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COLD FLOW HYDRATE MANAGEMENT METHODS

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Abstract. *Hydrate cold flow can be defined as flow of non-adhesive and non-cohesive hydrate particles dispersed in the production fluids at ambient temperatures. Cold flow related hydrate management strategies might significantly reduce the costs of oil and gas field development and production by removing or reducing the need for injection of chemicals, insulation and heating. One purposed method of producing hydrate dispersion is seeding of hydrate particles into the production fluids at hydrate equilibrium conditions to initiate controlled growth of hydrates as the dispersion is cooled to ambient temperatures. Use of anti-agglomerants combined with reducing viscosity by increasing water content have been proposed by other researchers. Alternatively, the water droplet size in water in oil dispersions can be reduced by utilizing static mixers or high velocity, which might facilitate readily conversion of the small water droplets into hydrate particles. Flow loop experiments indicate that cold flow works well for low to medium gas/oil ration and up to 20% water cut for both oil and condensate dominated systems. Experiments with crude oils containing wax show that cold flow could significantly reduce or eliminate wax deposition on pipeline walls. A field trial of the cold flow method in a once-through pipeline, which focuses on reducing droplet size, resulted in hydrate deposition.*

Keywords: *gas hydrates, cold flow, hydrate slurry flow, anti-agglomerants, hydrate deposition*

1. INTRODUCTION

Gas hydrates has been known as a challenge for the oil and gas industry since Hammerschmidt (1934) discovered that hydrates caused blockages of pipelines. Avoiding formation of hydrates by injection of thermodynamic inhibitors like methanol and glycols has been the traditional strategy to solve potential hydrate problems, which typically require 10-50 wt.% inhibitor added to the water phase. However, this approach might not be profitable in some cases because of the large inhibitor volume (Sloan *et al*., 2011).

During the past few decades, oil companies has also started using low dosage hydrate inhibitors (LDHIs) as means of inhibiting hydrate blockages, which might be efficient at concentrations as low as 0.01-1.5 wt.% (Mady and Kelland, 2018; Glenat *et al*., 2017a). LDHIs are divided into two main classes: Kinetic Hydrate Inhibitors (KHIs) and Anti-Agglomerates (AAs). The KHIs work by bonding to the hydrate surface and delaying significant crystal growth (Sloan *et al*., 2011). Recent laboratory experiments have demonstrated that certain blends of KHIs can delay measurable hydrate growth for more than 24 h at 15.9 °C subcooling (Mady and Kelland, 2018). AAs are surface active chemicals that prevents agglomeration of hydrates by reducing particle adhesion. Many AA blends contains quaternary ammonium salts as active components. These salts have one or two long chain hydrocarbon tails ($8 - 18$ carbon atoms) and a hydrate-philic head group consisting of two or three n-butyl, n-pentyl, and isopentyl groups. The long chain hydrocarbon tails dissolve in the oil phase and the shorter head group branches penetrate open $5_{12}6_4$ cavities on the hydrate surface (Kelland, 2006).

Researchers started experimental programs on hydrate cold flow in the late 1990s exploring the possibility of forming a dispersion of crude oil or condensate containing non-adhesive and non-cohesive hydrate particles that may be transported at ambient temperatures without using or with minimal use of chemicals. Agglomeration of hydrate particles due to capillary forces from liquid water trapped inside and between the particles is one of the central steps in the conceptual model for hydrate plug formation presented by Turner (2005). Hydrate particles in a cold flow hydrate in oil dispersion do not contain unconverted water, and will therefore not agglomerate and form hydrate plugs. Nicolas *et al*. (2008) measured the adhesive forces between cyclopentane hydrates and carbon steel. They concluded that hydrate particles 3 microns and larger would be removed from the carbon steel surface at flow rates that are typical for offshore pipelines. These non-cohesive properties between two dry hydrate particles, and non-adhesive properties between dry hydrate particles and the pipe wall, might be considered key factors making cold flow a promising alternative to conventional flow assurance strategies. Nevertheless, some of the main challenges with cold flow are connected to the formation of the hydrate in oil dispersion, which requires converting water to dry hydrate particles without agglomeration and deposition on the pipe wall with both water and hydrate present at same time during this conversion process.

The objective of this review is to summarize the research on hydrate cold flow from its beginning in the end of last century until recent years. The methods proposed by the various research groups are briefly explained and main results of autoclave tests, flow loop experiments and a full-scale field trial are presented. Explanations of the physical mechanisms in connection with the presented methods are proposed based on known mechanisms for hydrate formation and accumulation, and areas of application of cold flow are presented. The discussion about AAs is limited to the particular cold flow application that proposes use of AAs as an important component of the technology. Some suggestions are also given for further work to improve the understanding of mechanisms influencing cold flow and determine the window of operation for solid content, flow velocities and flow patterns in pipelines operating with hydrate cold flow.

2. CRYSTAL RECYCLING AND SEEDING

Starting experiments in the late 1990s and continuing through the first decade of this century, the research institute SINTEF developed and tested their patented cold flow process. The central idea of this process is seeding of hydrate crystals to initiate controlled growth of hydrate particles in the bulk flow (Lund *et al*., 2000). This cold flow process was further developed utilizing similar crystal seeding principals for wax, asphaltenes and other solids, which may form during flow of hydrocarbons, a process that is patented by SINTEF and BP in partnership (Argo *et al*., 2004).

Hydrate formation normally requires subcooling of the system to a temperature below the hydrate equilibrium temperature. In a survey involving various flow loops in the US, the average subcooling before hydrate formation was calculated to 3.3 °C (Sloan *et al*., 2011). The pipeline wall will be a natural location for hydrate nucleation both because the temperature of the wall is normally lower than the temperature in the bulk flow, and because the surface conditions require less subcooling to initiate hydrate formation at the wall than in the middle of the bulk flow (Sloan and Koh, 2008). However, in the cold flow process patented by SINTEF, a dispersion of hydrate particles in liquid hydrocarbon (hydrate slurry) is drained from a location in a pipeline at which the well stream has cooled down to a temperature close to the ambient temperature downstream the cooling zone where water is converted to hydrates. This slurry is then pumped upstream and injected into the flow at a location where the mixture product containing gas, liquid hydrocarbon, water and hydrate particles will have a temperature about at hydrate equilibrium. The water will be attracted to the hydrate particles, because of the hydrophilic surface of hydrates, and coat the particles with a thin water layer (Lund and Larsen, 2000). When cooled further while exposed to gas, oil or condensate containing the required guest molecules for hydrate formation, this water coated surface will be converted to hydrates, which results in dry particles as illustrated in Figure 1. In theory, the system will not reach a subcooling necessary for nucleation of new hydrate crystals at other locations than already existing hydrate particles, considering the hydrate formation conditions stay close to equilibrium throughout the growth.

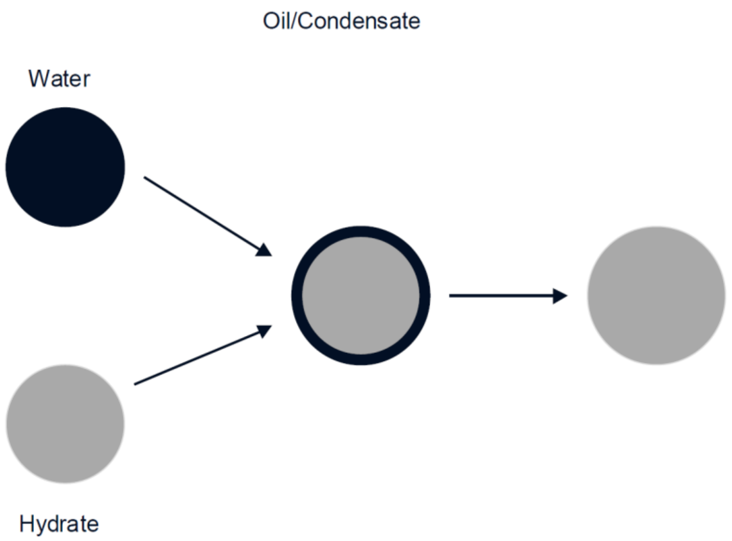

Figure 1. Water layer converting to hydrates (Larsen *et al*., 2001).

