow assurance challenges. These flow assurance challenges are sand production, multiphase flow, thermal issues, asphaltene, erosion, hydrate, scale, corrosion and wax formation. The challenges posed in this environment can also be complicated due to the changes in the prevailing conditions and production profiles over the field's life. It is worthy to also note that for effective subsea production, it is important to identify the potential for and quantify the extent of any solid deposition in the system.

It is difficult and costly to remove a plug in a pipeline especially in subsea environment. As the industry is moving into deep and ultra-deep-water environment which is more remote, the need for a technology that will enhance cost effective flow assurance becomes very imperative. This is so because development of new fields will demand long distance tiebacks to an existing infrastructure or onshore facility for processing.

In this thesis work I am going to mainly talk about hydrate formation in pipeline and chemical injection methods to mitigate it. Although there are a few methods to mitigate hydrate formation, we will be mainly focusing on chemical injection methods as it more widely used across everywhere by all the oil and gas industries.

Chapter 2 Literature Review

2.0 Overview of Literature Review

In combination with water, many of the components commonly found in natural gas form hydrates. One of the problems in the production, processing, and transportation of natural gas and liquids derived from natural gas is the formation of hydrates; however, the importance of natural gas hydrates was not apparent in the early era of the gas business, when gas was produced and delivered at relatively low pressure, thus hydrates were never encountered.

In the twentieth century, with the expansion of the natural gas industry, the production, processing, and distribution of gas became high-pressure operations. Under pressure, it was discovered that pipelines and processing equipment were becoming plugged with what appeared to be ice, except the conditions were too warm for ice to form.

Thermodynamic hydrate inhibitors are added at high concentrations (10-60 wt.%) and alter the chemical potential of the aqueous or hydrate phase so that the hydrate dissociation curve is displaced to lower temperatures or higher pressures. Examples are methanol and ethylene glycol.

Kinetic hydrate inhibitors are added at low concentrations (<1 wt.%) and do not affect the thermodynamics of hydrate formation. However, they do delay hydrate

nucleation and/or crystal growth. When the inhibition mechanism breaks down and fast, auto-catalytic hydrate formation begins, the hydrate agglomerates rapidly and can form a plug.

Anti-agglomerants are also added at low concentrations (< 1 wt.%) and prevent the agglomeration of hydrates so that all the hydrate crystals are transportable and do not build up in the pipe.

From review paper the inhibitors used are thermodynamic hydrate inhibitors and Low dosage hydrate inhibitors. Comparing results from different review papers, in thermodynamic inhibitors methanol and mono-ethylene glycol are the most preferred inhibitors in a pipeline and it is concluded that using 10-50% inhibitors for the pipeline could restrict the hydrate formation. LDHI's were also studied. They are divided into polymers and surface-active agents. LDHI's are found to be advantages over THI's because of its lower weight percentage used and also by reducing the operating cost of pipeline.

Chapter 3   Natural Gas Hydrates

3.0 Introduction to Natural Gas Hydrates

In the petroleum industry, the term hydrate is reserved for substances that are usually gaseous at room temperature. These include methane, ethane, carbon dioxide, and hydrogen sulfide. This leads to the term gas hydrates and to one of the popular misconceptions regarding these compounds. It is commonly believed that non aqueous liquids do not form hydrates; however, liquids may also form hydrates.

Gas hydrates are ice like crystals, but they are different in structure. Gas hydrates formation in gas transporting pipe lines causes clogging the pipe lines, and prevents transporting gas .therefore gas hydrates formation should be prevented.

Figure 1- Hydrate formation in a pipeline

It is a result of the hydrogen bond that water can form hydrates. The hydrogen bond causes the water molecules to align in regular orientations. The presence of certain compounds causes the aligned molecules to stabilize, and a solid mixture precipitates.

The water molecules are referred to as the host molecules, and the other compounds, which stabilize the crystal, are called the guest molecules. In this book the guest molecules are more often referred to as formers. The hydrate crystals have complex, three-dimensional structures in which the water molecules form a cage and the guest molecules are entrapped in the cages.

The stabilization resulting from the guest molecule is postulated to be caused by van der Waals forces, which is the attraction between molecules that is not a result of electrostatic attraction. As described earlier, the hydrogen bond is different from the van der Waals force because it is due to strong electrostatic attraction, although some classify the hydrogen bond as a van der Waals force.

Another interesting thing about gas hydrates is that no bonding exists between the guest and host molecules. The guest molecules are free to rotate. The stabilization resulting from the guest molecule is postulated to be caused by van der Waals forces, which is the attraction between molecules that is not a result of electrostatic attraction. As described earlier, the hydrogen bond is different from the van der

Waals force because it is due to strong electrostatic attraction, although some classify the hydrogen bond as a van der Waals force.

Another interesting thing about gas hydrates is that no bonding exists between the guest and host molecules. The guest molecules are free to rotate inside the cages built up from the host molecules. This rotation has been measured by spectroscopic means. Therefore, these compounds are best described as a solid solution.

To combat these issues, methanol has become the preferred method of chemical treatment to inhibit hydrate formation. However, the use of methanol, while effective at controlling hydrate growth when properly applied, has numerous drawbacks. These drawbacks can include salt and scale precipitation, increased corrosion risk due to dissolved oxygen, and an increased risk of hydrate formation if an insufficient volume of methanol is used.

Low dose hydrate inhibitors (LDHIs), such as kinetic hydrate inhibitors and anti-agglomerants, can be added to associated methanol injection or applied neat to reduce many of the drawbacks resulting from the use of methanol, while maintaining many of the benefits. The chemical methods covered will include thermodynamic hydrate inhibitors, kinetic hydrate inhibitors, and anti-agglomerants.

3.1 Typical Components in Natural Gas

Natural gas is a non-renewable resource that is expected to be widely expanded in the decades to come. It is considered a very safe energy source when transported, stored and used. It is a mixture consisting mainly (70-95 %) of methane (CH_4, a covalent bond composed of one carbon atom and four hydrogen atoms). It also contains other gaseous hydrocarbons such as ethane (C_2H_6), propane (C_3H_8), normal butane (n-C_4H_{10}), isobutane (i-C_4H_{10}), and pentane (C_5H_{12}), among other higher molecular weight hydrocarbons.
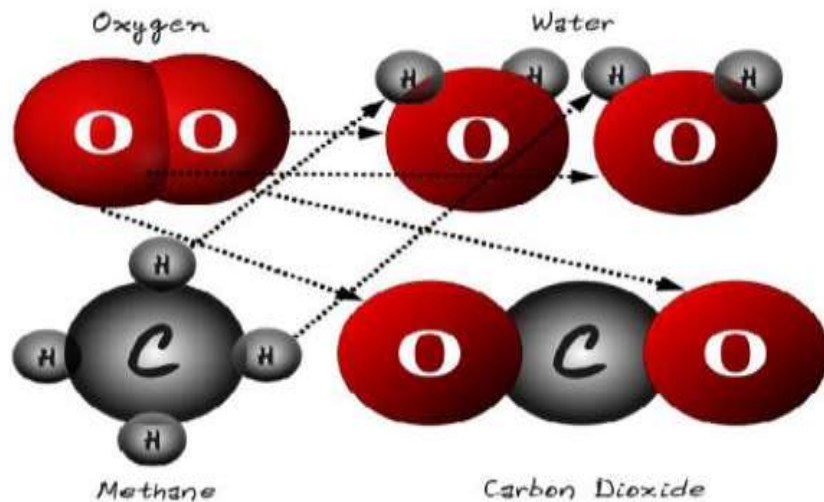
Figure 2 - Natural Gas Typical Molecule: Models of molecules of oxygen, water, methane and carbon dioxide

Natural gas also contains impurities or contaminants that have to be removed before it can be used as a consumer fuel after its extraction from the reservoir. These impurities include acid gases, such as hydrogen sulfide (H_2S), carbon dioxide (CO_2),

mercaptans (methanethiol – CH_3SH, and ethanethiol – C_2H_5SH), nitrogen (N_2), helium (He), and water vapor (H_2O).

Table 1 - Typical Natural Gas Components

Hydrocarbon Components (mole%)		Non- Hydracarbon Components (mole%)	
Methane	70 - 80	Nitrogen	15
Ethane	1 - 10	Carbon dioxide	20
Propane	5	Hydrogen Sulphide	20
Butane	2	Helium	Up to 5
Pentane	1		
Hexane	0.5		

3.2 Different Structures of Hydrates

There are three recognized crystalline structures for hydrates. In both, water molecules build the lattice and hydrocarbons, nitrogen, CO_2, and H_2S occupy the cavities.

