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Review Article

Gas Hydrate Formation: Impact on Oil and Gas Production and Prevention Strategies

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ABSTRACT

Formation of gas hydrates in oil and gas production systems continue to pose a serious concern particularly in the offshore environment. The formation and possible deposition of hydrates usually occur specifically as gaseous component of reservoir fluid interact with water molecules. Consequently, hydrates problems are commonly encountered during normal multiphase flow and the problem is often more significant in transient operations. Many researchers have extensively studied this subject, yet the extent to which the properties of reservoir fluids interact is still on-going, especially at low temperatures and high pressures. The fundamental technological features of hydrate formation and decomposition or dissociation processes have been poorly understood. Therefore, this paper studied and described the general phenomenon in which hydrates' formation occurs. It also discussed the mechanisms and analyzed the influencing factors that contributed to the formation of hydrates. The new remediation and prevention techniques for hydrates formation and blockages have been reviewed. The technical issues, level of protection, associated risks, and cost impacts were included in evaluating the techniques. The conclusion obtained from this research shows that further works are required to acquire substantial data for the development a new and robust prevention and control strategies, while improving the existing ones for optimum production, transportation and storage of oil and gas products.

1. INTRODUCTION

Currently, the positive aspects of gas hydrate as a new source of energy continue to drive more research and investment particularly in the offshore areas where hydrate reservoir formation is abundant. However, formation of gas hydrates during oil and gas production causes major flow assurance problems similar to other challenges resulting from wax, asphaltenes, slugging, naphthenates, scales, corrosion, erosion and emulsions (Tohidi et al., 1996; Turner, 2005; Bai and Bai, 2005; Sloan et al., 2009; Shuard et al., 2017). Studies by Sloan et al. (2009), Shuard et al. (2017) and Shi et al. (2018) have shown that hydrate plugging constitutes the largest concern by order of magnitude when compared to waxes asphaltenes and scales. The formation of gas hydrate occurs in two forms: a naturally occurring phenomenon (Kezirian and Phoenix, 2017) and action of industrial activities' technogenic gas hydrate', which forms in technological systems created and controlled by humans (Szamałek, 2004). Szamałek's study has shown that the earliest reported gas hydrates were produced in laboratory conditions by Sir Humphrey Davy in 1810 (chlorine hydrate). On the other hand, the first hydrate formation in the oil and gas system was identified in 1934 by an American chemist, E.G. Hammerschmidt. He found that a hydrate of methane in ice obstructed gas flow in natural gas pipes in Russia (Hammerschmidt, 1934).

The presence of hydrate in natural geological conditions, as reported by Szamałek (2004), was confirmed only in 1967 during the prospecting work in Siberia (Messiyakhi hydrocarbon field). Usually, the natural gas hydrate is discovered in permafrost and seabed (Makogon, 1965), with some of its compound postulated to be found in outer space (Iro et al., 2003). Over the last decades, the natural gas hydrate received so much attention due to its potential economic benefit. Tohidi et al. (1993) and Brewer et al. (1997) revealed some of the observed key attribute and potentials benefits of naturally occurring gas hydrate as follows: (1) they contain a great volume of methane, which indicates a potential as a future energy resource (2) they function as a source or sink for atmospheric methane, which may influence global climate, (3) they can affect sediment strength, which can initiate landslides on the slope and rise. Mogbolu and Madu (2014) revealed that the estimated volume of natural methane hydrate deposits is about 120 quintillion cubic meters at standard temperature and pressure. A comprehensive analysis of the production from these in-situ compound can be found in a study conducted by Moridis et. al. (2009).

On the other hand, the gas hydrates derived from industrial activities are prone to causing loss of revenue in oil and gas field, damage and blockages of processing subsea pipelines, valves or processing instrumentation and the overall shut-down of oil and gas system (Bai and Bai, 2005; Sloan et al., 2009; Shuard et al., 2017; Shi et al., 2018). Therefore, studies have shown that hydrate plugging is the most critical tasks that continuously challenges the oil and gas field, especially as oil and gas operations are moving into deepwater reserves. At this point, it is necessary to study the gas hydrate formation mechanism to identify the effective approaches for prevention, remediation and control of the phenomena. With this knowledge, oil and gas operators can ensure adequate hydrate management strategy are in-place during restart operations, particularly after an extended shutdown where the most favourable conditions for gas hydrate formation developed.

2. FORMATION OF GAS HYDRATES IN THE PROCESS FACILITIES

In general, gas hydrates are polycrystalline, non-stoichiometric, and clathrate-structured solid compounds formed by cages of hydrogen-bonded water molecules (which serves as a host) with low boiling gas (as a guest)—typically formed under low temperature (40 ^{o}F) and high pressure (>1000 psi) (Sloan and Koh, 2007; Gao 2008; Dorstewitz and Mewes 1995; Shi et al., 2018). The guest components are usually the light hydrocarbons such as methane, ethane, propane, butane (C_1-C_4) and other inorganic molecules such as H_2S, CO_2, and N_2 (Turner, 2005; Gao, 2008). In the process, water molecules, due to their hydrogen bonding properties, can form cavities, thereby accommodating low molecular weight materials. It is also revealed that the cavities of these hydrogen-bonded water molecules are typically in the form of pentagonal, hexagonal and square faces depending on the crystal structure (Sum, 2013). In the process, examining the size of guest molecules ratio to the cages they occupied can help understand hydrates (Sloan, 2003).

