

HYDRATE PLUGGING POTENTIAL IN UNDERINHIBITED SYSTEMS

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ABSTRACT

An underinhibited system is defined as a system where an insufficient amount of thermodynamic inhibitor is present to prevent hydrate formation. Underinhibition might occur due to malfunctioning of equipment, temporary limitations in the inhibitor supplies or operational limitations or errors. Understanding the plugging risk of such systems is important in order to take the correct precautions to avoid blocked flowlines. In this paper we summarize the experimental efforts for the last decade within StatoilHydro on the hydrate plugging risk in underinhibited systems. The flow simulator has been used as the main experimental equipment. The overall results for systems underinhibited with ethylene glycol or methanol show that the plugging potential increases up to a maximum at concentrations around 10-15 wt%. At higher concentrations the plugging potential reduces compared to the uninhibited system. The results can be explained as follows: As water is converted to hydrates in a system containing a thermodynamic inhibitor, the inhibitor concentration will increase until the remaining aqueous phase is inhibited. This self-inhibited aqueous phase will wet the hydrate particles, giving rise to the characteristic term of “sticky” hydrate particles. The aqueous layer surrounding the hydrate particles will form liquid bridges, by capillary attractive forces, upon contact with other hydrate particles or the pipe wall. During the hydrate formation period, there is also a possibility that some of the liquid bridges are converted to solid ones, strengthening the agglomerates. Depending on the oil-water interfacial tension, the phase ratio between the aqueous phase and the solid hydrates and the conversion of liquid bridges to solid ones, this leads to increased plugging risk at lower concentrations of inhibitor (< 20 wt%) and reduced risk at higher concentrations as compared to the uninhibited system.

Keywords: Hydrate plugging potential, underinhibition, agglomeration, capillary adhesion forces

INTRODUCTION

Hydrate control engineers have many different methods to avoid blockage of flowlines and process equipment by hydrates. One of the most used methods is the application of thermodynamic inhibitors. Thermodynamic inhibitors shift the hydrate formation boundary to higher pressures and lower temperatures by associating with the water molecules and preventing their arrangement into a hydrate lattice [1, 2]. There are two main types of thermodynamic inhibitors: salts and alcohols/glycols. Salts are seldom deliberately injected as hydrate inhibitors due to their negative

impact on corrosion and the need to use water as injection solvent. Of the alcohols, mainly methanol (MeOH) and monoethylene glycol (MEG) are used.

The injection rate of the inhibitor is chosen so that the pipeline operates outside the hydrate formation region during production or shut-downs. Safety margins are normally added to cope with possible uncertainties in predictions and rate measurements. In certain cases, however, the amount of inhibitor might be too low to give complete inhibition, this is called underinhibition.

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Underinhibition might occur due to malfunctioning of equipment, temporary limitations in the inhibitor supplies or operational limitations or errors. As underinhibition is a potential scenario with serious consequences, it is important to increase the understanding of the plugging risk of such systems.

During the Tommeliten field tests of hydrate plugging and dissociation in 1994 [3] it was discovered that systems with insufficient amount of methanol resulted in a worse plugging tendency than the uninhibited system. This was the first time it was observed that underinhibited systems could result in worse pipeline plugging than if no thermodynamic inhibitor was added. After the Tommeliten field tests, the hydrate plugging potential of underinhibited systems has been studied extensively for various concentrations and types of inhibitors [4-5]. These investigations showed that underinhibited systems at low concentrations of methanol, MEG or salt (~2.5 to 10 wt%) increased the plugging potential. Using MEG or MeOH the hydrates formed adhered more to the wall than for an uninhibited system, while the NaCl underinhibited systems plugged more frequently. The experimental findings by Statoil (now StatoilHydro) were followed-up by Yousif [6], who showed that both methanol and MEG enhanced the rate of hydrate formation when added at low concentrations to the water phase (1-5 wt%).