2.1 Experimental Results for Hydrates

The cold flow experiments of SINTEF were performed in a 50 m long flow loop with inner pipe diameter of 24.3 mm for the majority of the loop distance, 5 m with inner diameter of 49.3 mm, and with 100 bar operating pressure (Figure 2). The flow loop was contained in a temperature-controlled chamber with temperature set to 4 °C during experiments. The gas phase in the loop was a natural gas mixture dominated by methane with some propane. Both fresh and salt water were tested as water phase, and one condensate-like model oil and various crude oils were tested as oil phase.

The experiments focused on low to mid gas/oil ration (GOR) below 1000 Sm^3/m^3 and were successful at water cut (WC) up to 20% (Lund *et al*., 2010). Shut-in and restart experiments were performed in both the 1-inch flow loop (Figure 2) and the 5-inch wheel flow loop (Figure 3). The absence of hydrate deposition and hydrate plug formation in the experiments with circulation of hydrate particles or hydrate seeding supports the theory of only hydrate growth on existing particles, and that these particles do not agglomerate or deposit on the pipe wall. The shut-in and re-start experiments demonstrated that the hydrate slurry produced in the cold flow process was fully transportable and the apparent viscosity (pressure drop) was the same shortly after re-start as before shut-in. The hydrate slurry was heated to temperatures slightly above hydrate equilibrium during shut-in for some of the experiments in the wheel flow loop. Also in these experiments with controlled temperature fluctuations, the slurry was fully transportable after re-start and regained the same apparent viscosity as before shut-in a few hours after re-start (Larsen *et al*., 2009).

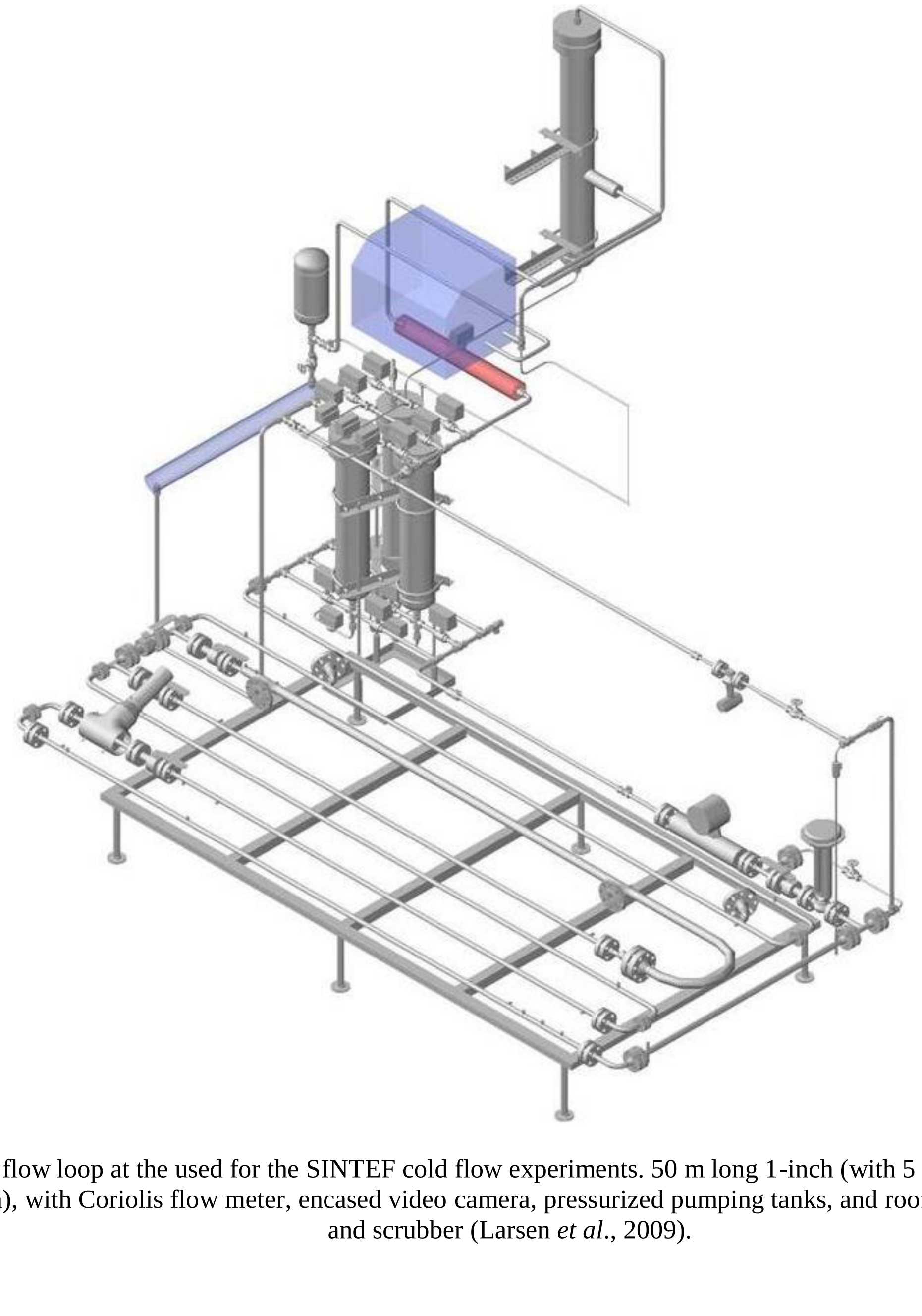

Figure 2. The flow loop at the used for the SINTEF cold flow experiments. 50 m long 1-inch (with 5 m long 2-inch section), with Coriolis flow meter, encased video camera, pressurized pumping tanks, and rooftop compressor and scrubber (Larsen *et al*., 2009).

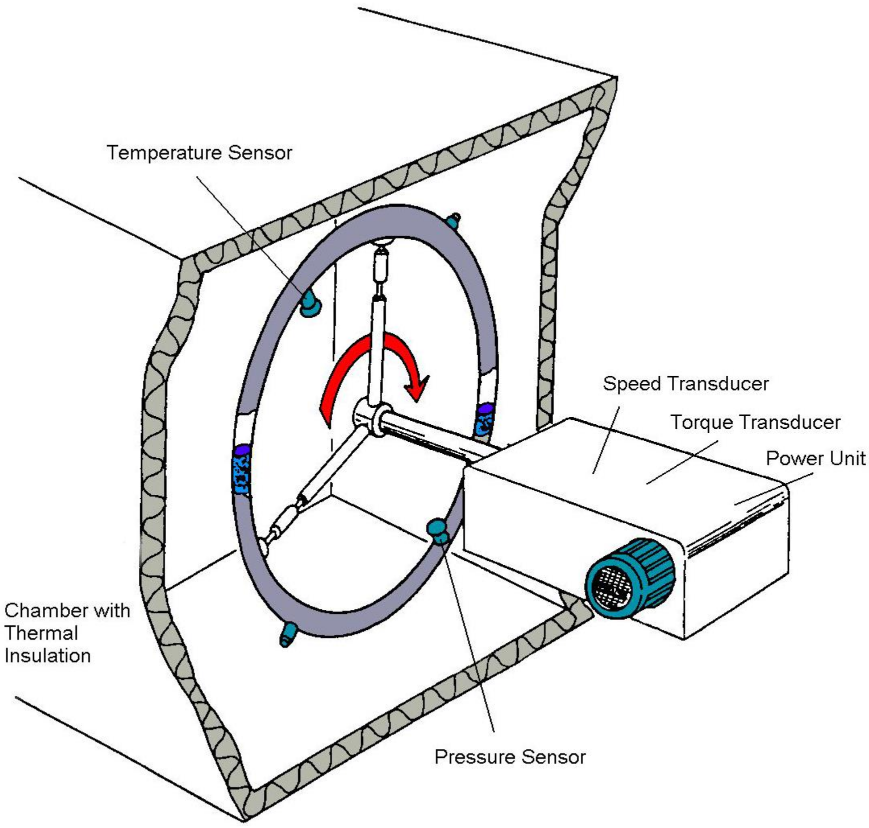

Figure 3. Principle sketch of the 5-inch wheel flow loop system. The wheel flow loop has a wheel diameter of 2 m and an inner pipe diameter of 121 mm. It is located in a temperature-controlled chamber and rotated with a motor with torque and speed measurements. The rotation of the wheel results in gravity driven flow in the wheel pipe due to density difference between the gas, oil and water phases (Larsen *et al*., 2009).