- Smaller molecules (CH_4, C_2H_6, CO_2, H_2S) stabilize a body – centered cubic called Structure – 1.

- Larger molecules (C_3H_8, i-C_4H_{10}, n-C_4H_{10}) form a diamond-lattice called Structure -2.

- Isoparaffins and cycloalkanes larger than pentane are known to form Structure H hydrates.

From the practical viewpoint, the structure point doesn't affect the appearance, properties, or problems caused by the hydrate but it has a significant effect on the pressure and temperature at which the hydrates form. Structure-2 hydrates are more stable than Structure-1 and this why gas mixtures having C_3H_8, C_4H_{10} form hydrates at a higher temperature than similar gas which do not contain these compounds. The presence of H_2S results in the substantially warmer hydrate formation temperature at a given pressure. CO_2 in general has a much smaller impact and often reduces the hydrate formation temperature at a fixed pressure for a hydrocarbon gas mixture.
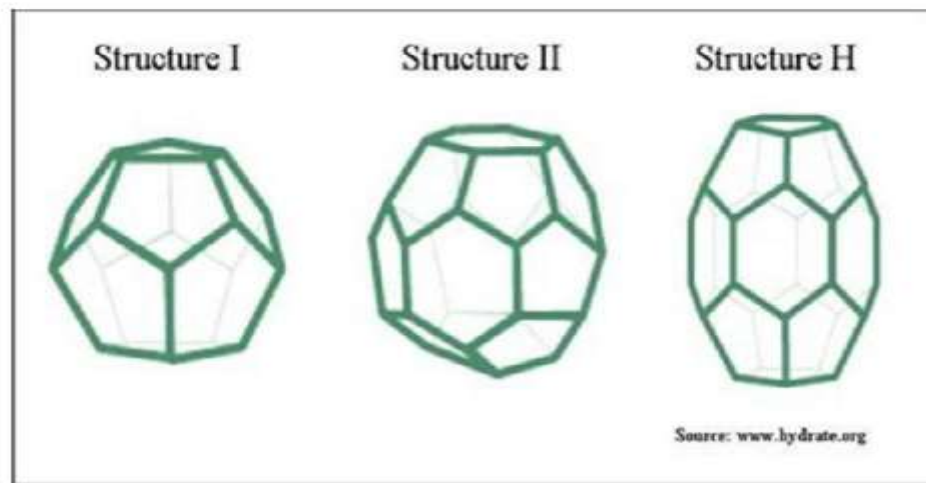
Figure 3 - Schematic representation of the structures of the hydrates

Structure I hydrates contain 46 water molecules per 8 gas molecules giving a hydrate number of 5.75. The water molecules form two small dodecahedral voids and six large tetra-decahedral voids. The sizes of the voids are relatively small meaning that the guest molecules are restricted in size to essentially methane and ethane.

Structure II hydrates contains 136 water molecules per 24 gas molecules giving a hydrate number of 5.67. The water molecules form 16 small dodecahedral voids and 8 large hexakaidecahedral voids. The larger voids are able to accommodate molecules including propane, isobutane, cyclopentane, benzene and others. However, while the larger cavities can accommodate larger molecules, the structure is only stable if small 'help' molecules are available to fill the smaller lattice cavities.

Structure H hydrates contains 34 water molecules for every 6 gas molecules giving a hydrate number of 5.67. The structure has three cavity sizes with the largest cavity able to accommodate larger molecules than both SI and SII. Once again, stability is only possible in the presence of smaller 'help' molecules such as methane or nitrogen.

These three structures commonly contain only one non-polar guest molecule within each cage. The guest molecule size has to be big enough to be stabilized in cavity, but not too big to fill the cavity. Therefore, under unusual conditions of very high pressure they can have multiple cage occupancy with unusually small guest molecules, example hydrogen and noble gasses.

Chapter 4 Conditions Necessary for Hydrate Formation Conditions

4.0 Conditions Necessary for Hydrate Formation

There are four major conditions necessary for hydrate formation

- Water as the liquid phase condensing out of the hydrocarbon.

- Hydrate formers. These are small gas molecules such as methane, ethane, and propane (gas composition).

- The right combination of low temperature and

- High pressure.
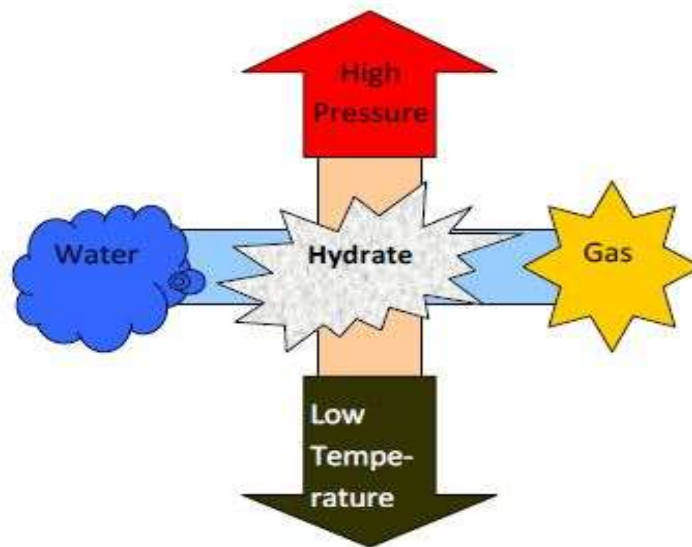
Figure 4 - Hydrate formation necessary condition

Hydrate formation is favored by low temperatures and high pressures typically 20°C and 100 bara. Solids formation phase diagram in the pressure-temperature plane is as shown in Figure 5. The right hand region covers pressures and temperatures at which hydrates are thermodynamically unstable and is therefore 'hydrate free' as indicated. On the left hand, the temperatures and pressures favour hydrate formation. In the 'hydrate region', the degree of subcooling is sufficient enough to promote hydrate formation spontaneously.
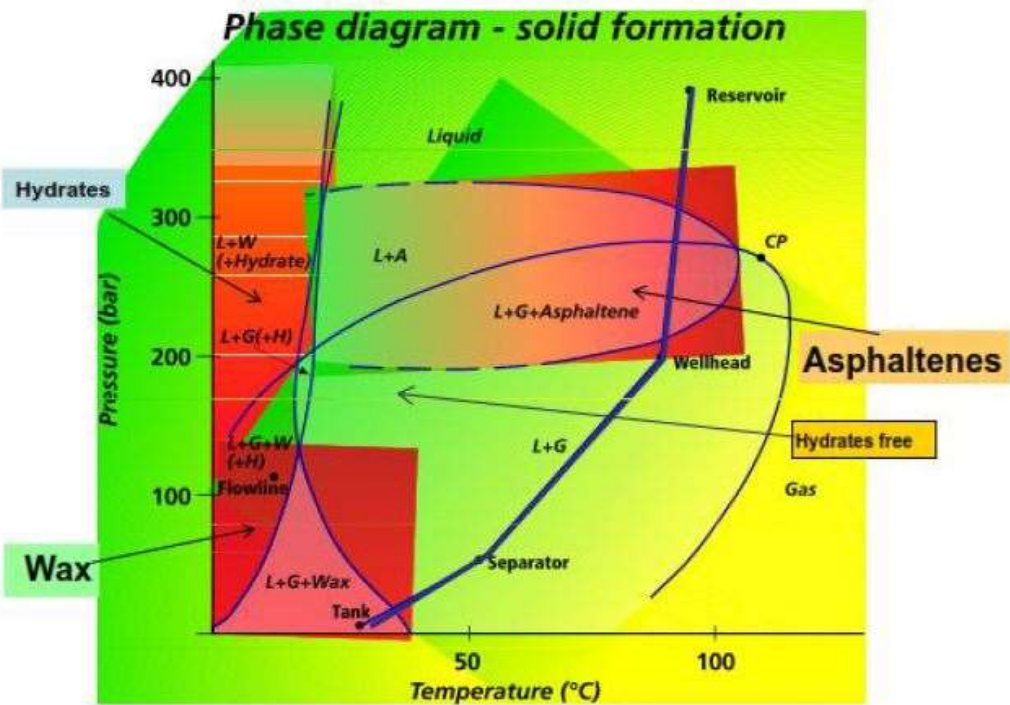
Figure 5- Hydrate formation phase diagram

Gas hydrate forms in water phase from gas molecules dissolved in that phase. Consequently, H2S and CO2 increase the temperature at which hydrates will form since they are more soluble in water than most hydrocarbons. Hydrate formation is enhanced during flow particularly in turbulence producing conditions (for example; flow through orifice meters, reduced port valves). However, hydrate also forms under static conditions.