The appearance of crystalline compounds of gas (clathrate) hydrates resembled snow or ice with densities smaller than that of ice (Rao et al., 2013). In some cases, the compound appears as a solid deposit on the cold pipeline surface, similar to wax deposition during production and transportation processes (Aspenes et al., 2010; Rao et al., 2013). Compared to other flow assurance issues such as sand, hydrates are less dense and accumulative when formed, while sand will either remain dispersed in the fluid or settle on the pipe wall depending on the flow rate. At a point and condition where sand forms a small deposit in the pipeline, hydrates formation can accumulate as highly as possible (Singh et al., 2000). Pressure-temperature diagram (Figure 1) have been used to forecast the possible occurrence of some flow assurance issues, such as hydrates, paraffin wax, and asphaltene (Sloan, 2003). For instance, as clearly shown in Figure 1, the right side of the hydrate's equilibrium curve represents the regions with no formation of hydrates crystals. The left of the curves are the regions with hydrate formation.

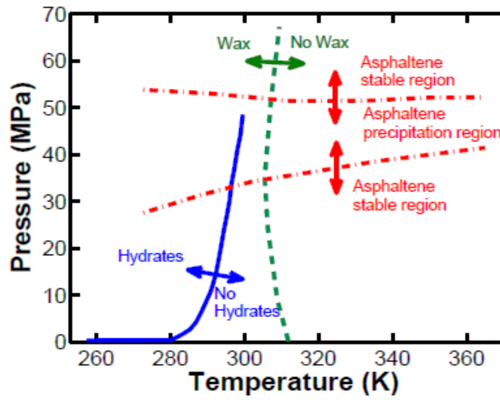


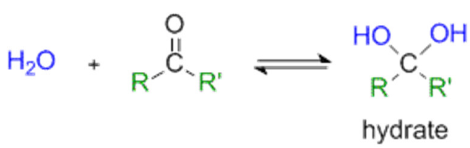
Figure 1: Pressure versus temperature diagram from the characterization of reservoir fluids during oil and gas production of the Gulf of Mexico (Sloan, 2003)

2.1. Structural Formation of Gas Hydrates

As clearly stated in the previous section, gas hydrates structures are formed when small non-polar gas molecules are enclathrated within water molecules. Sloan and Koh (2007) and Moridis et al., (2009) use Equation 1 to describe hydration reaction of a gas, (G) and hydration number, nH at suitable conditions. Complete hydration occurs when nH has an average value of 6.

$$G + n_H H_2 0 = G.n_H H_2 0 \tag{1}$$

For example, a nucleophilic addition reaction of Aldehydes and ketones with water gave 1,1-geminal diols known as hydrates (Equation 2).



(2)

Usually, gas hydrates are classified based on the different structural formation (shown in Figure 2) and further subdivided into three structures. The first two structures are popularly known as structures-I (sI, cubic) and II (sII, cubic) (Zerpa 2013), with the third newly developed hexagonal structure known as structure H (sH, cubic) (Ripmeester et al. 1987). Accordingly, studies on gas hydrate indicate that these structures have different chemical and physical properties formed from hydrogen-bonded water molecules as follows (Ripmeester et al. 1987; Bai and Bai 2005; Sloan and Koh, 2008):

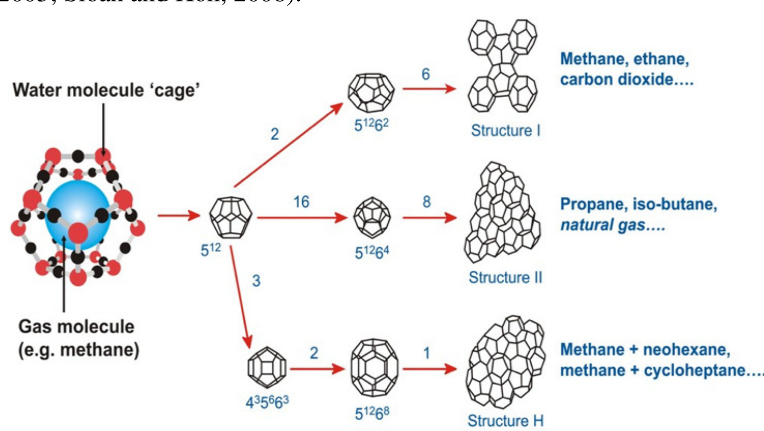


Figure 2: Three structural type of hydrates (Sloan, 2011; Ripmeester et al., 1987)

The structure I (sI): This structure is formed from a mixture of water and hydrocarbons lower than propane and other inorganic gases. The sI structure has a unit cell with 12 Å cube and 46 water molecules and consists of 2 small cages, each formed by 12 pentagonal faces (512) and six large cages, each formed by twelve pentagonal and two hexagonal faces (51262). Generally, small hydrocarbon molecules could quickly stabilize this structure, such as methane and ethane (Bai and Bai, 2005).

Structure II (sII): This structure forms from molecules larger than ethane but less than pentane. They are typical gas hydrate structure encountered in oil and gas pipelines because of the presence of larger hydrocarbon molecules such as propane and iso-butane that fit in the large cage of sII but will not fit in the large cage of sI (Sloan and Koh, 2008). The sII structure is being described with a unit cell with 17.3 Å cube and 136 water molecules. Their molecules consist of 16 small 512 cages and 8 large cages, each formed by 12 pentagonal and 4 hexagonal faces (51264).