2.2 Experimental Results for Wax

Experiments were performed with circulation of various crude oils with high wax content to investigate the effect of cold flow on wax deposits at the pipe wall with and without water in the system. After finishing a run, a section of the pipeline was pigged and the quantity of wax collected on the pigs (Figure 4) were measured. The quantity of wax deposition was reduced by an order of magnitude when the cold flow process was operating compared to blank tests without cold flow in the experiments that were performed without water in the system. Experiments with water present indicate that recirculation of slurry of cooled oil with dispersed hydrate particles almost eliminated the wax deposition on the pipe wall for oil with high wax content. The experiments showed that the dispersion of wax and hydrate particles in oil was easily re-mobilized following shut-ins, without agglomeration of particles, or deposition on the pipe walls, and with apparent viscosity the same as before shut-in (Larsen *et al*., 2007).

Figure 4. Pigs with collected wax deposit with cold flow (left) and without (right) (Larsen *et al*., 2007).

2.3 Limitations of the Experiments

The design of the flow loop and the manner the experiments were performed introduce uncertainty in extrapolation of the results and observations to a potential field implementation of the method. Considering the flow loop used in the experiments mainly consists of 1" pipe, the Reynolds number (*Re*) was low compared to typical *Re* for flow in an industrial scale pipeline, which influences both flow characteristics and heat transfer in the pipe. Another drawback in terms of realistic testing is that injection of warm fluid into the recirculating cold slurry had to be done batch-wise, as continuous operation would not allow fast enough cooling (Larsen *et al*., 2009). Testing in a field test or flow loop with higher diameter and sufficient cooling capacity for continuous experiments is needed to validate the process for industrial use.

Concerns have been raised about the fact that this is a recirculation process with growth of hydrate on existing particles, which could indicate that the particles will grow to larger size throughout the process (Talley *et al*., 2007). Growing particle size has not been reported as a problem in any of the experiments. However, detailed particle size measurements in continuous experiments are needed to verify that growth of particle size due to recirculation of hydrates will not be a problem in a field implementation.

2.4 Implementation for Oil and Condensate Fields

The experimental program of SINTEF has focused on developing cold flow as a concept for the subsea treatment of liquid-dominant (crude oil or gas condensate) well streams to avoid deposition and agglomeration of solids (e.g., wax and gas hydrates), and allow long-distance transport without using heating and without or with minimized injection of chemicals (Larsen *et al*., 2007). The field implementation of this method at an oil field with several templates could be as illustrated in Figure 5. Hydrates dispersed in oil, which are pumped from a position downstream, are injected at the template furthest away from the production platform, or onshore production facility. The warm oil and water produced from the wells at the first template are mixed with the cold hydrate in oil dispersion, and the mixture is cooled by heat exchange with the environment while flowing downstream the pipe until the water has been converted to hydrates. Some of the hydrate slurry is pumped upstream as described, while the main flow is transported further downstream. As this pipeline passes other templates, more warm oil and water is mixed into the flow, and the water is converted to hydrates. The hydrates will be dissociated when the dispersion of oil and hydrate particles reaches the processing facility (this dissociation process has not been described in detail).

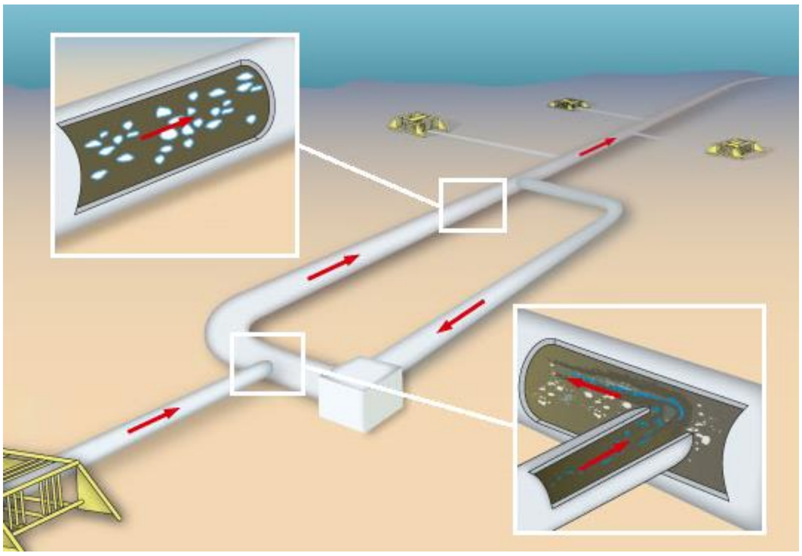

Figure 5. Example of cold flow in oil fields (Larsen *et al*., 2007).

An alternative to the field development illustrated in Figure 5 could be a long loop where hydrate slurry is pumped from the production platform or onshore facility. This would open the possibility for pigging of the whole pipeline. In cases where the fields have expectance of high water production, a subsea separator could be installed at the template that reduces the water cut to 10 to 20% before it enters the cold flow process. In this way SINTEF does not envision the cold flow technology as a very specific configuration which will be installed independently of local field variations. Rather, it envisions configuration of equipment being designed based on each individual field's characteristics implementing a collection of design and operation principles that will assure formation and flow of transportable hydrate slurry (Lund *et al*., 2010).

2.5 Cold Flow Dehydration of Natural Gas

One of the major components on the production platform at an offshore natural gas field is the glycol dehydration and regeneration process equipment. SINTEF has proposed using cold flow as an alternative dehydration process (Lund *et al*., 2011). This has not been tested experimentally but builds on the experimental results from cold flow experiments with a condensate like model oil. The simplified process diagram in Figure 6 illustrates one example of possible implementation of this method. The warm well stream from a natural gas well is mixed with excess slurry of condensate and hydrate particles from the cold separator. The hydrate dissociates and the majority of the water and condensate is separated from the natural gas in the warm separator. The condensate from the warm separator might be exported together with dehydrated natural gas in a wet-gas pipeline or separately. The water can be re-injected or sent through waste water treatment before discharge into the ocean. The warm natural gas with dissolved water and some condensate is mixed with slurry of condensate and hydrate particles taken from the cold separator, and this multiphase mixture is cooled by heat exchange with the environment. Because of the hydrophilic surface of hydrate, water vapor dissolved in the natural gas will form hydrates on the existing particles, and the natural gas will be dehydrated while the mixture is being cooled. The design criteria for the length of the pipeline and number of parallel pipelines in the cooling zone will be that the gas and hydrate slurry reach a temperature close to surrounding seafloor or air temperature before entering the cold separator. In the cold separator, the hydrate slurry is separated from the cold dehydrated gas and transferred upstream for dissociation and seeding of the cold flow process as described above. The dehydrated natural gas is sent to the gas export pipeline.

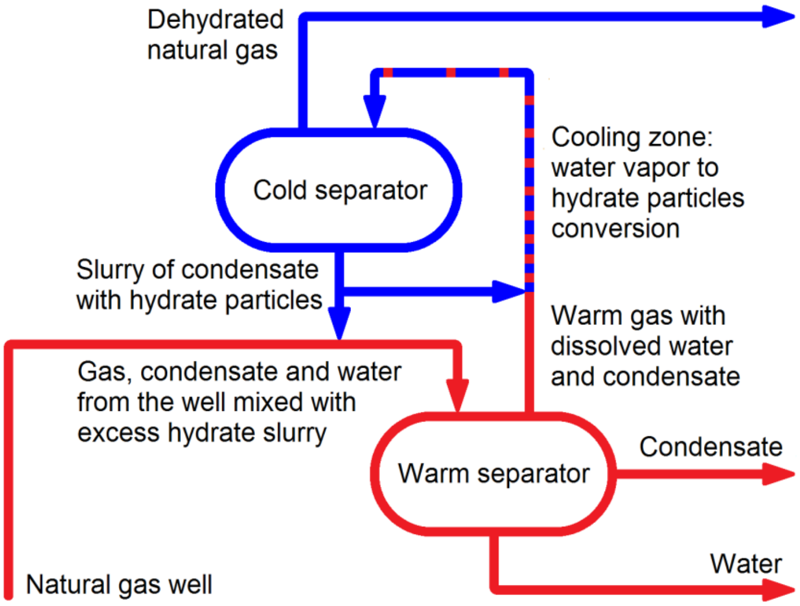

Figure 6. Simplified process diagram for cold flow dehydration. Red lines represent flow at temperatures above hydrate equilibrium and blue lines represents flow at has been cooled to ambient temperatures. Blue and read dashed line represents the cooling zone where water vapor in the gas phase is converted to hydrate particles dispersed in condensate.