Table 2 - Pressure Temperature Hydrate Formation Conditions

Temperature	Pressure	Composition (mol%)		
(^{o}c)	(MPa)	Aqueous	Vapour	Hydrate
0.0	2.60	0.10	0.027	14.1
2.5	3.31	0.12	0.026	14.2
5.0	4.26	0.14	0.026	14.3
7.5	5.53	0.16	0.025	14.4
10.0	7.25	0.18	0.024	14.4
12.5	9.59	0.21	0.024	14.5
15.0	12.79	0.24	0.025	14.5
17.5	17.22	0.27	0.027	14.5
20.0	23.4	0.30	0.028	14.5
22.5	32.0	0.34	0.029	14.6
25.0	44.1	0.37	0.029	14.6

Factors which contribute to the initiation of hydrate particles formation are :

Degree of subcooling – Hydrates may not begin to form immediately upon reaching the hydrate point. As much as 5 °C to 10 °C of subcooling is needed to form the first seed crystals of hydrates.

Presence of artificial nucleation sites – This is a point where a phase transition is favored, and in this case the formation of a solid from a fluid phase. Good nucleation sites for hydrate formation include an imperfection in the pipeline, a weld spot, or a pipeline fitting (elbow, tee, and valve). Scale and sand all make good nucleation sites as well.

Degree of mixing – System geometry and flow regime. This is to say that hydrate formation is favored in regions where the fluid velocity is high. This is because, there is high velocity while natural gas is passing through the narrowing in the valve and mixing in a pipeline, process vessel, and heat exchanger, enhances hydrate formation. There is also a high temperature drop when natural gas is choked through a valve due to Joule-Thompson effect.

Furthermore, once crystallization has begun, time is needed for the crystals to agglomerate and actually block the flow. In other words, hydrate formation is a transient process. Also, the exact hydrate formation point depends on the composition of the fluids involved; gas composition and water as well as brine composition. In

figure 6 the conceptual representation of hydrate formation is shown schematically as temperature drops along a pipeline with time in oil dominated system.
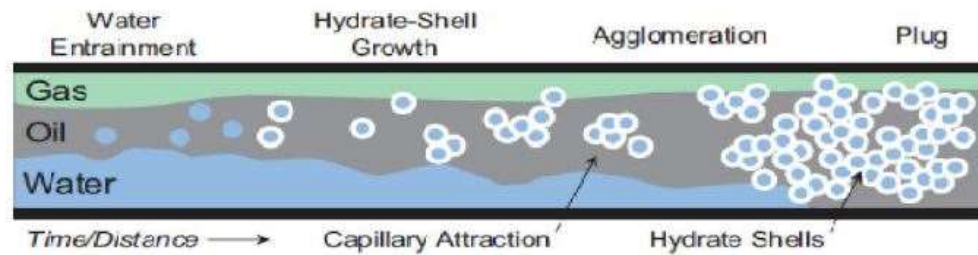
Figure 6 - Conceptual representation of hydrate formation in an oil domination Pipeline

4.1 Other Hydrate Formers

4.1.1 Freons

Freons, organic compounds of chlorine and fluorine, were once commonly employed as refrigerants. Because of environmental concerns, their use has been curtailed; however, many of the Freons are hydrate formers, especially the smaller ones. It is likely that the newer, more environmentally friendly Freons are also hydrate formers. Therefore, hydrate formation may be a problem in a refrigeration loop if it is not dry.

4.1.2 Halogens

The halogens are the elements in column 7A of the periodic table. Of these elements, chlorine and bromine are known hydrate formers. It is likely that fluorine also forms a hydrate based on its size and chemical properties. Historically, chlorine

was the first component definitely shown to form a hydrate. Iodine, another halogen, can form a hydrate only in the presence of another hydrate former (similar to nbutane).

4.1.3 Noble Gases

The following noble gases, also called inert gases argon, krypton, xenon, and radon all form hydrates. As was mentioned earlier, helium, another of the noble gases, does not form a hydrate. It is unlikely that neon, also a small gas, forms a hydrate. This group of gases is remarkable for its chemical stability. Only under extreme conditions can the noble gases be made to react to form compounds. The fact that they form hydrates is a good indication that no chemical bonding exists between the host and guest molecules in a hydrate.

4.1.4 Air

Among the other important compounds that form a hydrate is oxygen. Because it is known that nitrogen also forms a hydrate, then air also forms a hydrate. Both oxygen and nitrogen form hydrates at very high pressures; therefore, it was once thought that they did not form hydrates.

4.1.5 Others

Sulfur dioxide also forms a hydrate. This is somewhat surprising because SO_2 is fairly soluble in water. This is probably the most soluble component that still forms

a hydrate. As a rule of thumb, gases more soluble than SO_2 do not form hydrates. Small mercaptans (e.g., methanethiol, ethanethiol, and propanethiol) are also hydrate formers. Another interesting compound that forms a hydrate is ethylene oxide. Ethylene oxide is an important industrial chemical, usually as a precursor to other chemicals.

Other hydrate formers include N_2O, H_2Se, SF_6, PH_3, ASH_3, SbH_3, and $C10_3F$. Obviously, this list of compounds is of little interest to the natural gas industry. It is interesting, however, to see the wide spectrum of components that do form hydrates.

4.2 Hydrate Formation and Growth in Pipeline

Hydrate formation begins when temperature drops below a certain level and starts to nucleate close to the hydrocarbon phase on a water droplet in gas, oil or condensate phases. Along the surface of a droplet, hydrate will grow until it is completely covered with a thin hydrate layer. Then, from the interior of the water droplet to the surface of the hydrophilic hydrate, water will penetrate next to the hydrocarbon phase through micro perforations or small cracks in the hydrate film as shown in Figure 1. Hydrate formation rate will decrease with the increase in the thickness of the hydrate layer, depending on the shear forces on the droplets and the hydrate formation driving force, within a relatively short time.
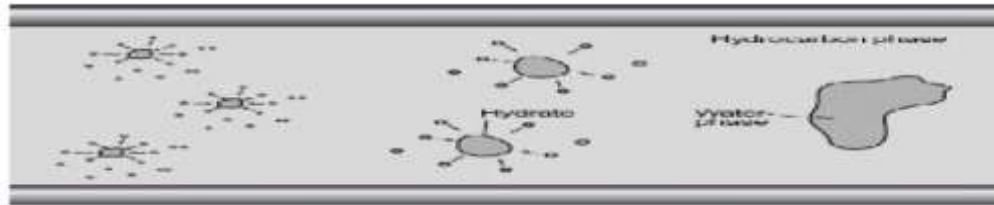
Figure 7 : Agglomeration of water droplets after hydrate initiation

When the water droplets covered by a hydrate film hits the pipe or a reactor's wall in a turbulent system, the impact created may create a large crack in the film. The sub cooled water inside the droplet will then drain out through these cracks, and spread on the dry hydrophilic hydrate film, creating a sticky film. This can often result in hydrate deposition on the wall of a pipeline.

The water phases in turbulent liquid systems are often distributed in the hydrocarbon phase as rough, unstable water-in-oil emulsions. As the surface tension of the droplets increase due to the hydrate layer, the water droplets agglomerate to larger droplets in order to minimize surface area, as shown in Figure 2.

Figure 8 : Hydrate covered with water droplet inside larger water lumps

The surface area and the volume of water lump will continuously change its form in a turbulent liquid systems. This will result in breaking down of the thin hydrate layer on the water lump, giving new water-hydrocarbon interfaces where more hydrates form quickly. Also, the turbulent forces would as well create small hydrate covered with water droplets as shown Figure 3. These droplets will be absorbed in the water lumps giving a slush-like appearance due to hydrophilic nature of the hydrate surface.
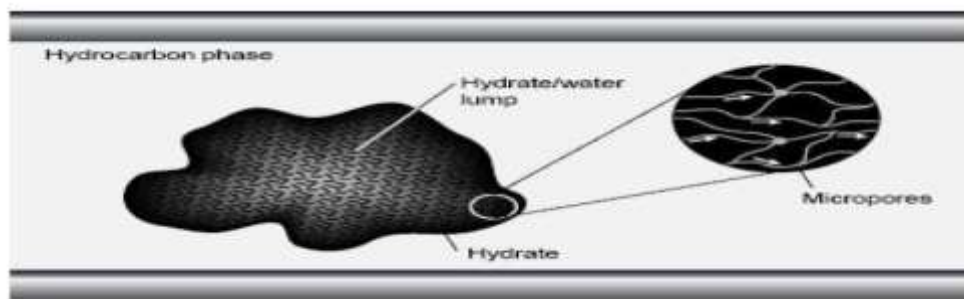
Figure 9 : Conversation of water hydrate by water transport to surface of large lumps

Further growth and particle accumulation will cause the outer area of the lumps to stiffen. When these lumps collide with one another and the walls of the pipe, free water from the lump interior will spread out to the surface of the hydrate and will act as glue to enhance agglomeration in further collisions. The hydrate layer covering lumps or plugs increases in thickness until internal pressure gradients due to capillary forces and volume changes, break it down to smaller hydrate particles as shown in Figure 4. This process continues until the lumps have been broken down to a powder-

like appearance, assuming that the flow conditions can be maintained throughout the process. In a reality, the pipeline will likely be plugged before this stage is reached.