Structure H (sH): The size of structure H (sH) type of hydrates allows larger molecules (8–9Å) such as n-butane, it is however, uncommon to the oil industry but has been suggested to exist in the Gulf of Mexico. The unit cell of this structure has 34 water molecules forming a hexagonal lattice with parameters a = 12.26 Å and c = 10.17 Å. Also, consists of 3 small 512 cages, 2 small cages, each formed by three square, six pentagonal and three hexagonal faces (435663) and 1 large cage formed by twelve pentagonal and eight hexagonal faces (51268) (Ripmeester et al. 1987). A specific hydrate structure's stability depends on how easily the guest molecule (gas) would fit inside the host cage (water). Hence, Sloan (1998) summarized the hydrate structure for the three-unit crystal sI, sII, and sH, as shown in Table 1.

Table 1: The geometry of cages in three hydrate crystal structures I, II, and H (Sloan, 1998)

Cavity	sI		sII		sH		
	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^{2}$	5^{12}	$5^{12}6^{4}$	5^{12}	$4^{3}5^{6}6^{3}$	$5^{12}6^{8}$
No. of cavities/unit cell	2	6	16	8	3	2	1
Average cavity radius	3.95	4.33	3.91	4.73	3.91C	4.06^{c}	5.71^{c}
no. of waters/unit cell	46		136		34		

Where superscript ^{c} is the estimates of structure

2.2. Conditions for the Formation of Gas Hydrates

As reviewed in the published literature, if hydrates' formation during production is non-avoidable, then it is necessary to know how they are formed, where they are likely to occur, how much can be expected and how they would influence flowline (Jacobs and Writer, (2015). The studies by Gbaruko et al. (2007), Jacobs and Writer (2015), John (2017) and Lim *et al.* (2020) outlined the following as the key conditions that influence the formation of gas hydrates in a system. (i) Presence of free water: The presence of free water is necessary for the formation of hydrates. It is generally believed that no hydrate formation can be formed without the existence of free water. Therefore, to avoid this problem, it is always significant to remove water vapour from natural gas to avoid the formation of hydrates. (ii) Low temperatures: Temperatures of about 39 °F or higher are critical in any system that desires to avoid hydrates formation. Studies by Jacobs and Writer (2015), John (2017) and Lim *et al.* (2020) has shown that hydrates form when the temperature is below or at the hydrate formation temperature for a given pressure and gas composition. (iii) High operating pressures: Gas hydrates require pressure greater than 166 psig. It is also reported that in some cases, the formation of hydrates does occur at a higher temperature > 70 °F if the pressure is high enough (around 2900 psig or above). (iv) Flow pattern: Studies have shown that hydrodynamic slug flow increases the rate of the formation of hydrates at the head of the slug. This is because of the greater gas-water interfacial area existing at this location. (v) Presence of H_2S and CO_2: These acid gases accelerate hydrate formation. Studies have shown that these are more soluble in water than other hydrocarbons.

Other factors such are high velocities or agitation and/or pressure pulsations, in other words, turbulence is regarded as the catalyst for hydrates formation (John, 2017). Experimental study by Lim *et al.* (2020) revealed a model (Equation 3) that measure the initial hydrate growth rate (*Gi*) under isochoric cooling condition. Gi = (-dn/dt), which is calculated from $\delta p \equiv p_{meas} - p_{isochor}$, where p_{meas} is the measured cell pressure and $p_{isochor}$ is the temperature-pressure trend associated with isochoric cooling. The study by Lim *et al.* uses pressure detection-based technique for hydrate formation detection which enables an extraction of the gas consumption rate, *(-dn/dt),* following formation onset, where n is the molar quantity of gas.

$$\mathrm{G_i} = \left(-\frac{dn}{dt}\right) = \left[\frac{n_g d(\delta p)}{pf dt}\right] \tag{3}$$

Where n_g is the number of moles of methane in the gas phase and *pf* is the formation pressure

2.3. Gas Hydrates Formation Interfaces

Gas hydrates are considered as a multiphase flow problem involving gas, liquid hydrocarbon, water, and hydrates as solids. Therefore, a study by Turner et al. (2015) highlighted five different interfaces where gas hydrates may form and aggregate during oil and gas production: gas/liquid, liquid/liquid, gas/solid, liquid/solid, and solid/solid. Therefore, the gas here is referred to as hydrocarbon gas, while the liquid is oil, water or condensate, and solid is referred to as gas hydrate or pipe wall surface. Consequently, the three-driving force in the process was highlighted by Sloan and Koh, (2007) and Turner et al. (2005) as water entrainment, cooling and pressure elevation. Besides this, the formation process has two major stages, namely, nucleation (nanoscopic) and growth (macroscopic), which occurs in the following way:

$$Water\ Entrainment \rightarrow Hydrate\ Nucleation \rightarrow Hydrate\ Growth \rightarrow Agglomeration \rightarrow Plugging$$

Figures 3 and 4 illustrate the various stages and a conceptual view on how hydrates may form and agglomerate to block the flow line containing gas, oil and water. The model was originally adapted by Sum (2013) from Turner (2005). Turner (2005) developed this model with input from J. Abrahamson (University of Canterbury, Christchurch, NZ).