Based on these initial findings, more experimental work was performed on underinhibited systems with up to 40 wt% inhibitor concentration. These studies show that at very high inhibitor concentrations the system formed a more gel-like slurry, giving lower plugging potential than for the uninhibited system. Most of the experimental work referred here has been performed in the flow simulators (2" and 5") at the StatoilHydro R&D Center in Trondheim, but unpublished data from other types of test facilities also give similar indications.

This paper summarizes the results obtained in the StatoilHydro experimental studies. Mechanisms to explain the experimental observations are suggested.

EXPERIMENTAL

Description of the StatoilHydro Flow Simulator

The 2" Flow Simulator is a wheel-shaped loop made of stainless steel (see Figure 1). The inner diameter of the steel tube is 52.5 mm, the wheel diameter is 2 m and the volume of the wheel is 13.4 litres. The maximum operating pressure is 100 bar. A high-pressure window (PMMA-glass) allows visual inspection using a video camera. The Flow Simulator is placed in a temperature-controlled chamber [0 – 60 °C].

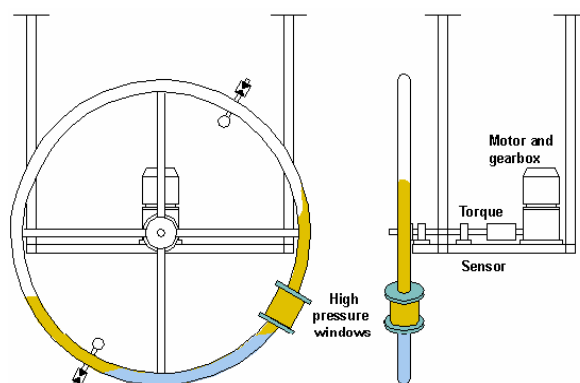


Figure 1. Schematics of the Flow Simulator.

The wheel is attached to a motor/gearbox system, enabling rotation between 0.3 m/s and 5.0 m/s peripheral velocity. A torque sensor is installed as part of the rotating shaft assembly to provide torque measurements during rotation. The temperature in the chamber, the temperature and pressure inside the wheel and the torque on the shaft are measured at preset intervals. The accuracy of the measurements is estimated to be ± 0.2 Nm for the torque, ± 0.2 bar for the pressure, ± 0.1 °C for the fluid temperature in the wheel, and ± 1.0 °C for the temperature in the chamber.

Operating procedure

The Flow Simulator was operated with three phases present: condensate, gas and water. During all the tests reported here, the following applies: The gas was composed of methane, ethane and propane in ratio 74.5:17.5:8 (mol%). Distilled water and the synthetic condensate Exxsol D60 were used. The water + MEG content (based on dead oil volume) was 20 vol%. To avoid liquid carry over during the experiments, the maximum amount of liquid in the wheel was set to about 40 vol%. Between two subsequent experiments with the same fluids, the wheel was always heated to 55°C for several hours to ensure no hydrate and wax residues before the next experiment.

Observation of hydrate plugging potential and formation kinetics

A fluid system capable of transporting hydrate particles with minimum risk for plugging should have the following characteristics in the flow simulator:

- Finely dispersed hydrate particles
- No hydrate lumps
- No hydrate deposits
- Low and stable torque when the temperature and pressure have stabilized

A fluid system is defined to have a high plugging potential if large deposits, lumps or plugging occur during the experiment, even if it is more or less transportable at the endpoint. For gas-condensate systems, the hydrate plugging potential has always been observed to be high, where deposits, lumps and plugging are normally observed within the typical experimental time frames.