Figure 10 : Break-up of large hydrate lumps

Chapter 5   Hydrates Mitigation

5.0 Methods to Mitigate Hydrates

The formation of the hydrates can be prevented by dehydrating the gas or liquid to eliminate the formation of a condensed water (liquid or solid) to eliminate the formation of the condensed water (solid or liquid) phase. There are four methods to prevent hydration:

- Controlling pressure (the lower pressure the less hydration but in gas transporting lines it's impossible because of reinforcing gas pressure for transporting it)

- Controlling temperature (heating the system by electrical heating so as to prevent from reaching hydrate formation point)

- Removing water (water in pipe lines should be removed. In spite of this, there is always some water along with gas.)

- Injecting chemical inhibitors (these inhibitors prevent hydrate formation and are prior to other methods)

In some cases dehydration may not be practically or economically possible. In these cases, chemical inhibition will be the effective method of preventing the hydrate formation.

As mentioned earlier, the formation of hydrates requires four essential elements to be present. A supply of hydrate forming guest molecules, a supply of water and a combination of high pressures and/or low temperatures. Strategies for hydrate

mitigation and remediation often modify one or more of these elements to destabilise the hydrate and thus remove the problem.

However, hydrates can also be prevented by the injection of chemical inhibitors which seek to modify the chemistry of hydrate formation such that the system is operated outside the hydrate envelope or the kinetics of hydrate formation do not allow hydrates to form blockages during transit through the production system. The various methods of hydrate control can be summarized as follows:

5.1 Pressure Control

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

5.2 Temperature Control

Maintain the temperature of the production fluids by either passive insulation or active heating (e.g. direct electrical heating) in order to prevent the system entering the hydrate envelope. The use of insulation to maintain the temperatures of production fluids outside the hydrate envelope at system operating pressures is an

established approach to hydrate prevention during normal operation, particularly in black oil systems where hydrate prevention may often be a 'byproduct' of wax prevention.

However, temperature control by passive insulation only offers hydrate control during normal operation when the system is being continually heated by hot production fluids. Following a shutdown the production fluids will cool down and can enter the hydrate envelope. Under these circumstances the traditional approach has been to depressure the system as discussed above, although recently active heating has been installed to prevent cooldown into the hydrate region by maintaining temperatures.

5.3 Remove Supply of Water

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.

5.4 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 processing facilities in separate pipelines. The gas pipeline still requires hydrate

inhibition (through chemical inhibitors) but the liquids line (containing oil and water) is able to operate satisfactorily without forming hydrates due to the absence of hydrate formers. It is not known whether such a system has yet been installed and operated in this way.

5.5 Inject Chemical Inhibitors

Inject chemical inhibitors into the system which modify the hydrate phase diagram or the kinetics/morphology of hydrate formation. Along with the use of insulation for temperature control , the injection of chemical inhibitors has also found widespread application. The use of chemical inhibitors is a main focus of this paper and is discussed in more detail in the next section.

Hydrate inhibition using chemical inhibitors remains the most widely used method in the industry. The development of cost effective alternative and environmentally acceptable hydrate inhibitors is a technological challenge for the oil and gas industry. Inhibitors are added into processing lines to inhibit the formation of hydrates.

Types of Chemical Hydrates Inhibitors are

- Thermodynamic inhibitors
- Low dosage hydrate inhibitors (LDHIs)
    - ✓ Kinetic hydrate inhibitors (KHIs)
    - ✓ Antiagglomerants (AAs)

Chapter 6 Thermodynamic inhibitors

6.0 Introduction to Thermodynamic inhibitors

Thermodynamic inhibitors prevent hydrate formation by shifting the freezing /hydrate- formation point of water. If enough of a thermodynamic inhibitor is in place, typically hydrate formation should not be a problem. Common thermodynamic inhibitors are methanol and ethylene glycol. In glycol ethylene glycol (MEG), diethylene glycol (DEG), and triethylene glycol (TEG) glycols have been used for hydrate inhibition. The most popular is been ethylene glycol because it has low viscosity, lower in cost, and lower solubility in liquid hydrocarbons. Besides the above-mentioned organic inhibitors, inorganic acid solution (dilute electrolyte solution), including those of sodium chloride, calcium chloride, and lithium chloride, can also be used. As far as effectiveness, nonpoisonous nature and low cost are concerned, calcium chloride is the best choice. Sodium chloride is also frequently used. But the corrosivity of its dilute electrolyte solution restricts its applications under many conditions.

The thermodynamic hydrate inhibitors (THIs) have been used for a long time in the industry and they act as antifreeze. The most commonly used THIs are methanol and mono-ethyleneglycol (MEG). Other chemicals such as diethylene glycol (DEG), and triethylene glycol (TEG) are also used but will not be specifically considered in this work.

The main principle behind this method is that, it prevents hydrate formation by shifting the equilibrium conditions so that lower temperatures and higher pressures are required to form hydrates. This implies that with the addition of THIs (methanol or MEG), hydrate equilibrium curve will be shifted to the left (lower temperature and higher pressure). This alters the thermodynamic equilibrium of water and hydrocarbon molecules and reduces the risk of hydrate formation in the system. This is essentially because, the chemical potentials of hydration are reduced and correct volumes of injection must be ensured. They do not affect the nucleation of hydrate crystals and the growth of crystals into blockage. They only change the temperature and pressure conditions, thereby shifting operating conditions out of stable hydrate region, as illustrated in Figure11 .
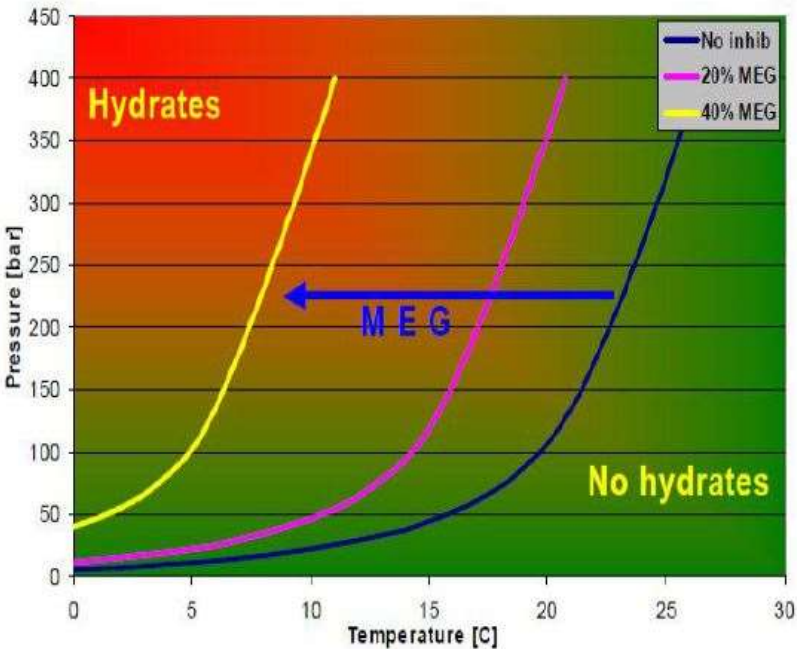
Figure 11 - Gas Hydrate equilibrium curve

6.1 Technical Evaluation of Thermodynamic Inhibitor

Advantages of using methanol

- Methanol is as much cheaper than glycol

- At cryogenic conditions (below -40^0F) methanol usually is preferred because glycol's viscosity makes effective separation difficult.

Limitations of using methanol

- Methanol has become the preferred method of chemical treatment to inhibit hydrate formation. However, the use of methanol, while effective at controlling hydrate growth when properly applied, has numerous drawbacks. These drawbacks can include salt and scale precipitation, increased corrosion risk due to dissolved oxygen, and an increased risk of hydrate formation if an insufficient volume of methanol is used

- Due to the above factors, maintenance cost of the pipeline increases

- Methanol cannot be regenerated as glycol

- Methanol has been found to reduce the effectiveness of some corrosion inhibitors

- Methanol losses to the gas and hydrocarbon phases can be significant

Advantages of using glycol

- For continuous injection in services down to -40^{0}F, one of the glycols are usually used because it offers an economic advantage versus methanol recovered by distillation

- Glycol systems can be preferably used because it can be regenerated, but again the problem lies with the transportation of the regenerated glycol to the offshore systems and the cost of building the glycol regeneration unit

- Maintenance cost of the pipeline decreases

Limitations of using glycol

- A common environmental concern with operating glycol units is the rate of harmful emissions from the glycol regenerator. In many cases, the inlet feed to the glycol unit contains small quantities of aromatic hydrocarbons that are quite soluble in the glycol. The aromatics are primarily composed of benzene, toluene, ethylbenzene, or xylenes (BTEX). These aromatics travel to the regenerator where the application of heat removes virtually all volatile gases.