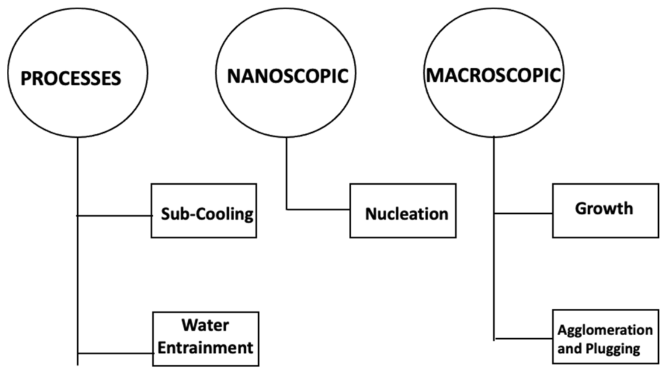


Figure 3: Stages of hydrate formation and plugging (adapted from Mogbolu and Madu, 2014)

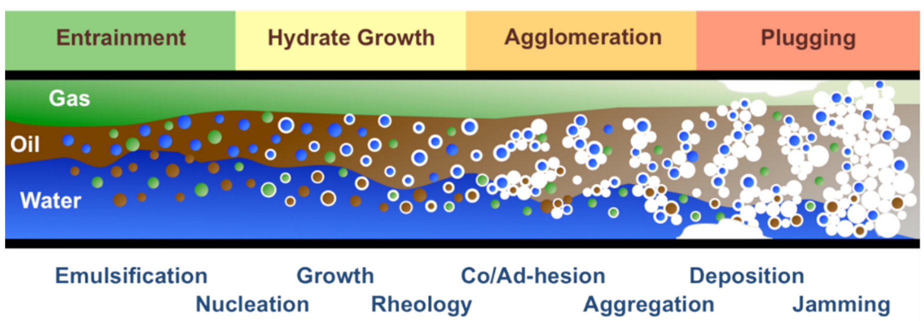


Figure 4: Typical conceptual hydrates formation model in a multiphase flow system (Turner 2005; Sum 2013)

As pointed out by Turner (2005) and Sum (2013), Figure 4 revealed that at the beginning of production, three-phases (involving oil, water and gas) are emulsified, which creates gas bubbles entrained in the oil and water, oil emulsified in water, and water emulsified in oil, which consequently developed a surface area for hydrate formation. Hydrate's formation begins as soon as the system's temperature and pressure reach a point within the hydrates stability region. This occurs at the interface between the water and hydrocarbon fluid (oil or gas), forming a shell structure around the water/oil droplets (emulsified in oil/water). Sum (2013) reported that pipe walls are another possible location for hydrates to initially form in the form of deposits, as these will be wet and exposed to the gas. As a typical mass transfer and/or heat transfer limited process, the growth of hydrates continues after this stage. Comparably, in the former stage, water and/or gas must diffuse to the interface, and in the latter stage, heat must be removed as the hydrate formation is an exothermic process (Sloan and Koh, 2008). It is paramount to mention that hydrate slurry in the system changes the rheology behaviour of the flowing fluid when a sufficient hydrate is formed (Camargo and Palermo, 2002).

Once hydrate particles interact and agglomerate into larger aggregates, the particles continually grow and form larger hydrate masses and deposition, leading to increased slurry viscosity, causing an unacceptable large pressure to drop in the line, prohibiting flow and eventually creating a plug. Sum (2013) and Turner (2005) revealed that if the hydrate particles are dispersed in a water-continuous phase, the binding force between the hydrate particles is minimal, and they will remain dispersed. On the other hand, if the particles are dispersed in an oil-continuous phase, the particles may bind to form large aggregates due to the water capillary bridging formed between the particles. The last stage of the conceptual model is the jamming of hydrate particles and continual deposit on the pipe wall. These are said to be responsible for the flowline blockages under steady-state operation, as these particles can slowly and continuously build-up over time (Rao et al., 2013), similar to wax/asphaltene deposition (Singh et al., 2000). Understanding how these particles jam is vital to the oil and gas field to develop a strategy that can prevent, manage, and remediate the system.

3. HYDRATE PREVENTION, REMEDIATION AND CONTROL

As an essential flow assurance problem, the formation of gas hydrate and possible blockages in petroleum transportation systems have attracted significant attention from both academic and industrial communities (Sloan, 2003; Shi et al., 2018) The standard remedies for hydrate flow assurance include the traditional control methods of injecting thermodynamic inhibitors/anti-agglomerant or applying thermal insulation that assure the operational conditions outside of the hydrate formation region (Shi et al., 2018; Chua and Kelland, 2018). On the other hand, the conventional strategy to manage hydrates during restart operations is aimed at preventing the formation of hydrates entirely using a combination of chemical inhibition and thermal control. However, the cost and technical limitations of this technique increase with increase in depth particularly for deep-water offshore petroleum exploitations. A paradigm shift is currently underway that is challenging the notion that complete avoidance of hydrate formation is a necessary step to provide adequate flow assurance. Authors such as Turner et al. (2015), and Zerpa et al. (2012) have provided the basis to explore alternative solutions that reduce the risk of hydrate plugging in flowlines, without the explicit requirement that hydrates need to be avoided entirely.