Analysis of logged data

The temperature, pressure and torque data were logged during all the experiments. The pressure and temperature curves give information of both the amount of water converted to hydrates and the conversion rate. Figure 2 shows the basic steps for calculating the pressure drop due to hydrate formation and the rate of the pressure drop. The discontinuity in the PT curve shown in Figure 2 a) is due to the formation of hydrates. Extrapolation of the smooth PT curve before hydrate formation gives the PT curve for no hydrate formation. The difference between this extrapolated PT curve and the experimental PT curve gives the pressure drop due to hydrate formation (see Figure 2 b)). The relation between the amount of water converted and pressure drop can be estimated using a thermodynamic program packages such as PVTsim (Calsep):

1. Calculate a hydrate flash at the experimental pressure and temperature prior to hydrate formation. This gives the amount and composition of hydrate at equilibrium conditions.
2. Update the composition in the flow simulator by subtracting the components in the hydrate phase.
3. Update the volume by subtracting the volume of the formed hydrate phase from the flow simulator volume.

4. Perform a volume-temperature flash using the new volume and new composition at the experimental temperature. This gives the pressure after the hydrate formation at equilibrium conditions.
5. Calculate the ratio of the pressure drop to the amount of water in the formed hydrates.

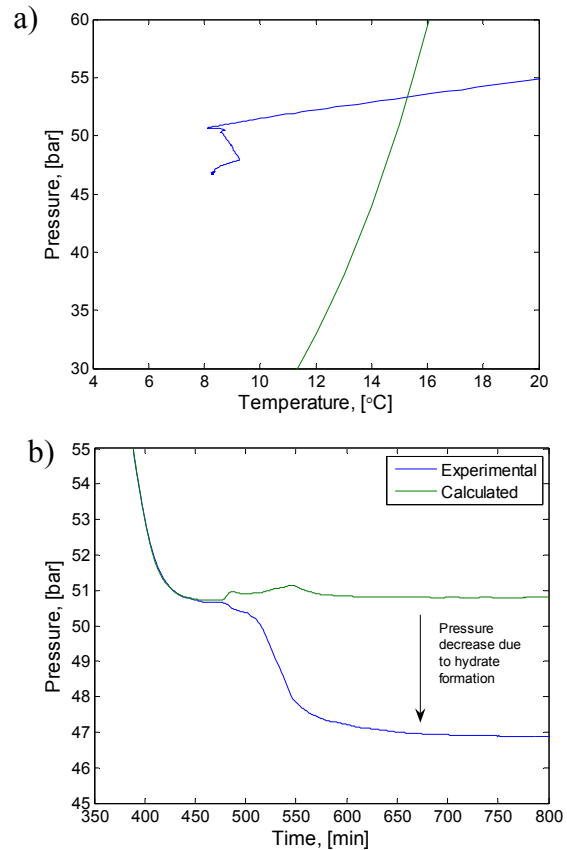


Figure 2. Analysis steps: a) Experimental P-T curve (blue) and hydrate equilibrium curve (green), b) Experimental pressure curve and calculated projected pressure curve for no hydrate formation

Using this scheme, an average value of 6.6 moles of water converted per bar have been estimated for all the studied fluid systems. This is in good accordance with Kelland et al [7], which estimated 6.2 to 6.9 moles of water per bar for a condensate system at 85 bar and 4 °C using an identical flow simulator. However, the quality of the calculated water to hydrates conversion depends on the precision in both the experimental composition and the equation of state used for flash calculations. In this work we have used PVTsim with the Soave-Redlich-Kwong equation of state, with its known limitations for water containing systems [8].

RESULTS AND DISCUSSIONS

Hydrate plugging potential

The hydrate plugging potential is determined by a combination of visual observations and the torque measurements. Figure 3 shows a representative logging of the hydrate formation kinetics and plugging for a system without any inhibitor. The pressure and the two torque measurements are all stable before the hydrate formation starts (around 860 min). The torque is measured in two ways, as the mean torque per rotation and as the maximum torque per rotation. Hydrate formation is indicated as the pressure decreases with increasing torque. Hydrate plugging is detected as the mean torque curve peaks and then drops to a lower level, while the maximum torque are at high levels. Such torque logging is expected for plugs which follow the rotation of the flow simulator. Sometimes part of the plug can be observed through the high pressure window (see Figure 4).