If the export pipeline requires higher pressure than the pressure of the cold separator without compressor in the system, a compressor might be located between the warm separator and the cooling zone. The higher partial pressure of water vapor will result in extraction of more water from the gas during hydrate formation. The partial pressure of water vapor and dew point temperature in the natural gas will always be lower in the export pipeline than in the end of the cooling zone, because of pressure drop in the pipeline. A simplified version of the process could be implemented without the warm separator and with export the excess slurry of condensate and hydrate particles in a separate pipeline. The cold flow dehydration process could be designed as a subsea development or it could be in part located on a production platform and in part subsea. Hence, in a similar way as envisioned for oil fields the cold flow dehydration process can be designed based on each individual field's characteristics.

Multiflash® (Infochem/KBC Advanced Technologies plc., 2014) predictions and experiments by Nicholas (2008) indicate that the quantity of water dissolved in hydrocarbon will be lower for a system with hydrocarbon and hydrates than for systems with hydrocarbon and liquid water or ice. It is therefore likely that the water content in the natural gas dehydrated by the cold flow dehydration process will correspond to a dew point temperature significantly lower than the temperature in the pipeline and the ambient seafloor temperature.

2.6 Empig Induction Heating and Magnetic Pig

During the present decade, the Norwegian company Empig has developed their patented technology for cleaning of wax and hydrate deposits from the pipe wall in the cooling zone in a cold flow hydrate seeding process patented by SINTEF. One version of their technology consists of a hallow pig, which may remove deposits inside the pipe while it is moved using a magnetic sled outside the pipe (Lund, 2013). Another version consists of a sled with an inductive coil providing local induction heating of short segments of the pipe while moving along the outside of the pipe. The heating at regular intervals will cause melting and sloughing of deposits in the whole cooling section before any deposits grow to a critical thickness (Lund, 2016; Empig AS, 2018). In both versions, the pipe wall cleaning procedure is planned to operate in a compact cooler module in which warm fluid is cooled to ambient temperatures while hydrates and wax are forming (Figure 7). The cold flow seeding process is implemented by cold fluid with hydrate and wax particles being pumped from the cold outlet and mixed with warm production flow at the inlet of the cooler. Empig envision their process as one component of a subsea production unit, which might also include production wells, manifold, subsea separator to lower the water content to acceptable level for cold flow transport of hydrate slurry, and water injection well as illustrated in Figure 7. Empig plan to perform large scale technology testing in 2019 (Empig AS, 2018).

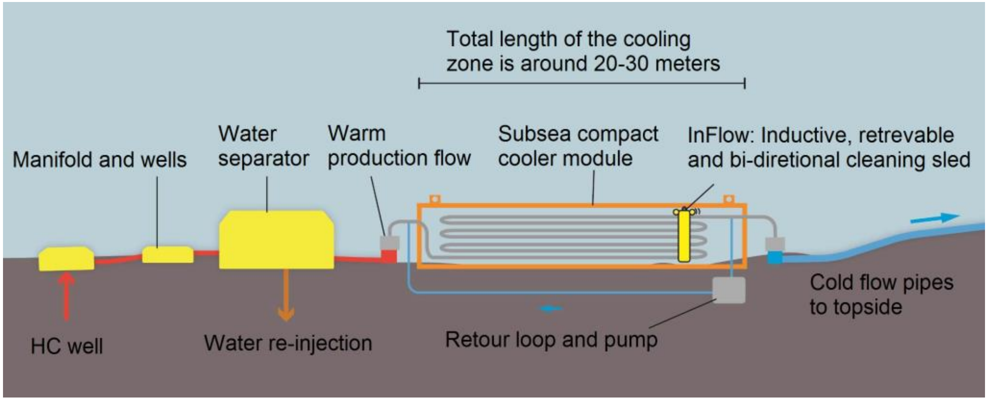

Figure 7. Subsea compact cooler module converting warm production flow to hydrate slurry with Empig cleaning sled installed (Empig AS, 2018).

3. COOLING OF LIQUIDS SEPARATELY BEFORE MIXING WITH GAS AND HYDRATE FORMATION

The cold flow process proposed by Norwegian University of Science and Technology (NTNU) consider separating of liquid phases from gas at temperatures above hydrate equilibrium, then cooling the liquid phases, and mixing all phases for hydrate formation in a reactor as illustrated in Figure 8. The wellhead unit (WHU) consist of valves, connection and other equipment normally located at the wellhead. The separator unit (SU) separates the gas phase from the liquid phases. Water and oil with dissolved gas is cooled from wellhead temperature to seafloor temperature (−2 to 4 °C) in the heat exchanger unit (HXU). The cooled mixture of liquids is then mixed with the gas in the reactor unit (RU) and hydrate particles dispersed in the oil phase is transported downstream in the cold flow pipeline (CFP) (Gudmundsson, 2002).

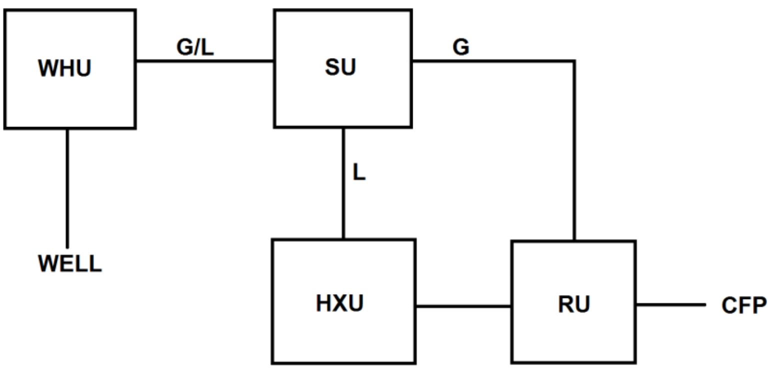

Figure 8. Block diagram of cold flow hydrate process proposed by NTNU, illustrating wellhead unit (WHU), separator unit (SU), heat-exchanger unit (HXU) and reactor unit (RU), feeding into a cold flow pipeline (CFP) (Gudmundsson, 2002).

The paper describing this method mentions in the introduction chapter that produced fluids without associated gas, which means that the in-line pressure is above the bubble point pressure of the oil, will not form hydrates (Gudmundsson, 2002). However, this assumption does not agree with later published conceptual models for hydrate formation that consider hydrate formation at all hydrocarbon – water interphases as long as the oil phase contains a sufficient quantity of dissolved gas. (Sloan and Koh, 2008; Sloan *et al*., 2011). The oil phase will be saturated with hydrate forming natural gas components after the separator unit, which makes it reasonable to assume that hydrates will form also in the heat exchange unit of a cold flow process flowing the process proposed by NTNU (Figure 8). In a once through operation, it is likely that the hydrate formation in the heat exchanger would have caused deposition, as documented in other once through experiments (Lachance *et al*., 2012). The lack of deposition in the hydrate formation experiments presented in the paper might be attributed to the fact that the experiments were performed in a flow loop (Gudmundsson, 2002). This experimental design suggests that hydrate particles were circulated during the experiment, which likely resulted in hydrate formation on existing particle in these experiments similar to the hydrate seeding experiments of SINTEF.

4. CONVERTING THE GAS PHASE INTO HYDRATES

Researchers at the Centre for Gas Hydrate Research at Heriot-Watt University have developed a patented cold flow method named “HYDRAFLOW” that aims to convert all or most of the gas in a hydrocarbon fluid system into hydrates that can be transported dispersed in hydrocarbon liquid, water or a mixture of these two liquid phases (Tohidi, 2006). AAs may be added to the system to control hydrate crystal size and prevent blockage formation. The patent presents reduced slugging and pressure drop in the production pipeline in addition to reduced risk for hydrate blockage formation as some of the benefits of converting the gas to hydrates.