A risk-management technique, as pointed out by Shi et al. (2018) is by utilizing cold flow, and hydrate slurry, which was proposed by Gudmundsson (2002), and Turner and Talley (2008), wherein hydrates are allowed to form and made to flow with the help of anti-agglomerants (AAs) (Turner et al. (2015). As reported by Shi et al. (2018), significant effort have been devoted by several researchers to promote the application of this technology, including studies on the mechanisms of hydrate formation, deposition, blockage, dissociation, and remediation (Kakati et al., 2017; Song et al., 2017). Others include the studies of the rheological properties of hydrate slurry (Raman et al., 2016) and the flow characteristics of hydrate slurry (Ding et al., 2016; Pandey et al., 2017).

3.1. Hydrate Prevention Methods

Basically, there are four ways hydrate formation could be prevented: separation of water to reduce the gas dew point, the use of inhibitor, controlling the system temperature and pressure These methods are used independently or in combination with one another. However, studies have shown that the most favourable and desired option for the oil and gas industry is to avoid operating within the hydrate formation region (Forsdyke, 1997; Sloan, 2003). However, this is an inevitable requirement due to an unplanned shut-down or abnormal operating conditions originating from equipment malfunction (Sum, 2013). Therefore, over many years, several industries have employed different approaches to prevent gas hydrates formation in flowlines. Studies have indicated the following as the most promising method.

3.1.1. Injecting hydrates inhibitors

The chemical inhibitors commonly used are thermodynamic hydrate inhibitors (THIs) and low-dosage hydrate inhibitors (LDHIs) (Bai and Bai, 2005; Kakati et al., 2017; Song et al., 2017; Shi et al., 2018; Lim *et al.*, 2020). It is worth noting that the selection of the hydrate inhibitor is an important decision in the oil and gas field, especially at the early Front-end engineering and design (FEED) (Bai and Bai, 2005). Bai and Bai (2005) outline the following criteria involved in the selection of inhibitors for prevention and remediation strategy:

- Capital costs of topsides process equipment (especially for regeneration)
- Capital costs of subsea equipment
- Topside’s weight/area limitations
- Environmental limits on overboard discharge
- Contamination of the hydrocarbon fluid and impacts on downstream transport/processing
- Safety considerations
- System operability
- Local availability of inhibitor

The thermodynamic Hydrate Inhibitors (THIs): THIs such as methanol (MeOH), monoethylene glycol (MEG) or ethanol has traditionally been used in the industry to inhibit hydrate formation in the free water phase. In choosing the effective THI inhibitor, the cost implications, the quantity of chemicals required, suitability due to health, safety, and environmental (HSE) together with deployment issues may be crucial. Studies have shown that, as production from offshore gas wells moves into the colder and deeper region, the conventional methods using THI face challenges such as high injection rate and large storage requirement.

Figure 5 shows hydrates equilibrium boundaries curves with and without THI (methanol) in the free water phase. As shown in the Figure below, the thermodynamic hydrates inhibitors (THI) shift the hydrate equilibrium curve to safe conditions, allowing the flowline to operate outside the hydrate stability region. This is observed by adding 10 to 30% MeOH concentration. From this Figure, it is clearly shown that a methanol concentration >20% is required to completely inhibit hydrate formation in this system. According to Cha et al. (2013), there have been little works that measured the hydrate equilibrium conditions with MEG concentrations higher than 30 wt%.

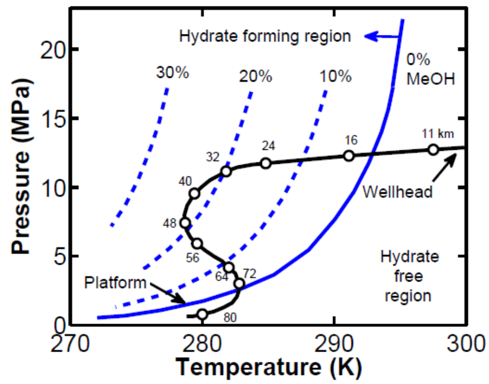


Figure 5: Subsea flowline operation conditions curve for hydrates formation with and without methanol as THI (Sloan and Koh 2008)

If health, safety, and environmental (HSE) issues are to be considered, the use of MEG over methanol is favored mostly by the oil and gas industry as shown in Table 2 (Cha et al., 2013). Based on their studies Cochran and Gudimetla, (2004) and Bai and Bai (2005) summarized the advantages and disadvantages of methanol and MEG inhibitors as shown in Table 2.

Table 2: Comparison of methanol (MeOH) and MEG (Cochran and Gudimetla, 2004)

THI	Advantages	Disadvantages
Methanol	i. Move hydrates formation temperature more than MEG in a mass basis	i. Losses of methanol to gas and condensate phases can be significant, leading to a lower recovery (<80%)
	ii. Less viscous	ii. Impact of methanol contamination in downstream processing
	iii. Less likely to cause salt precipitation	iii. Low flashpoint
	iv. The relative cost of the regeneration system is less than MEG	iv. Environmental limitation on overboard discharge.
Monoethylene glycol	i. Easy to recover with the recovery of 99%	i. High viscosity impacts umbilical and pump requirements
	ii. Low gas & condensate solubility	ii. Less applicable for restarts stays with aqueous phase at the bottom of pipe
	iii. Approximate Gulf of Mexico cost of 2.5$/gal	iii. More likely to cause salt precipitation.