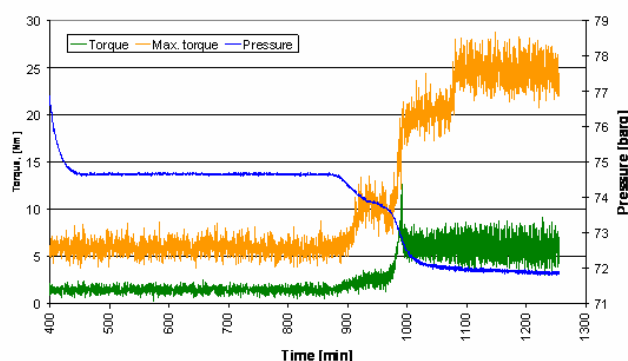


Figure 3. Exxsol D60 system without any inhibitor; dynamic cooling test at subcooling 3.7°C.



Figure 4. Hydrate plug formed in Exxsol D60 system without any inhibitor.

For systems with low MEG content, between 5 and 20 wt%, deposits are formed readily in the Flow Simulator. Figure 5 shows typical hydrate deposition in a 10 wt% MEG system. The picture was taken while the window was in the gas phase.

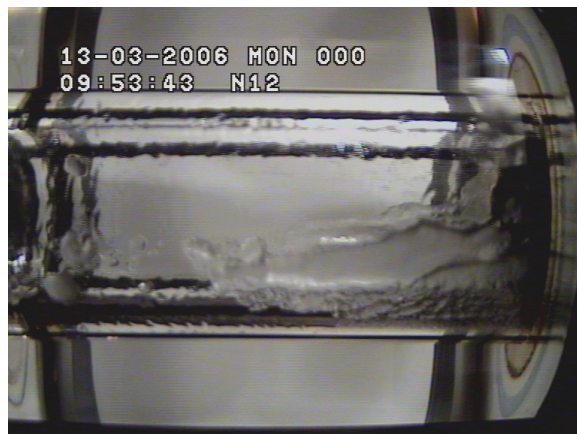


Figure 5. Hydrate deposits on high pressure window. Exxsol D60 with 10 wt% MEG in aqueous phase.

Since the flow simulator is a closed system, the amount of deposits is limited by the amount of water present. In a real pipeline the danger of clogging would be larger.

Although results presented here are for specific Exxsol D60 systems, the overall understanding is based on both published [3-5] and unpublished data including two light oils and seven condensates. The behaviour of the MEG and MeOH uninhibited hydrate systems is very similar for all these light oils and condensates. The overall results from the MEG or MeOH uninhibited systems show that the plugging potential increases up to a maximum around 10-15 wt% and then decreases at higher concentrations compared to the uninhibited system. The properties of the hydrates go through large changes when moving from uninhibited towards full inhibition. First the hydrates are forming large but relatively dry lumps. With an increasing inhibitor concentration from 5 to 20 wt% the hydrates become more adhesive depositing on the wall and agglomerating into larger chunks in the bulk fluid. At higher concentrations up to the full inhibition point smaller hydrate particles form a gel-like structure in the bulk fluid. Figure 6 summarizes the overall experimental findings.

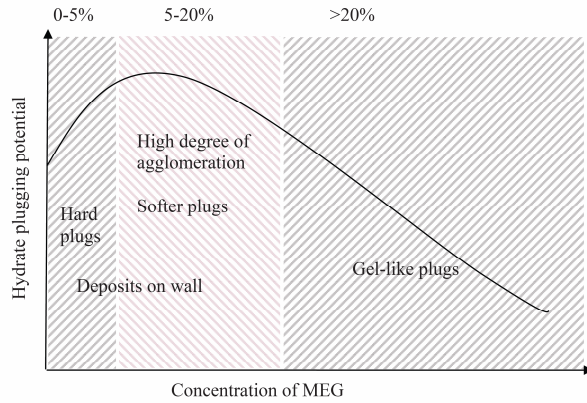


Figure 6. Hydrate plugging potential as a function of MEG concentration.