- Since the regenerator is usually vented to the atmosphere, the plant may have a serious environmental impact

- Regeneration cost as well as the maintenance and operating cost of the pipeline from the regenerating point to the pumping station are to be considered and economic analysis verses methanol is to be considered

- Cannot achieve dew point low enough for cryogenic applications

- Glycol can be easily contaminated and will become corrosive

Advantages of using Potassium Formate

Due to their high density, HCOOK solutions are the most effective hydrate inhibitors on a volumetric dosing basis and as a consequence the storage volume requirements for formates should be lower than for methanol or MEG. Reduced transport costs will bean advantage for HCOOK, but it will probably have no practical consequences except in circumstances where inhibitor transportation in supply boats is a significant operational cost element. HCOOK has minimal volubility in hydrocarbons, and so contamination of the hydrocarbon phases will not be an issue. HCOOK does not have a scaling tendency and is, in fact, a sulphate scale dissolver at high concentrations, One disadvantage of this scale-dissolving activity is that the fluid might gradually pick up contaminating ions which could eventually cause corrosion problems, together with the deposition of insoluble solids and an accumulation of radioactive isotopes from the scale.

HCOOK is hardly corrosive at alkaline pH but it would be prudent to formulate the product with a pH buffer and corrosion inhibitor if the gas phase of the pipeline contains acid gases. Ethylene glycol and HCOOK are both readily biodegradable, but the biological oxygen demand of HCOOK is ten times lower than for the glycol. The volubility of hazardous volatile aromatic (BTX) compounds is higher in ethylene glycol than in HCOOK. Hence formate is more favorable from an environmental perspective. From an overall safety perspective formates are also much

more desirable than the other hydrate inhibitors. These Health Safety and Environmental benefits provided by HCOOK are not easy to measure economically, but they are nevertheless important factors to be considered in the process of choosing the best hydrate inhibitor for a gas pipeline.

6.1.1 Hydrate Formation Temperature Calculation Method

The minimum inhibitor concentration in the free water phase may be approximated by Hammerschmidt's equation

$$d = \frac{K * X1}{MW(1 - X1)}$$

Where K is constant with respective to each inhibitor (glycols = 2335 to 4000 and methanol) = 2335

d is the temperature lowering for the formation of hydrate

K is a constant specific to each inhibitor

MW is the molecular weight of the inhibitor

X is the mole concentration of the inhibitor.

Hammerschmidt's equation cannot be used beyond 20-25 wt% for methanol and 60-70 wt% for the glycols. For methanol and 60-70 wt% for the glycols. Foe the

methanol concentration up to about 50%, the Nielsen-Bucklin equation provides the better accuracy.

Nielsen-Bucklin equation

$$d = -129.6\ln(Xh)$$

Where Xh is the mole fraction of water.

The mass of inhibitor required in the water phase may be calculated from

$$d = \frac{X(R) - m(h)}{X(L) - X(R)}$$

Where X_R is the mole concentration of the inhibitor

m(h) is the amount of water condensed

X_L is the mole fraction of the inhibitor injected.

6.1.2 Economic evaluation of THI's

Hydrate prevention with methanol or MEG can be very expensive due to high effective dosages required, 20 to 50 percent of the water phase. MEG is usually recovered downstream and recycled while methanol is not usually recovered. But the selection of either methanol or MEG for deep water hydrate inhibition usually involves comparison of many factors such as capital and operating costs, site-specific conditions and previous experiences.

Methanol is less expensive per gallon than MEG. Typically, methanol is used without regeneration because it reacts with the gas phase and its total volume can be as high as twice the volume of water. This results in the allocation of large amount of storage and transportation volumes. As earlier said, it needs to be injected in very large quantities, from 30 weight percent to 60 weight percent. This can cause price escalation around $60,000 per day for using THIs. The respective cost of Methanol, MEG and TEG is NOK 3, 5 and 7 per litre (sources according to 2005 statistics).

The controlling factor is the product of chemical cost and gallons consumed. Thus, chemical losses rather than price per gallon can have the greatest bearing on chemical costs. MEG is added in equal amount to the amount of water in the petroleum. This drives the cost for MEG injection system up, in addition to a costly pipeline diameter. MEG is recovered, regenerated and reused when utilized for hydrate inhibition. For subsea production systems, separation of produced water on the sea floor is not normally possible as salt water associated with the produced gas will distribute into and be separated with the rich glycol phase. Since all the MEG cannot be regenerated, extra cost will be acquired as MEG will be reclaimed and new MEG slowly added. MEG is generally associated with high CAPEX because of the equipment needed to regenerate it. An oil system will need even larger pipeline diameter, thus increasing the price of the pipelines. It is normal to use an insulated pipeline in combination with injection of methanol. The price of a thermal insulated pipeline is around $1 million per kilometer. Also, a large portion of heat is required to regenerate MEG, as all the water needs to be boiled out and this again can add to the cost acquired.

However, since large quantities may be necessary to suppress the equilibrium temperature below the lowest operational temperature expected in the system, the infrastructure cost may add up to significant or humongous amounts. Necessary considerations to make when designing for a hydrate strategy with thermodynamic inhibitors are storage volumes and regeneration facilities. It will cost from around $7,000 million and upwards for a system with regeneration facilities. Depending on the regeneration needed, the cost will be from $180 million and up and cost will reduce without a regeneration system.

The reinjection pipeline cost can be calculated relative to length and diameter of other pipelines. Moreover, the need for injection valves, a tank to store the chemicals and powerful pumps will also add to the cost of the system. This would cost around $1 million, $27 million and $1.6 million respectively.

Chapter 7   Low dosage hydrate inhibitors

7.0 Introduction to Low dosage hydrate inhibitors (LDHIs)

LDHI's have made an impact in the industry as a viable, and in some cases, required treatment methodology for hydrate control. LDHI's consist of two different classes of compounds, kinetic inhibitors and anti-agglomerants. The term "LDHI" was coined because these products can be used at comparatively low concentration levels (0.25 – 0.50 % by volume in produced water) compared to the higher required concentrations of more traditional thermodynamic inhibitors such as methanol. A further difference between LDHI's and thermodynamic inhibitors is the inhibition mechanism. Neither of these two methods alters the hydrate equilibrium point of a system as thermodynamic inhibitors do. Kinetic inhibitors will alter the reaction rate while anti-agglomerants will allow hydrate formation but not agglomeration.

Low-dosage hydrate inhibitors (LDHIs) have recently been developed and their usage modifies the rheology of the system rather than changing its thermodynamic state. The low dosage hydrate inhibitor is divided into kinetic hydrate inhibitors (KHIs), and Antiagglomerant (AAs). These types of chemicals would be considered in this section.

Low dosage hydrate inhibitors (LDHIs) was coined because they can be used at comparatively low concentration levels (0.25 – 0.50 percent by volume in produced water), when compared to the higher concentrations required of more traditional

thermodynamic inhibitors such as methanol. LDHIs do not significantly change the hydrate equilibrium curve unlike thermodynamic inhibitors. They rather work at low Concentrations , lower than or equal to one (1) weight percent. Therefore, the use of this technique reduces the environmental concerns and since no regeneration units are required, it results in reduction of capital cost. LDHI was initially produced to prevent hydrate formation in deep-water, and also to transport multiphase hydrocarbon. But is now also used when transporting wet gas in pipelines in the Middle East since hydrate can easily form due to the condensation of water from the gas.

7.1 Kinetic hydrate inhibitor

Kinetic hydrate inhibitors (KHI) work by delaying hydrate crystal nucleation and/or growth until the fluids in question are brought to a zone where hydrates are unstable. Kinetic inhibitors are chemicals that have the ability to increase the induction time for a hydrate crystal to begin growing. Their unique chemical structure significantly reduces the rate of nucleation and hydrate formation without altering the thermodynamic hydrate formation conditions. This mechanism is different from methanol and glycol. KHI blends are usually applied in one of two different methods. One method is to apply the blend neat without a supplementary methanol injection. Another method is to apply it, along with methanol, either through separate injection points or mixed into methanol and applied as a single injection. KHI's used as an

additive to methanol injection provide both an increase to the sub cooling tolerance of the treatment while routinely reducing the overall injection rate by 40 – 60% to that of methanol alone, or more, depending on the system treated.