Low-dosage hydrates inhibitors (LDHIs): In recent times, the industrial standard shifts from time-independent method of hydrate prevention towards time-dependent hydrate management; these include Low Dosage Hydrate Inhibitors (LDHIs) that offered significantly lower concentration to prevent the formation of hydrates than thermodynamic inhibitors (less than 1 % by weight) (Bai and Bai 2005; Kelland 2006). These inhibitors interfere either with the formation of hydrate crystals or the agglomeration of crystals into blockages. According to different studies LDHIs fall into two categories: kinetic hydrates inhibitors (KHI) and anti-agglomerants inhibitors (AAs) (Forsdyke, 1997; Kelland 2006). KHI was reported to be water-soluble polymers used to suppress nucleation. These include homo- and co-polymers of the N-vinyl pyrrolidone and N-vinyl caprolactam (Kelland, 2006; Chua et al., 2012). However, the main drawback of KHI is that they only suppress nucleation without prevention. However, after having a successful field trial in the Southern North Sea, the Kinetic inhibitors are now used commercially in the wet gas system (Corrigan et al., 1995; Argo et al., 1997).

Bai and Bai (2005) described anti-agglomerants as surfactants, which cause the water phase to be suspended as small droplets. He also states that anti-agglomerants can provide protection at higher subcooling than kinetic hydrate inhibitors, but the drawback is that they are more expensive than KHI and are not recoverable at low dosage. This type of inhibitor (AAs) inhibits hydrate plugging rather than hydrate formation, which is sufficient for deep-water applications and has completed successful field trials in deep-water Gulf of Mexico production system as reported by Bai and Bai (2005). However, the effectiveness of this inhibitor can be affected by the type of oil, the salinity of the water, and the water cut. Cochran (2003) summarized the following drawback of AA's which include:

- High cost per unit volume
- Toxicity concerns
- Less effective at high water cuts
- May need to break the water-in-oil emulsion
- Materials and chemical compatibility
- Testing with a representative fluid sample recommended
- Potential impacts on downstream facilities

3.1.2. Heat retention

This involved heating the gas stream and maintaining flow lines and equipment at a temperature above the hydrate region. However, according to Forsdyke (1997), these can be very effective for short subsea flowlines, likely to be inadequate for flowlines with significant length. One major example is a 30km pipe-in-pipe system currently installed in the North Sea. No matter the kind of insulation considered, another complementary form of technique will always be required. In another development, heat is added through (1) Electrical heating: – This technique can be applied for continuous operation, shut-down, and restarts. (2) Hot fluid circulation: – This method is usually applied in a bundle plan, which contains production lines and heating lines together. Similarly, the method can be used for continuous operation, shutdown, and restarts. (3) Hot oil circulation: – Hot dead oil is circulated to warm flow lines and risers prior to restarting wells or during a shut-down until the system is restarted (Cochran, 2003). All these possible technologies are able to prevent and remediate (as described in a subsequent section) hydrates formation, but all are somewhat not economical and, as yet, do not have an acceptable record of accomplishment (Forsdyke, 1997).

3.1.3. Low-pressure operation

If hydrates formation prevention is desired, the operating pressure of the system must be kept lower than the pressure corresponding to $\leq$300 psia at the ambient temperature around 4 ^{o}C for deep-water operation (Cochran, 2003).

3.1.4. Water removal

Water is the main component for hydrates formation, without water in the system no hydrate formation will occur (Cochran, 2003). According to studies by Bai and Bai (2005) water can be reduced from the separation system in a flowline using a common method called dehydration. This method can also increase recovery of reserves and decrease the topsides water handling, treatment and disposal. One of the advantages of this technique is its suitability in a long-distance tieback (Cochran, 2003).

3.2. Remediation Method

While industrial design intended to prevent hydrate formation and plug the pipeline, the design also considers provisions for remediation of the blocked (Figure 6) pipeline, which may occur as previously mentioned due to unplanned shut-down or abnormal operating conditions originating from an equipment malfunction. A hydrate blockage remediation plan should be developed where hydrate formation is predicted and/or consider to be an issue of concern. The remediation methods are similar to the prevention methods, which include (Bai and Bai 2005; Turner, 2005):

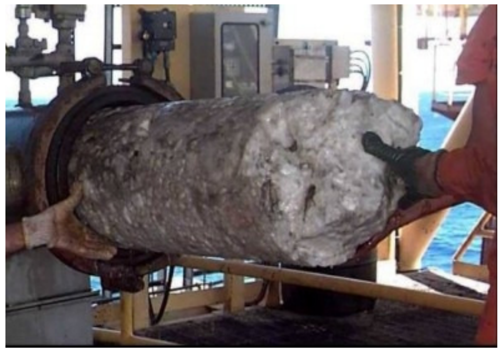


Figure 6: Gas hydrate blockages formed in a subsea hydrocarbon pipeline (Heriot-Watt University, 2014)

3.2.1. Depressurization of pipeline

Generally, depressurization entails reducing the pressure below the hydrate formation pressure at an ambient temperature sufficiently enough to reverse the equilibrium reaction (Zou, 2013). However, rapid depressurization should be avoided as this can worsen the hydrate problem and form ice (Bai and Bai, 2005). The technique is economically feasible and is suitable where gas hydrates is in contact with conventional gas reservoir, particularly for a gas bearing formation that has higher permeability and at higher depth (700m) (Zou, 2013).