Articles presenting this method propose using a loop concept (Figure 9) that allows circulation of liquid phases and additives when this is profitable (Azarinezhad *et al*. 2008; Azarinezhad *et al*., 2010). Water can be added to the system and/or recirculated if this is necessary for conversion of the gas to hydrates and when increased water cut will reduce the slurry viscosity and pressure drop. Some oil can be recirculated to improve the performance of AA for gas fields or high GOR systems. This loop concept does not intend to recycle hydrates for seeding and controlled hydrate growth like the method patented by SINTEF, but allows circulation of fluids like oil, water, AAs and other chemicals for the purpose of increased liquid content of the slurry and recycling chemicals. Moreover, HYDRAFLOW should be distinguished from “dry” hydrate cold flow concepts, because it allows hydrate formation in the presence of excess water, but prevents solids agglomeration using AA when necessary. The recycled oil and water both serve as carrier fluids collecting produced fluids from various wells, and forms hydrates with the gas phase. Hydrate particles dispersed in oil and/or water are transported to processing facilities (Figure 9). The articles also suggested that hydrates reduce wax deposition by maintaining the fluid temperature for a longer time due to heat released from hydrate formation, by providing solid seeds for wax nucleation dispersed in the liquid phase rather than on the pipe wall, and by erosion of deposited wax from the wall by the moving hydrate particles (Azarinezhad *et al*. 2008; Azarinezhad *et al*., 2010).

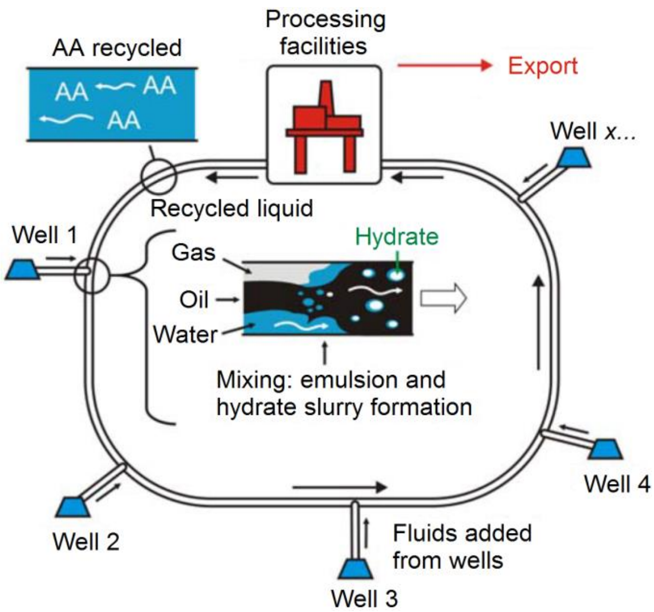

Figure 9. Illustration of the HYDRAFLOW pipeline loop concept for recycling of fluids and chemicals (Azarinezhad *et al*. 2010).

Hydrate formation experiments were performed in rocking cells after which water, oil and hydrate phase were separated to measure the AA distribution between the different phases. These experiments showed that the majority of the AAs remained in the free water and hydrate phase with more residual AA in the free water than AA trapped in the hydrate phase. AA components did not enter oil phase significantly (Azarinezhad *et al*. 2008). The results indicate that the majority of the AA can be reused by recycling the water phase according to the HYDRAFLOW loop concept.

An experimental study was performed in an autoclave cell to evaluate how AAs performed at different salinities and water cuts (Azarinezhad *et a*l., 2010). The results showed that the presence of salt together with AAs can reduce significantly the viscosity of hydrate slurries at both high and low water cuts. This might be explained by strengthening performance of the quaternary ammonium salt AA in saline water phase because of ion paring. It might also be related to the inhibiting effect of the salt, which decreases the hydrates formation rate and thus decreases the agglomeration. Hydrate growth rate, subcooling, heat transfer and mixing were studied in the same experimental study. The GOR for the system was 60 and 150 vol/vol in these experiments. The water cut was 43% with 4 wt% salt and 1 wt% AAs present. For the low GOR tests, the initial hydrate growth at 12 °C subcooling rate was more than an order of magnitude higher than at 6 °C subcooling, which was a much more pronounced effect than the effect of the mixing rate and heat transfer rate. The hydrate formation rate was significantly higher in experiments with high GOR than in experiments with low GOR. The mixing rate and heat transfer had also more impact on the results with high GOR (Azarinezhad *et al*., 2010).

The HYDRAFLOW method and results presented by Heriot-Watt University confirm and quantify the effect of AAs on formation of transportable hydrate slurry. The economic saving from recycling of AAs and liquid phases need to be weigh against the investment cost in installing a loop for recycling of fluids. This method might be a viable alternative for some fields. The idea to increase water cut to decrease viscosity could be useful for fields with water cut close to the oil-water inversion point. Studies of other research groups show that a water continuous hydrate-oil-water slurry might have much lower viscosity than an oil continuous slurry with slightly lower water cut (Glenat *et al*., 2017b).

5. ONCE-THROUGH OPERATION

ExxonMobil has proposed a once-through method of generating non-plugging hydrate slurry (Talley *et al*., 2007). This patented method involves the use of static mixers to reduce water droplet diameter in order to facilitate instant conversion of the entire water droplet to hydrates when hydrate formation occur as illustrated in Figure 10. Static mixers are non-mechanical devices, which mix flow in tubes by diverting flow, rotating flow, and reversing the flow rotation. Since this is a once-through process, it will not require any pump for recirculation of hydrate seeds as the process patented by SINTEF. This reduces the need for power supply to only include power to control valves and possible other moving part like the static mixers that can be bypassed as proposed in another patent by ExxonMobil (Broussard *et al*., 2012). The patents also include the option of hydrate seeding, but in that case, the hydrate seeds are produced in a branch of the main pipe before the slurry is mixed into the main pipe downstream to facilitate hydrate formation. Thus, it is also considered a once-through process.

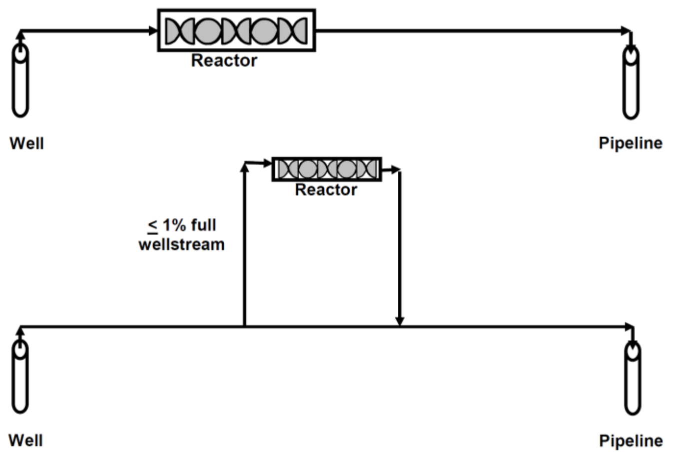

Figure 10. Once-through hydrate formation with static mixers without and with seeding (Turner and Talley, 2008).

5.1 Flow loop experiments

ExxonMobil performed the following three classes of flow loop experiments: (1) hydrate slurries produced in bare piping, (2) hydrate slurries produced through static mixers, and (3) hydrate nucleation by seeds (Turner and Talley, 2008). The experiments were performed in a 4” and a ½” flow loop that were connected to enable seeding of the fluids in the 4” loop with hydrate slurry produced in the ½” loop. The 4” loop (Figure 11) was 95 m loop with an inner pipe diameter of 97.2 mm and pressure rating 83 bar. It was contained in a chamber with temperature controlled between -6.7 and 32.2 °C. The ½” loop was 42 m with an inner pipe diameter of 12.7 mm and pressure rating 310 bar, and was placed in a temperature bath with temperature range -6.7 to 37.8 °C. The typical experimental temperature was 4.4 °C for both flow loops. The pressure was maintained constant during the experiment by hydraulically controlled piston accumulators. Particle size, mass flow and differential pressure were measured. To avoid shifting equilibria during hydrate formation, methane gas with 99.9 % purity was used as gas phase. Hydrocarbon liquids used include dodecane, King Ranch Condensate, and Conroe Crude. The fluid properties of these hydrocarbon liquids estimated at 4.4 °C are given in Table 1.