A kinetic hydrate inhibitor (KHI) delays hydrate formation for a period of time, also known as the induction period. This period is system specific and as such, KHIs are designed to meet individual facility requirements. It can delay the onset of hydrate formation time from hours to days. Residence time should be shorter than the induction time as illustrated in Figure 24. This implies that, as induction time is increased to a value higher than the residence time, hydrate will not be formed during its passage through the pipeline. But if the transit time through the pipeline is sufficiently long, and during shutdown for instance, hydrates will be formed and plugged the pipeline.

KHIs are typically most effective in low-to-moderate hydrate formation conditions. They are applicable to both gas and oil systems and are able to prevent hydrates up to around 18 -20 °F subcooling. Subcooling is the difference in temperature between the actual working conditions of a system to the hydrate formation point. The first generations of KHI were very effective in controlling hydrates up to 8 °C subcooling and with extension of induction time to 24 hours. For the latest technology, the application window has expanded to 13 °C subcooling and for at least a 48 hours shut-in protection.

The limit of subcooling for best KHI is 14 – 15 °C. KHIs have subcooling limits rather than water-cut limits, and can work even at 100% water cut . KHIs are

not limited by gas oil ratio and water cut experienced in the produced fluids, but high water cut and high gas oil ratio, will result in difficulty of fluid transportation.
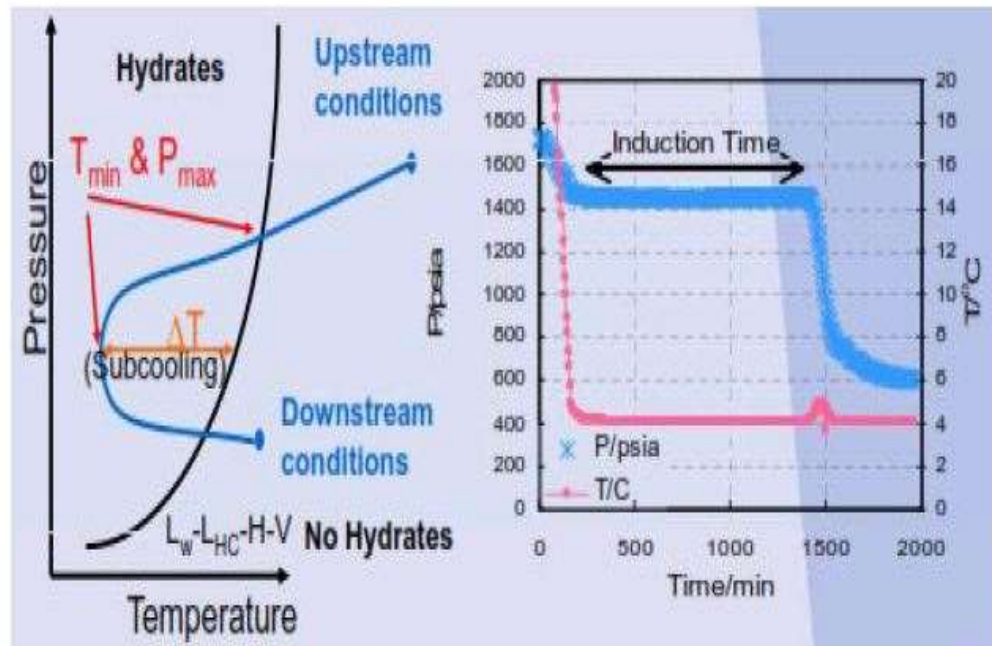
Figure 12 - Hydrate prevention with KHI's

KHIs are commonly water-soluble polymers which delays the nucleation and growth of hydrate crystals until the produced fluids are brought to a zone where hydrates are unstable. Some KHIs also are incompatible with corrosion inhibitors. Kinetic hydrate inhibitors are injected in much smaller quantities compared to thermodynamic inhibitors. Therefore it offers a significant potential costs savings, depending on the pricing policies of major chemical suppliers. A hydrocarbon liquid

phase as a carrier is not necessary for KHIs, as it is not limited by the water cut as long as it is in sufficient amount in the aqueous phase, but $20 - 30$ percent of water cut is preferred in normal operations for KHIs.

Two different methods are usually adopted in the application of KHI blends. One method is to apply the blend neat without a supplementary methanol injection. Another method is to apply it along with methanol, either through separate injection points or mixed into methanol and applied as a single injection. KHIs used as an additive to methanol injection provides both an increase to the subcooling tolerance of the treatment while routinely reducing the overall injection rate by $40 - 60$ percent to that of methanol alone, or more, depending on the system treated. The selection of injection method is based primarily upon cost-to-treat and the required effectiveness of the program. Typical examples of KHIs include: polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap).

Advantages of KHIs

- Significantly lower inhibitor concentrations and therefore dosage rates. Concentrations range from 0.1 to 1.0 weight percentage polymer in the free water phase, whereas alcohols can be as high as 50 %

- Lower inhibitor loss caused by evaporation, particularly compared to methanol

- Reduced capital expenses

- Reducing operating expenses

- Increased production rates

Limitations of KHIs

Although KHIs are applicable under most producing conditions, certain conditions should be considered when evaluating a potential application, which include water salinity, freezing conditions, hold time, water saturation, and high temperature process.

- At water salinity levels greater than approximately 17% NaCl, the polymer may not be so effective.

- A solution of KHI in water does not provide protection from freezing or icing conditions, neither in the line being treated nor in the KHI storage tank.

- A solution of KHI cannot be used for melting ice or hydrates plugs.

- KHI delivery system must be capable of providing sufficient dosage to achieve the hold time greater than the water residence time in the piping.

- If the gas is unsaturated with respective to water, the water in KHI solution will evaporate and leave a high viscosity fluid.

- Any fault associated with the pouring system and the well not closed regularly or the insufficient use of inhibitor will cause hydrate blocking, and under these conditions, Kinetic inhibitor cannot be applied. The hydrate blocking can be prevented by the addition of methanol or by adopting the

pressure drop method. Therefore, in actual application a combination of kinetic inhibitor and thermodynamic inhibitor are used to solve the hydrate-plugging problem.

7.2 Antiagglomerant inhibitors

Unlike KHIs, which delay the formation of the hydrates, Antiagglomerant (AAs) allow the formation at normal rates, but as small nonagglomeranting hydrate crystals that are dispersed into oil or condensate thus preventing the formation or accumulation of the large hydrate crystals. It was developed put of the necessity to extend the range of sub cooling of LDHIs beyond that of that of KHIs. AAs can achieve sub cooling of greater than $40\,^0$F.

Anti-agglomerants (AAs) are surface active chemicals (surfactants). They allow hydrate crystals to form but prevent them from agglomerating and adhering to pipe walls. This means that, they allow hydrates to form, but as tiny, non adherent particles that are easily dispersed into the liquid hydrocarbon phase. As the viscosity remains low, this will allow the hydrates formed to be transported with the produced fluids. AAs do not have subcooling limitations but have been found to be effective in low to extreme hydrate stable regions, even during extended shut in periods.

The design of the AA molecule is similar to foaming surfactants used for gas well deliquification. A foaming surfactant has a hydrophilic (water-attracting) head and a hydrophobic (water-repelling) tail. The molecule's head is attracted to the

hydrate and becomes part of the hydrate crystal. The tail portion is dispersible in hydrocarbon liquids and causes the crystal to be dispersed into a hydrocarbon phase. The dispersion hinders the formation of larger crystals which would then be less likely to cause plugs.
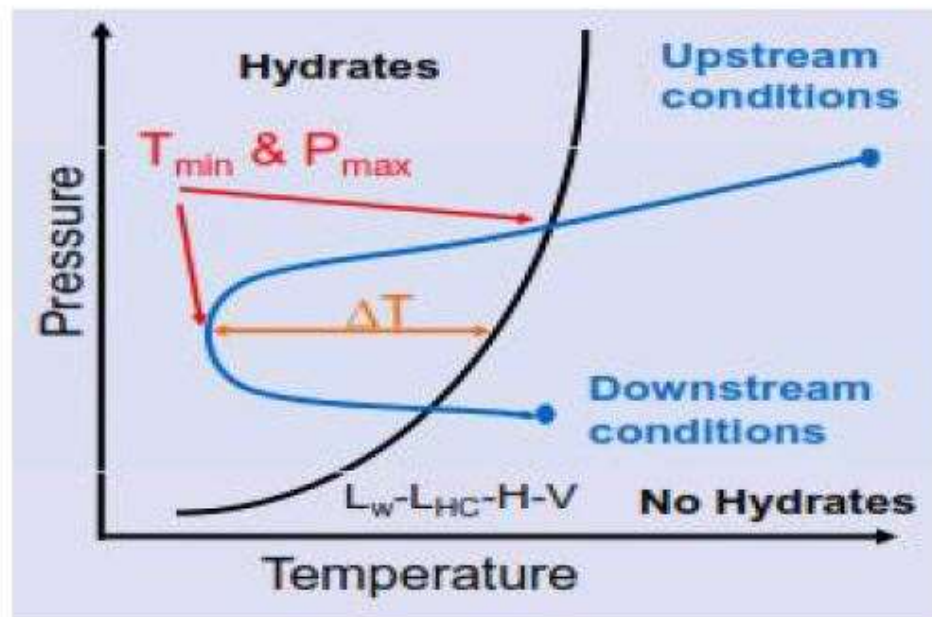
Figure 13 - Hydrate Prevention with AA's