3.2.2. Thermodynamic inhibitors

If chemical inhibitors are designed for the purpose of remediation, essentially, they act by melting the blockages of solid hydrates with direct contact. Studies have shown that methanol can be pumped down the tube to the target blockage point with coiled tubing that reached as far as 14800 ft (Bai and Bai, 2005).

3.2.3. Active heating

Similarly, active heating is also reported as another remediation method (Cochran, 2003 and Bai and Bai, 2005). This method is carried out by increasing the temperature of the system above the hydrate dissociation temperature. Therefore, an adequate amount of heat is required to quickly dissociate the formed solid hydrate to prevent build-up pressure and possibly flowline rupture. Similar to the prevention method; electrical heating, and/or hot fluid circulation in pipe bundle to the system can be used as remedial action following a shut-down.

3.2.4. Mechanical methods

Unlike wax deposition remediation techniques, a pigging method is not recommended for removing blockage system with hydrates because they can cause more harm. Previous studies show that drilling, pigging or scraping has been attempted without fruitful result (Turner, 2005; Bai and Bai, 2005). Therefore, these methods are generally not recommended. However, a coiled tube is recommended, installed and tested with the support of a lubricator (Turner, 2005; Bai and Bai, 2005).

3.3. Control Methods

Understanding the pressure and temperature conditions and/or the locations in which the gas hydrates form is paramount. It forms the basis of any model designed for controlling hydrate formation in a system. Several computer modelling and simulators were reported for this purpose (Edmonds et al., 1996; Tohidi et al., 1996; Turner et al., 2015). A state of the art "OLGA®" modelling and simulation software developed by the Institute for Energy Technology in Norway in 1979 is used for transient analysis to study the behaviour of a system during start-up and shutdown operations. OLGA was the oil and gas industry's first transient multiphase flow model that has been used to predict temperatures and pressures in the production system. It can signal an alarm for any hydrate formation conditions and other flow assurances problem. Other modelling software includes tools like CSMHyFAST and CSMGem, which predict the necessary thermodynamic conditions for hydrate stability (Ballard 2002), and hydrate kinetics model called the Colorado School of Mines Hydrate Kinetics model (CSMHyK), which is integrated into the OLGA multiphase simulator (Turner 2005). Another tool that is developed to estimate the dissociation of the hydrate plug is CSMPlug (Sum, 2013). Therefore, in order to fully comprehend the system behaviour and control the formation of hydrates, this paper highlighted the general philosophy and the guidelines to hydrates control that have been employed in the subsea hydrocarbons system design and operations as follows (Cochran, 2003 and Bai and Bai, 2005):

- Keep the entire production system out of the hydrate formation envelope during all operations, which may be accomplished by various means. Current knowledge is insufficient to design a system to operate in the hydrate region without hydrate or blockage formation
- Use chemical inhibitors only for start-up/shut-down operations and not for continuous operation
- Insulate flowlines and risers for heat retention during normal operation and provide reaction time during the shut-down. Consider insulating subsea equipment (trees, jumpers, and manifolds)
- Consider wellbore insulation to provide fast warm-up during restart operations and to increase operating temperatures during low-rate operation
- Determine minimum production rates and flowing wellhead temperatures and check consistency with technical and economic criteria
- Establish well, and flowline start-up rates to minimize inhibitor injection while assuring that the system warms in an acceptable amount of time
- Ramp-up well production rates sufficiently fast to outrun hydrate blockage formation in wellbores
- Provide system design and operating strategies to ensure the system can be safely shut down. These strategies are not intended to cover true emergencies
- Provide protection for wells during shutdowns
- Monitor water production from individual wells
- Located surface control subsurface safety valve (SCSSV) at a depth where the geothermal temperature is higher than hydrate temperature at shut-in pressure
- Consider self-draining jumpers and manifolds
- Remediate hydrate blockages via depressurization or heating
- Provide remediation procedures for all locations in the production system
- Provide for depressurization on both sides of a blockage

Other development includes a novel insulation technique known as deep-water flowline burial. This method was successfully applied by the Shell (Angus field flowlines) (Cochran, 2003). The main flow assurance advantage to burial is that it can potentially give very long cool downtimes and long warm-up times during restart (Cochran, 2003).

As shown in Table 3, this paper summarized some of the hydrate control techniques employed by the oil and gas field, in accordance with a survey reported by Cochran (2003). This summary captured most of the developed practice used by different fields. It is obvious that trends were identified, insulation is almost always the most promising and usually applied to flowlines and risers. Another trend has shown that the use of methanol as a chemical inhibitor for restarts, spot treating during the shut-down, or displacement is commonly used. However, ethanol (as an alternative) has been used in Brazil because of the cost. As pointed out, all the developments are designed to permit injecting chemical inhibitors into the system. Whereas hot oil circulation, which is also a commonly used technique to warm deep-water flowlines and risers in a cold restart. However, depressurization or displacement is frequently followed after shutdowns to protect flowlines and risers. For blockage remediation, depressurization is the most commonly used technique, whereas active heating is the main alternative method.