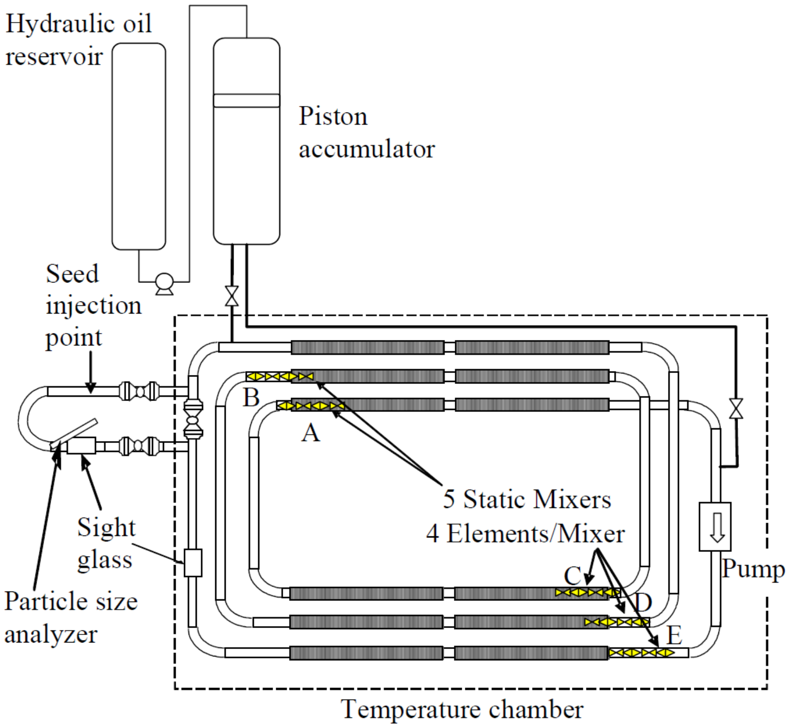

Figure 11. Diagram of the 4” flow loop with static mixer locations indicated (Turner and Talley, 2008).

Table 1. Liquid hydrocarbon properties estimated at 4.4 °C (Turner and Talley, 2008).

Property	Dodecane	King Ranch Condensate	Conroe Crude
Specific Gravity (kg/m3)	790	683	845
Viscosity (cP)	2.0	0.4	6 − 11
Oil-Water Interfacial Tension (mN/m)	51	38	25
Wax appearance temperature/ Wax dissolution temperature (°C)	N/A	N/A	12.5/ 21.5

A number of different parameters were studied to investigate their effect on water droplet size and pressure drop. The experiments showed that higher gas void fraction (GVF) resulted in high pressure drop and slushy hydrate agglomerates that caused plugging upon restart, while hydrates produced with low GVF dispersed readily as a suspension after restart and did not accumulate on the pipe walls. Higher liquid velocity resulted in more flowable hydrate slurry. It is believed that flowable hydrates are promoted by a mechanism caused by the higher share rate, heat transfer and mass transfer. Higher share rate produces smaller water droplets and gas bubbles, which results in rapid hydrate formation. It also breaks aggregates that may form. Higher heat and mass transfer increase hydrate growth rates. Static mixers had a similar effect as higher velocity. Static mixers caused the droplet size to decrease significantly at low velocities. Necessary velocity for production of 20 − 30 μm diameter droplets is decreased from 1.2 – 1.5 m/s to well below 1.0 m/s by using static mixers. At velocities above 2.7 m/s in the 4-inch loop, there was no additional effect using static mixers. The static mixers increase mass and heat transfer from the surroundings. For $Re < 2000$ the Nusselt number (Nu) was 2.5 times higher utilizing static mixers. Nu was more than 3 times higher using static mixers for $Re > 2000$. The oil properties also affected the water droplet size and transportability of the hydrate slurry. Oil with high viscosity and low interfacial tension between oil and water produce smaller water droplets, which are desired for rapid and complete hydrate conversion. An experiment in the ½-inch loop with 9 % water cut (WC) in dodecane ended in total blockage of the pipe an hour after hydrate formation started while similar experiments with 9 % WC in Conroe crude resulted in a flowable hydrate slurry.

Hydrate seeding was tested by first producing seeds in the ½-inch loop and transferring the seeds to the 4-inch loop, which was filled with Conroe oil without water present, pressurized with methane to 69 bar and cooled to 4.4 °C before transfer of hydrate seeds. Fresh water was filled to a total WC of 34% after the seeds had been transferred and the hydrate slurry had circulated for about 15 hours. The GVF was 44% in the experiment, oil velocity was 0.9 m/s and 4 static mixers elements were installed in the flow loop. Filling of additional water resulted in a higher but constant differential pressure probably caused by the increased amount of hydrate particles in the oil. The relative viscosity was constant at 1.0 for the rest of the experiment, which lasted about 24 hours after water injection. A baseline run without seeding was run under the same conditions and the relative viscosity increased to 7.7 before plugging of the flow loop 22 hours after hydrate onset. The method used and the experimental results are similar to the results in the experiments performed by SINTEF. The results suggest that seeding of hydrate particles promotes the growth of flowable hydrate slurries (Turner and Talley, 2008).

Flowable hydrate slurries also seem to erode wax from the pipe wall particularly at high liquid velocities, and liquid loadings. Flowable hydrate slurry was observed to successfully restart after a 26-day shut-in period in the 4-inch loop without significant increase in pressure drop. Both of these results also agree with the results from the experiments performed by SINTEF (Larsen *et al*., 2007).

5.2 Once-through operation field trial

ExxonMobil also conducted a field trial in a once-through, 4-inch diameter, 3.2 km pipeline facility with the focus on: (1) comparing hydrate slurry performance in a once-through flow system versus a 4-inch flow loop at various operating conditions and scenarios, (2) determining the effect of long-term operation while mimicking actual field life conditions during hydrate slurry formation, and (3) characterizing transient performance during rate changes and shut-in/startup with hydrate slurry formation (Lachance *et al*., 2012).

The basic process flow in the field trial equipment is shown in Figure 12. The flow of oil, water and gas entering the system were controlled by flow meters to achieve the desired GOR, water cut and liquid loading required for an experiment. The mixture of oil and water was cooled to hydrate equilibrium temperature (~10 °C) in heat exchanger EX1, after which the cooled liquids were mixed with the gas. The mixture could continue through static mixtures installed after EX1 or bypass the static mixtures. At this point the oil, gas and water continue through one of the two parallel heat exchangers EX3 and EX4 that cooled the mixture into the hydrate region (3 − 6 °C). The flow was periodically swapped between the two heat exchangers during an experiment to perform wax/hydrate remediation on them. These heat exchangers could also be bypassed by most of the flow and a minor part of the flow could be cooled in the heat exchangers for production of seeds and mixed into the main flow afterwards according to the principals illustrated in Figure 10. After leaving EX-3/EX-4 the fluid could either pass through a static mixture or bypass the mixtures after which the particle size was analyzed before the fluid entered the test section. After the test section, the hydrate slurry flowed through the line heater HX-1 for dissociation of hydrates before separation. Erosion/corrosion probes monitored the effect of hydrate slurry compared to flow conditions without hydrates. Span 80 obtained from Sigma-Aldrich was used as emulsifier in some experiments. It was also possible to inject methanol.

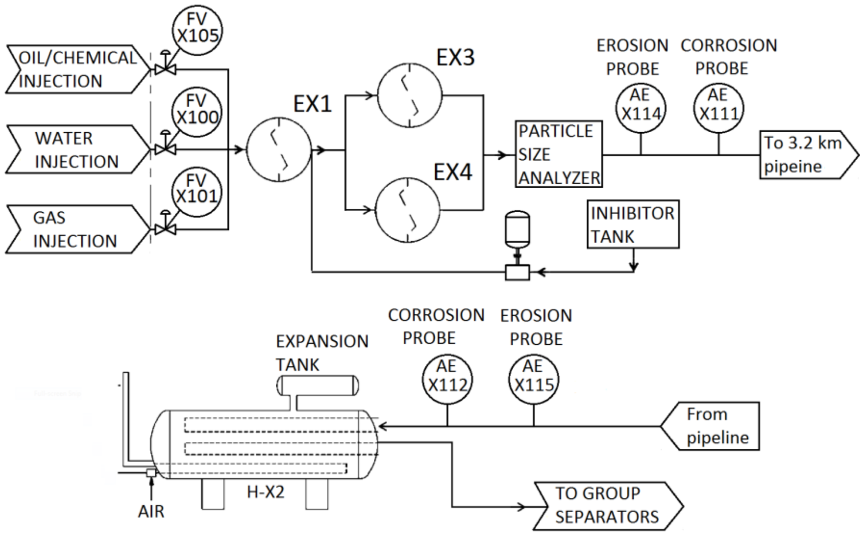

Figure 12. Simplified process flow diagram for the field trial system (Lachance *et al*., 2012).