Since hydrate crystal is formed and dispersed, subcooling or residence time limitations has been eliminated, as shown in Figure 13. There are two classes of AAs commercially in use. These include; pipeline or production AAs and gas well AAs. The former allows formation of hydrates as transportable non-sticky slurry particles dispersed in the liquid hydrocarbon phase while the later disperses hydrate particles in excess water. However, as a side effect on dispersion requirement, AAs requires the presence of a liquid hydrocarbon phase to provide effective inhibition. Typically, the water cut must be below 25 – 50 percent for AAs to be effective. It also shows a gas-

to-liquid (GOR) limitation. Above this range, hydrate particles concentration in the slurry becomes so high that AAs are no longer able to allow the transport of the suspension. A rule of thumb for AAs to be effective is that a GOR should be less than 100,000 scf/stb.

Consequently, AAs effectiveness is dependent on the type of oil/condensate, the salinity of the formation water and the water cut. Pipeline operation can also be of importance as dispersion of small hydrate crystals will be favored by higher velocities. At low flow rates and during shutdown conditions, the crystals may settle out and agglomerate when the oil density difference is sufficient. The anti-agglomerants provide protection up to 40:60 water oil ratios. Typical examples of AAs include alkyl aromatic sulphonates or alkylphenylethoxylates

As such, AA inhibitor is an economically attractive option under severe hydrate-forming conditions and is also very effective where production is shut-in for extended periods.

Advantages of AA's

- Significantly lower inhibitor concentrations and therefore dosage rates. Concentrations range from 0.1 to 1.0 weight percentage polymer in the free water phase, whereas alcohols can be as high as 50 %

- Lower inhibitor loss caused by evaporation, particularly compared to methanol

- Reduced capital expenses

- Reducing operating expenses

- Increased production rates

Limitations of AAs

- Some AAs have a maximum salinity criterion that is normally not exceeded with produced water

- Since AAs are based on dispersing polar hydrate crystals in a nonpolar oil or condensate phase, they may sometimes require a de-emulsifier for oil and water separation. Further heat coil inside a separator may be required to melt the hydrate crystals

- Since AAs are dispersed in the liquid hydrocarbon, viscosity included with the steady state flow are considered

- AAs can impact the performance of some metallurgy and elastomers, so impacts on existing hardware should be reviewed

- They require a continuous oil phase and therefore only applicable at lower watercuts.

7.3 Economic evaluation of LDHI's

LDHIs are more cost effective than THIs, and the shift from THIs to LDHIs is driven by economics. Among these economic drivers include: facilitation of higher production rates in THIs (Methanol) volume-limited system, CAPEX and OPEX reduction through system designs where fewer umbilical lines, smaller and lighter

storage capacity, and smaller pumps are required. Drastic reduction in volumes required of LDHIs leads to a whole host of potential cost savings when compared to Methanol. Insulated pipeline are normally used with chemical injection which costs around $1 million per kilometer.

Though the chemicals are expensive, only less than one percent by weight is required of LDHIs to prevent hydrate formation. LDHIs cost approximately NOK 65 to 100/ kg or $4 – 6/lb. It takes 0.5 weight percent of LDHI to treat 11^0C subcooling which is equivalent to using 25 weight percent methanol or about 40 weight percent MEG. Also, an average cost KHIs is $5 – 6 per Litre, which makes it nearly the same as operational expenditure as using THIs. The selling prices of specialty chemical LDHIs are significantly higher than the commodity chemicals (Methanol and MEG). LDHIs are typically sold for tens of dollars per gallon, whereas Methanol is typically $0.30 - $0.90/gal and MEG is typically $1.75 - $3.75/gal.

Table 3 -Cost comparison of KHI's and AA's

CHEMICAL INJECTOR	COST PER LITRE IN ($ US)
Methanol	0.13$
Mono Ethylene Glycol	0.64$
Tetra Ethylene Glycol	0.89$
Potassium Formate	0.68$
Kinetic Hydrate Inhibitor's	5-6$

Chapter 8   Case Studies on KHI and AA

8.1 Case History on KHI - 1

A large sweet gas field was operated by a producer in northern British Columbia that had winter access-only roads for the majority of the field. During the warmer months, when the winter roads could not be used, methanol was required to be flown in to replenish tanks. The cost to fly in methanol during the summer months was high; therefore, alternatives to straight methanol injection were sought.

A system assessment was performed and a hydrate equilibrium curve was generated. Subcooling for the field were found to be between 3 to 5^0C during summer months. Methanol injection rates were originally between 50 to 100 L/day for the majority of the field. A KHI mixture with methanol was selected as the most economic means of treatment. A KHI blend was mixed into the methanol tanks to make a 5% solution and was applied initially to selected well sites as a test of viability. It was discovered that the test wells were able to lower the overall treating rates by 60% and not result in hydrate formation. Over time, the program was expanded to encompass the majority of the field with little to no issues.

The hydrate inhibitor program was considered a success as the methanol injection rates were lowered sufficiently to allow onsite tankage to be sufficient to

control hydrate formation throughout the summer months. In many cases, fly-in methanol / KHI tank fills were not required until winter access was resumed.

8.2 Case History on KHI – 2

A producer in central Alberta operated a 5 km long sales line requiring on average 600 L/day of methanol to prevent hydrate formation. Production through the flow line was 400 e^{3}m^3/day of sweet gas along with 10 m^3/day of condensate. Water production through the line was estimated by the producer to be approximately 1m^3/day, although this was not accurately metered. The line was mostly downhill with few liquid hold ups. Pigging was conducted monthly or as required, whichever came first, and no hydrates were ever discovered. Hydrate formation was not a typical issue for the line, but was generally avoided at all cost through high methanol injection rates.

The production parameters were reviewed and it was decided that a KHI would be a good option to trial to reduce the daily methanol injection volume. A KHI blend was added to methanol to make a 10 percent solution. Initial optimizations were able to reduce the methanol rate to approximately 250 L/day with no hydrate formation issues. Optimizations are ongoing and lower injection rates are expected to be reached. The program was considered a success as the methanol injection rate was dropped considerably and hydrate formation was not observed.

8.3 Case History on KHI – 3

A producer in central Alberta operates a sales line that typically carries 100 e^3m^3/day of gas production containing 2000 ppm H_2S, along with approximately 50 L/day each of condensate and water. Prior to entering the line, production is separated to remove hydrocarbon liquids and water. . Saturated gas entered the flow line at 27^oC and exited the line at 8^oC. The line temperature was determined to be stable throughout winter and summer. Line pressure was again fairly stable at 4350 kPa. Subcooling for the system was determined to be 8^oC. The calculated methanol volume required to inhibit hydrate formation was approximately 64 L/day. Historically hydrates were found during the pigging operation. The flow line was periodically pigged, but was not on a regular basis.

Upon calculating the methanol partition volumes for the production, a KHI blend was applied neat without methanol injection. Initial injection rate was set at 10 L/day. Optimizations brought the neat KHI injection down to 6 L/day. The neat KHI hydrate inhibitor.

8.4 Case History on AA – 1

A producer drilled a number of new oil wells in northern Alberta. As they began to bring them online, it was discovered that they were prone to both extreme paraffin and hydrate issues. The wellhead temperature was found to be below the

cloud point of the oil, causing the production of a paraffin stabilized emulsion. One such well-produced on average 9 m^3/day of 19,000 ppm TDS brine, 36 m^3/day oil, and 4 e^{3}m^3/day of sour gas into a flow line over 9 km long. If the well was allowed to flow, it would produce, on average, one hour before the flow line would plug with hydrates and then production would cease. Additionally, no convenient location for methanol injection was available for injecting methanol to dissolve the hydrate blockage. To remove hydrate plugs, the lines required depressurizing on both sides of the plug to portable pressure vessels and flare stacks. The hydrates were then allowed to disassociate naturally under controlled, depressurized conditions. This proved to be a slow process, requiring long production down times and significant operator time.