Table 3: Hydrate control techniques used by industries from an open literature (Cochran 2003)

Operator and field	Hydrate control technique	Comment	References
BP Troika Gulf of Mexico	• Insulated dual flowlines with target overall heat transfer coefficient of 1.0 W/m^2/°C (pipe-in-pipe design with pressurized nitrogen at 99 bara in the annulus). Insulated trees, jumpers, manifold. Vacuum-insulated tubing in a wellbore • Methanol injection downhole and/or manifold during restart until the system has warmed. Methanol injection for spot treating following the shut-down • Depressurization for the shut-down • Depressurization for blockage remediation	• Oil development • Water depth 825 m and 22.5-km tieback distance • Note that arrival temperatures were lower than anticipated. Greater than expected heat loss due to convection of high-pressure nitrogen and the nature of the open cell insulation foam	Beckmann et al. (2001)
Petrobras Roncador Offshore Brazil	• Single rigid flowlines insulated with sold polypropylene. Required UID of 5.95 W/m^2/K for the flowlines • Some continuous operation within the hydrate region is tolerated. Based on previous operating experience and flow loop tests with oil samples, it is believed hydrate crystals will form but will not form blockages. • Later life at higher water cuts (>19%) injection of a kinetic inhibitor is planned for some wells	• Oil development • 31° API oil, the cloud point of 14 °C. • Water depths from 1400 to 2000 m • Tieback distance averages 8 km • 31° API oil, cloud point of 14 °C	Minami et al. (2000) Azevedo et al. (2000)
Petrobras Marlim Offshore Brazil	• Flexible flowline sand risers; some are insulated • Prior to restart, pig to displace water from flowlines • Ethanol injection at the tree • Wax control is a more significant design driver • Remediation via depressurization.	• Oil development • Tieback distance averages 8 km • Water depths from 620 to 1100 m • Minimum ambient seabed temperatures range from 4 to 6 °C	Silva et al. (1999) Porciuncula et al. (1999)
Petro-Canada Terra Nova North Atlantic	• Dual flexible flowlines and risers with insulation. Flowlines are trenched and backfilled. Trees, jumpers, and manifolds are insulated to provide cool down time equivalent to flowlines. • Normal operation is above hydrate conditions. Minimum arrival conditions are 23 bara and 46 °C • Hot oil circulation for the warm-up of flowlines/risers prior to restart. • For planned shut-downs, methanol will be injected prior to shut down if water cuts are low or the flowlines will be displaced with dead oil, or the flowlines will be depressurized. • For unplanned shutdowns, the flowlines will be depressurized.	• Oil development • Water depth 94 m • Minimum seabed temperature of -2°C • Tie back distance 2 km • In determining methanol requirements, the design does not take credit for inhibition due to salts in the formation water.	Stephens et al. (2000)
Norsk Hydro Troll Oil North Sea	• Thermal insulation to avoid continuous methanol injection during normal production and to provide minimum 8-hour cool downtime following the shut-down	• Oil development • Water depth 310 m	Fadnes et al. (1994)

Operator and field	Hydrate control technique	Comment	References
	• Depressurization of flowlines during unplanned and planned shutdowns. • Displacement and circulation with hot stabilized oil through the gathering lines for all clusters to warm up the lines and reduce methanol consumption during restart. • Removal of hydrate plugs by depressurization from both sides, combined with methanol if possible.		
Shell Serrano / Oregano Gulf of Mexico	• Single flowlines for each development. • Insulation is pipe-in-pipe for continuous operation. • Electrical heating for short-term shutdown and/or restart. Electrical heating is not applied while system is producing. • Depressurization for long-term shutdown. • Electrical heating for remediation (faster than depressurization).	• Multiple field gas and oil development • 9.7 km and 12 km tieback distance • Water depth ~1040 m	Von Flatern (2001)
Total Fina Elf Girassol Offshore West Africa	• Insulated bundle containing dual production flowlines and a service line surrounded by syntactic foam. Bundle filled with inhibited water. • Insulated riser tower containing multiple flowlines (production, water injection, gas lift, service), syntactic foam, and inhibited water. • Insulated subsea equipment. • Insulation to provide arrival temperatures greater than 40 °C and cooldown time of 16 hours. • Methanol for inhibitor	• Oil development • Water depth 1350 m • Tieback distance up to 7 km	Cochran (2003)

4. CONCLUSION

Pipelines hydrate formation and blockage is a critical problem in oil pipeline transportation and its severity increases in deep-water offshore environment. This work illustrates and explains the formation of gas hydrates particularly during the oil and gas production. The study has demonstrated the conditions for the formation hydrates and defined different modelling software that can be used to predict the on-set of hydrate formation in the pipeline, such as OLGA multiphase simulator, CSMHyK, CSMHyFAST and CSMGem. It is worth noting that these prediction tools are essential in developing hydrate's prevention and remediation strategies. Similarly, the study discussed the relationships among reservoir and flowline conditions (e.g., phase equilibria and fluid properties) that must be met for the formation or prevention of gas hydrates – includes chemicals inhibitors, active heating and pigging process (as remediation method). On the other hand, the study has explicitly demonstrated how time-independent properties such as cavity size ratio, geometrical properties of structure sI and sII are determined. Based on the understanding of the mechanism of hydrate formation, a significant development of the knowledge of gas hydrate treatments in oil and gas pipelines has been made. However, further study is suggested to fully establish the sH structure of hydrates. Similarly, it is important to stress out the need for further research and development; for instance, there is need for a new and robust prevention and control strategies, while improving the existing ones for optimum production, transportation and storage of oil and gas.

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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