The experiments in the once-through field trial gave exponential rise in pressure drop mainly caused by wall deposits of hydrates in various sections of the field trial system. This result differed from the flow loop experiments in the 4” loop even though the fluids used were the same and the run conditions were similar to the flow loop experiments. However, bulk fluid slurry behaviors were similar for the flow loop and field trial. The water dispersion characteristics of the flowing fluids were the most important factors in hydrate transportability and depositional rates. The water dispersion properties were adjusted by changing water cut, concentration of chemical (Span 80) for emulsion stability, and the fluid velocity. Higher shear flow patterns tended to delay hydrate deposition on the pipe wall, with the most rapid slug frequency delaying deposition the most. Geometry had some effect on deposition. Based on X-ray tests, the main contributor to increased pressure drop was depositions around bends, especially downstream of the bend in the stagnation zones. The field trial included a successful restart with fluids entering the pipeline in the hydrate region after a 7-day shut-in. No large spikes in differential pressure were observed, indicating that hydrate aggregates did not appear to be jamming. As the flowline warmed along the 3.2 km length, a steady decrease in the pressure drop was observed indicating that some deposition, which had occurred earlier, dissociated at this point (Lachance *et al*., 2012).

5.3 Differences between flow loops and field trial

Lachance *et al*. (2012) note that the flow loop experiments could be considered short-duration “snapshots” corresponding somewhat to the state of fluids in a once-through pipeline before a steady-state condition is achieved in the pipeline, and that steady-state conditions in the flow loop are not the same as steady-state conditions in the once-through pipeline. In the flow loop, the quantity of water available for hydrate formation is limited, and when the available water is converted, the measured parameters will in many cases plateau. However, in a once through pipeline, “new” water continually arriving at the location of hydrate deposits at the pipe wall cause a steady growth of the deposit.

The circular nature of a flow loop may also have some influence on the quantity of hydrates forming as deposits on the pipe wall and particles in the bulk flow. Flow loops circulate hundreds of times while water converts slowly to hydrates. In the beginning, hydrates mostly form on the wall as a film until they grow thick enough to slough off and then seed the bulk water. The sloughing may result in more hydrate particles and hydrate growth in the bulk flow in a flow loop than in a once through process, because circulation of fluids will distribute hydrate particles throughout the loop. However, due to the low quantity of hydrate particles, the effect of these particles in the bulk flow in a flow loop without seeding will be much smaller than in a flow loop that has been seeded with hydrate particles in the beginning of the experiment. In a seeding cold flow apparatus, bulk water sees seeds immediately and hydrates start growing at existing hydrate particles when the system enters conditions where hydrates are stable. This may result in much less or absent of hydrate growth on specific locations at the pipe wall, and consequently much less wall deposition compared to the non-seeded flow apparatus. A once-through pipeline in which there is no recirculation of any hydrate particles will require subcooling to a temperature below hydrate equilibrium, similar to the previously mentioned nominal subcooling of 3.3 °C before hydrate formation in flow loops (Sloan *et al*., 2011), and the pipeline wall will be the natural location for hydrate nucleation. This could also be part of the explanation of the difference between flow loop experiments and the Once-through operation field trial.

6. SUGGESTIONS FOR FUTURE STUDIES OF HYDRATE COLD FLOW

The cold flow experimental campaigns discussed in the previous chapters demonstrate various categories of conditions enhancing formation of transportable hydrate slurry. Experiments performed by Heriot-Watt University and others show that adding of a small percentage of AAs promotes formation of hydrate slurry for both oil and water continuous systems. Experiments performed both by SINTEF and by ExxonMobil showed that seeding of powder-like hydrate particles result in formation of transportable hydrate slurry and no deposition of hydrates at the pipe wall. The experiments of ExxonMobil in addition showed that effects increasing water dispersion or reducing water droplet size also enhance formation of transportable hydrate slurry. It would therefore be natural to address AAs, hydrate seeding, and methods reducing water droplet size and increasing water dispersion, in possible future flow loop experiments and field trials.

It is essential for further studies to understand the causes for the differences between the successful flow loop experiments and the once-through field trial experiments with hydrate deposits at the pipe wall. The comparison of the various types of tests has identified a few differences based on the nature of flow and hydrate formation in flow loops and once through processes. Finding explanations for these differences supported by theory and experiments focusing on specific topics concerning hydrate formation, deposition and hydrate slurry flow will give important input for design of future test facilities, experimental procedures, and field implementation of cold flow hydrate management methods.

6.1 Hydrate deposition studies

Designated laboratory studies have been performed during the present decade attempting to better describe and understand mechanisms involved in hydrate deposition. Rao *et al*. (2013) studied deposition on the outer surface of a cooled pipe exposed to water-saturated natural gas. Growth of hydrates with high porosity was detected in the beginning of the experiments until the hydrate layer reached a certain thickness at which the growth stopped, because the insulation of the hydrate layer resulted in hydrate equilibrium temperature at the deposit surface. After this, water started filling the porous space decreasing porosity and hardening the deposit. Di Lorenzo *et al*. (2014) performed experimental studies of hydrate deposition in annular gas-water flow in a pipe testing section at various subcooling conditions suggesting that particle deposition from the liquid or deposit sloughing from the wall made significant contributions to the pressure drop.

Grasso *et al*. (2014) performed laboratory experiments in a rocking cell studying hydrate deposition. The experiments indicated that water would reach the deposition surface by direct contact between the water phase and the cold surface, by condensation of water on the surface, and by liquid capillarity. Straume *et al*. (2016) demonstrated experimentally in the same rocking cell apparatus that non-emulsifying oil and condensate systems, in which the oil and water phases formed a shear stabilized dispersion before hydrate formation, could separate upon hydrate formation onset under constant oscillation conditions. Experiments with AA resulted in absence of wall deposit. Hydrate sloughing was not detected in a narrow operational window defined by both subcooling lower than 4 °C and temperature gradient in the rocking cell lower than 1 °C in these experiments (Straume *et al*. 2018). Hydrate deposition experiments performed in a flowloop with temperature gradient between the wall and the fluids showed that hydrates deposits gradually over time with hydrate particles present in the flow in the beginning of the experiment. Experiments preformed at the same temperature gradient, water cut and flow conditions without hydrate particles present before the deposition experiment was initiated resulted in agglomeration and rapid hydrate build-up in the beginning of the experiments (Straume *et al*. 2017).

These studies have added valuable knowledge and understanding of mechanisms involved in hydrate deposition. The studies show that temperature gradient in the system and the subcooling during hydrate formation could be important parameters for hydrate deposition. The effect of AA and the effect of adding hydrate particles on hydrate deposition are topics that also would be interesting for further studies. The influence of the wall surface properties on hydrate deposition is another topic that could be investigated further by designing the experiments. The pipe wall could be oil wetted in some experiments, water wetted in some, and with hydrate film that has started growing on the pipe wall in the beginning of some experiments. Such small-scale laboratory experiments would give valuable input for future field trials by identifying conditions that promote hydrate deposition, and conditions that limit and prevent hydrate deposition.

6.2 Important parameters in future experiments

Parameters that are necessary to measure in potential future large-scale flow loop or field trial experiments should be carefully considered and selected during the planning of the experiments and design of test facility based on results and observations from small-scale laboratory experiments. Some parameters of interest for future studies can be suggested based on previous experimental results. Parameters influencing hydrate equilibrium conditions should be measured at some selected locations in the flow loop or field trial pipe. These parameters are: pressure, temperature, gas composition and water composition. By measuring the temperature and pressure at various positions along the pipe, the hydrate equilibrium conditions and subcooling, which might be viewed as the driving force for hydrate formation, can be calculated for different locations in the cooling zone where water is converted to hydrates. It may be sufficient to measure the gas and water composition at the start and the end of the cooling zone if multi-component gas and water phases are used. Radial temperature gradient in a pipeline might influence deposition on the pipe wall. It would therefore be useful to measure the temperature in top, center and bottom of the pipe and run experiments with different cooling temperature applied to the top and the bottom of the pipe. This allow evaluation of which temperature gradient conditions that might cause deposition in the pipe.