The production parameters were investigated and a hydrate equilibrium curve was generated. It was discovered that the system subcooling was approximately 16°C for the produced gas. Calculations showed that the system required a minimum of approximately 4800 L/day of methanol to inhibit hydrate formation effectively.

The following is a timeline of events for the hydrate inhibitor trials:

1. Methanol injected at steadily increasing rates until 6000 L/day reached, hydrate plugs formed.

2. It was determined that wax may be inhibiting ability of methanol to reach water phase. Attempts made to mitigate wax formation unsuccessful.

3. AA blend injected at 200 L/day, no hydrate formation noted.

4. 25% KHI blend in methanol solution injected up to 6000 L/day, hydrate plugs formed.

5. AA blend injection re-instituted, again, no hydrate formation resulted.

Optimizations were performed and it was found that the AA injection rate was able to be dropped by 55% (optimized injection rate 90 L/day) without hydrate plug formation being noted. The AA blend was brought in to use at more wells displaying similar production issues to the initial well and all responded to the treatment like the first well. The AA application was considered a great success. Wells were able to produce continuously without hydrate plug formation using a relatively low injection rate in an application where even high volumes of methanol, and a KHI and methanol mixture, were proven unsuccessful.

8.5 Case History on AA – 2

A producer operated a number of wells in central Alberta that were found to be prone to severe hydrate blockages during the winter when flow line temperatures dropped. It was not economical for the wells to be flowed from November through May due to the hydrate issues. With relatively high methanol injection rates, weekly hydrate blockages would still result. Therefore, from November through May, the

wells would be shut-in and the flow issues avoided. Typical daily production on one such well in operation was 2 m^3 of water, 3.5 m^3 of oil, and 0.5 e^{3}m^3 of gas. Line pressure for the gathering system was low at 1000kPa although the flowing temperature was expected to be highly variable.

Production data was used to develop a hydrate equilibrium curve. After reviewing the data and the curve it was decided that the wells would be a good candidate for a trial using an AA blend. An AA was selected for this treatment due to the low water rate and the unknown day- to-day flow line temperature. For one such well, an AA blend was initially trialled at 15 L/day to make a blend concentration of 7500 ppm in the produced water. The AA was applied with no supplementary

methanol injection. No hydrate blockages were noted and the chemical was optimized down at regular intervals. The end result was that the minimum pump rate of 3.5 L/day was realized with no hydrate blockages noted during the entire winter. This injection rate resulted in a blend concentration of 1750 ppm in the produced water. The AA application was considered a success because wells that would typically be shut in for winter were able to be flowed with a low injection rate of neat hydrate inhibitor.

8.6 Results and discussions on case histories

Currently, LDHIs are now widely used in the industry and as such can be regarded as proven technology, following a number of successful trials and field experience. The usage of KHI was primarily limited to onshore fields and relatively shallow offshore system, but several deepwater projects have now been considered.

As shown by several case histories, hydrate inhibitors can be excellent alternatives to the use of straight methanol. With proper implementation and optimization, significant reductions to methanol volumes can be introduced to a hydrate inhibition program. In some cases the use of neat methanol can be completely replaced by low injection rates of the correct hydrate inhibitor.

It has been shown that this new type of additive can bring significant benefits in terms of additional production, HSE improvements and OPEX savings. Both KHI's and AA's alone or in combination with methanol were evaluated. A step methodology for evaluation of LDHI's for field implementation was developed and implemented. The combination of KHI+methanol was identified as the best option.

Chapter 9   Conclusion

Today's Kinetic Inhibitors (KIs) have limited applications as they only work down to certain subcoolings, perhaps 10"C at most. The oil industry would obviously like a chemical that is twice as effective for many subsea and/or cold climate applications.

Anti-agglomerators (AAs) could solve this problem as they do not appear to be dependent on the subcooling, and so theoretically can be used at any line pressure and temperature. However, they have several possible drawbacks. The effect of the AA appears to be dependent on a) the hydrocarbon fluid composition, b) the brine concentration and c) the water cut. This may mean different AAs need to be developed for different crudes. The AA must also remain active at varying brine concentrations and increasing water cuts as water breakthroughs occur and the field matures.

As today's AAs cannot handle very high water cuts, KIs may be the only new option at very high water cuts as long as the subcooling is not too high. Consequently, the new generation of hydrate inhibitors may find their limitations for very high water cut with very high subcoolings. Technology development should concentrate on extending these limits always bearing in mind cost-effectivity and environmental considerations.

Two types of inhibitors are described in this article, they are thermodynamic hydrate inhibitors and Low dosage hydrate inhibitors. From the economic evaluations

of methanol and mono-ethylene glycol as the inhibitors in a pipeline it is concluded that using 10-50% inhibitors for the pipeline could restrict the hydrate formation. LDHI's were also studied. They are divided into polymers and surface-active agents. LDHI's are found to be advantages over THI's because of its lower weight percentage used and also by reducing the operating cost of pipeline. In practice it is better to use LDHI's along with the THI's for the better results.

Chapter 10 References

1. Gas Processing and Suppliers Association (GSPA) 12th Edition FPS version – 'Engineering Data Book'.

2. KIMBERLY C. COVINGTON, JOHN T. COLLIE III, Bryan Research & Engineering, 'Selection of Hydrate Separation Methods for Gas Streams'.

3. Zarinabadi, Soroush, Samimi, Amir, "Problems of hydrate formation in oil and gas pipes deal," Australian journal of basic and applied science, 2011

4. Hammerschmidt, E.G.: "Formation of Gas Hydrates in Natural Gas Transmission Lines," Ind. & Eng. Chem. (1934) v. 26, 851.

5. Clathrate, Merriam – Webster.com, Retrieved Sept. 02, 2009, http://www.merriam-webster.com/dictionary/hydrate

6. Hydrate, Merriam – Webster.com, Retrieved Sept. 02, 2009, http://www.merriam-webster.com/dictionary/hydrate

7. Buzatoiu, B. and Popp, V.V.: "Hydrate Problem in the Oil Production Industry," SPE 50749, 1999.

8. J. E. Paez, R. Block, H. Vaziri and M. R. Islam: "Problems in Hydrates: Mechanisms and Elimination Methods." SPE 67322, 2001.

9. Len. W. Clark, Joanne Anderson: "Low Dosage Hydrate Inhibitors (LDHI): Further Advances and Development in Flow Assurance Technology and Applications Concerning Oil and Gas Production Systems." IPTC 11538, 2007.

10. Boxall, J. and May, E. (2011): Formation of Gas Hydrate Blockages in Under-Inhibited Conditions. 7th Int'l Conference on Gas Hydrates (ICGH 2011), Edinburgh, July 17-21, 2011.

11. Carroll, J.J. (2009). Natural Gas Hydrates: A Guide for Engineers. Gulf Professional Publishing, Elsevier, 30 Corporate Drive, Suite 400, Burlington, MA 01803, USA. 2nd Edition.

12. M.B Tomson, A.T. Kan, G. Fu, M. Al-Thubaiti, Dong Shen and Heather J. Shipley: "Scale Formation and Prevention in the Presence of Hydrate Inhibitors." SPE 80255, 2006.

13. M.H. Yousif: "Effect of Under inhibition With Methanol and Ethylene Glycol on the Hydrate-Control Process." SPE 50972, 1998.

14. Tohidi, B. (2006): Novel Hydrate Based Systems. International Patent No. WO 2006/048666A2.

15. Tohidi, B. (2011): Gas Hydrates Challenges in Oil and Gas Industry. Centre for Gas Hydrate Research, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh, EH14 4AS, UK.

Chapter 11   Appendix

MATLAB Coding for Calculation of Freezing point Temperature and Weight percentage of Methanol Injection

Ms=18.015;

R=8.314;

Tm=273.15;

hsl=6006;

Mi=32.042;

Wi=10;

delta_T=((Ms*R*Tm*2)/hsl)*(Wi/((100-Wi)*Mi));

W=(100*32.042*10)/(1297+(32.042*10));

MATLAB Coding for Calculation of Freezing point Temperature and Weight percentage of Glycol Injection

```
Ms=18.015;

R=8.314;

Tm=273.15;

hsl=6006;

Mi=32.042;

Wi=10;

delta_T=((Ms*R*Tm*2)/hsl)*(Wi/((100-Wi)*Mi));

W=(100*62.07*10)/(1297+(62.07*10));
```