Fluid specific properties like density, viscosity and interfacial tension for the phases are parameters needed for any multiphase flow model. Fluid flow in which solid particles are present is also influenced by properties of the particles like density and surface energy. Velocity or mass flow rate, differential pressure, liquid hold up, flow pattern, water droplet size and solid particle size are important input parameters for both understanding the cold flow process and development of multiphase flow models involving hydrate particles. Hydrate particle size measurement over time in a possible future field trial of the SINTEF patented hydrate recycling and seeding process will determine if this method results in growing particle size, which could be a problem for implementation of this cold flow process. It is important to know the rates of hydrate crystal growth at all locations (e.g., walls, films, bulk water, shrinking core droplets, gas/water and water/hydrate interfaces). It would therefore be desirable to develop and implement methods to measure these parameters both in small scale laboratory experiments and in large scale flow loop and field trial experiments. Considering hydrate deposition has been identified as a challenge in previous experiments, measurements of hydrate deposit thickness and growth rate in long duration steady-state and transient experiments are essential for the validation of cold flow as a flow assurance strategy. Measurement of accumulation of hydrates as bedded hydrate particles in the pipe could be helpful in determining solid content and velocity limits for transportable hydrate slurry.

Wax related parameters that are of interest for measuring influence of cold flow on wax deposition may include: wax appearance temperature, wax dissolution temperature, thickness of wall deposit of wax without recirculation of cooled oil, and with recirculation of oil with and without hydrate particles present. Measurement of water vapor content in the gas phase or dew point temperature could be included to evaluate the efficiency of the SINTEF patented cold flow dehydration process.

6.3 Design of future flow loop or field trail

Possible design options for a field trial test pipe or flow loop are dictated by available equipment and flow rates from a production field, and the economical limitations of the project. However, a future test facility should have characteristics that would help give decisive answers on the efficiency of cold flow. One of the main operations that need to be tested for the methods proposed by the various research groups is long term continuous run of cold flow. The parameters of interest mentioned in previous paragraph should be measured in the cooling zone during conversion of water, oil and gas into the water to hydrate slurry with non-adhesive and non-cohesive hydrate particles, and in the downstream pipeline.

In addition to testing of the proposed processes for conversion of warm well fluid to hydrate slurry under constant flow operation, various types of transient operation should be tested. This may include controlled shut-in, emergency shut-in, and restart after several days or weeks of shut-in. The test facility should have capability of performing experiments at several different pipe diameters and a sufficient range of GOR, water cut and content of solid hydrates in the liquid. The fluid velocities should have a range that makes it possible to reproduce a variety of different flow patterns for development of hydrate slurry flow models. However, the available field production rate or compressor capacity may limit the option of performing experiments with certain flow patterns. These measurements for various steady state and transient conditions can establish operational windows for cold flow with low risk of high pressure drop and plug formation caused by deposition, agglomeration and accumulation of hydrates.

The pipe configuration of the test facility should be such that it will be possible to run the suggested configurations of the once-through process proposed by ExxonMobil and the process with crystal recycling and seeding proposed by SINTEF. The test facility could also implement an option of adding and recycling water, AA and other chemicals as proposed by Heriot-Watt University to test the influence of these chemicals on the formation of hydrate slurry. Static mixers of different design could be included to evaluate how this will affect water droplet size and the efficiency of the proposed cold flow processes. The efficiency of other equipment and methods related to cold flow, like the pipe wall deposition removal systems proposed by Empig, could also be tested in such facility. Running all proposed processes in the same test facility under similar conditions will give a better understanding of advantages and limitations of the various processes and facilitate further development of combination of the various proposed methods.

Realistic once through operation of hydrate formation in a flow loop requires continuous formation of hydrates of all the water passing through cooling zone and continuous dissociation of all hydrate slurry in a dissociation section of the loop to produce mixture of warm oil and water. Some heat exchange between the two processes could be implemented, but the cost of heating and cooling systems and the energy consumption would become a substantial part of the cost performing experiments in a flow loop with flow rates and pipe diameters close to field conditions. It is therefore likely that it would be a better option to perform a field trial in which the cooling zone of the test facility receive warm oil, gas and water from the well, and exchange heat with the environment for cooling of the cold flow process to produce hydrate slurry.

6.4 Model development for hydrate cold flow

The cold flow experimental campaigns of SINTEF and ExxonMobil focused mainly on validating the cold flow concept by producing transportable hydrate slurry containing non-adhesive and non-cohesive hydrate particles. Later studies have also focused on development of correlations for hydrate slurry flow (Glenat *et al*., 2017b). Results from future experiments and theoretical studies identifying flow characteristics of multiphase flow of gas, oil, water and hydrates for both oil continuous and water continuous systems could contribute to further development of models describing hydrate cold flow. A model should include prediction of parameters that normally are of interest for multiphase flow in addition to hydrate specific parameters.

Such parameters could be pressure drop, liquid hold-up and flow regime at various flow rates of gas, liquids and hydrates, at various pipe inclinations and diameters. Determining conditions that result in bedding and build-up of hydrate particles in the pipe, and determining maximum hydrate content in the liquid for transportable hydrate slurry should also be included. In addition to predicting steady state conditions, a model should include prediction of transient scenarios that might occur during field operation like, shut-ins and re-starts. Calculations from such model for the expected variation of production conditions like water cut gas-oil ration and pressure during the lifetime of the field will give information for field design decisions in the development of the field. In some cases, there might be a need for separation of water from the oil to decrease hydrate content before hydrate formation to decrease pressure drop, or adding water to make the system water-continuous. In some cases, pumps or compressors might be required because of high pressure drop or for recirculation of hydrates for seeding of hydrate particles.

6.5 Development of hydrate management strategies

Planning of economically viable hydrate management strategies involving cold flow would be an important part of the further development of this method. As presented earlier, SINTEF has suggested various field implementations of cold flow depending on the characteristics of the various oil and gas fields, for which this technology are considered. Cold flow could be viewed as the main hydrate management strategy for some fields and one piece of the overall strategy under certain operational conditions for other fields.

As an example of the later, cold flow for hydrate blockage prevention during long duration shut-in and start-up operations can be considered for some fields. An oil production pipeline that will not enter hydrate formation conditions under normal steady-state flow might be cooled down during shut-in, which increases the risk for hydrate plug formation. The traditional approaches of hydrate avoidance require either inhibitor injection before shut-in or replacement of the fluids in the pipeline with dead oil or diesel. The previous reported experiments of both SINTEF and ExxonMobil show that hydrate slurry produced in the cold flow process can easily be remobilized after a long duration shut-in (Larsen *et al*., 2007; Turner and Talley, 2008). Given these experimental results, it might be possible to replace the fluids in a pipeline with hydrate slurry before a planned shut-in. This hydrate slurry could be generated from the produced fluids in the pipeline utilizing the methods successfully tested in the experiments, and circulated until the slurry is cooled to ambient temperatures before shut-in. After re-start, the pipeline will be heated to temperatures higher than hydrate equilibrium, and the hydrates will be dissociated in the separator and other process equipment downstream.

Choice of hydrate management strategy influence the design of pipelines, separators, pumps and other infrastructure that need to be installed during the development of a field. The costs of additional or different field infrastructure when utilizing cold flow as part of the hydrate management strategy compared to other traditional solutions must be evaluated as part of the further development of the method. In some cases, injection of AA could be a strategy with lower investment and risk than installing pumps and pipelines for recirculation and seeding of hydrate particles. In some cases, reducing slurry viscosity and pressure drop by recirculation of water and AA could be economical even though this requires installation of more pipelines. A combination of the methods discussed in this paper could be a viable approach for some field developments. The determining factor in the end will be the investment and operational cost for the various methods.

7. CONCLUSION

Hydrate cold flow has the potential of becoming an important flow assurance strategy in oil and gas exploration. It may reduce cost, exploration complexity and use of chemicals. Experiments performed by various research groups show that adding of a small percentage of AAs promotes formation of hydrate slurry. Flow loop experiments without chemicals have demonstrated that seeding of powder-like hydrate particles results in formation of transportable hydrate slurry. Static mixers, increased velocity and other effects increasing water dispersion or reducing water droplet size also enhance formation of hydrate slurry. A field trial of once-through operation has indicated pipeline wall deposition of hydrates. Further studies of hydrate deposition have been performed in recent years to gain more knowledge about mechanisms involved in this phenomenon. Measurement of various parameters, which could increase the understanding of the cold flow conversion of warm well fluid to hydrate slurry in particular and hydrate slurry flow in general, are proposed for potential future experiments. Development of hydrate slurry flow models along with large scale experiments testing the methods for producing hydrate slurry are important for validation and implementation of cold flow as a reliable hydrate management strategy.

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