The inhibitor concentration ranges given above are only meant to be indicative and will depend on several other parameters like the degree of sub-cooling, water cut and the fluid dynamics of the system. For example, a flow loop test (performed for StatoilHydro) showed plugging behavior with 30 wt% MEG at 30 vol% water cut.

Thermodynamic considerations

Once inside the hydrate region, an uninhibited system has the potential to convert all of the water to hydrates. This is not the case for an uninhibited system, since the inhibitor concentration will increase in the aqueous phase as more water is converted to hydrates. This is shown in Figure 7 where, at equal sub-cooling, the maximum water fraction possible to convert to hydrates decreases as the MEG concentration increases.

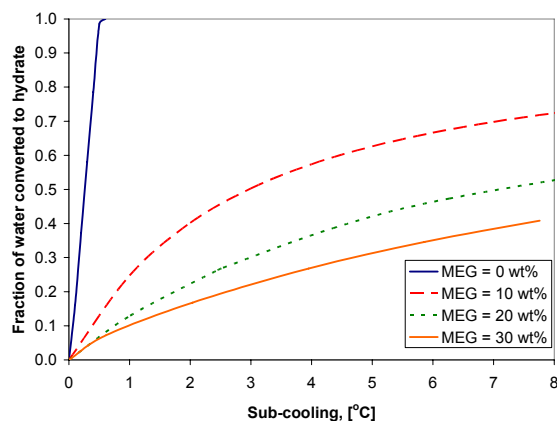


Figure 7. Maximum calculated fraction of water converted to hydrate for different concentrations of MEG at 70 bar, at thermodynamic equilibrium.

However, in real systems and also in experimental flow lines, loops and simulators, plugging may occur at conversions as low as 10-20 %. During hydrate formation, water will be enclosed within hydrate particles and lumps, preventing hydrate formers to meet liquid water molecules. This will cause the hydrate formation to end at lower degree of conversion.

Hydrate formation kinetics

Most of the earlier experimental studies on uninhibited systems have focused on two experimental results, the amount of deposits and how the hydrates behave in the bulk fluid, i.e. large lumps, smaller particles etc. Information about the hydrate formation rate and the degree of water to hydrates conversion would give better understandings of the observations. Here we report the hydrate induction time, formation rate and water to hydrate conversion which have been extracted from the experimental temperature and pressure curves. The induction times, although with some scattering, show an interesting pattern (Figure 8). The system with 10 wt% MEG shows overall shorter induction times than the uninhibited system and the higher concentration MEG systems.

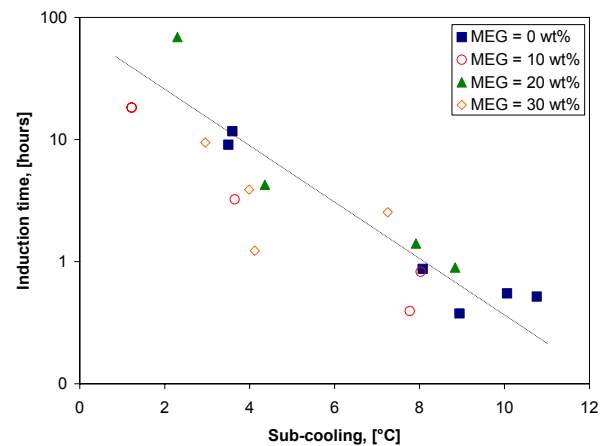


Figure 8. Induction time as a function of sub-cooling for uninhibited and underinhibited Exxsol D60 systems at 70 bar. Dynamic cooling experiments. Rotational speed of flow simulator: 1 m/s.

Yousif [6] investigated the hydrate kinetics of low concentration MeOH and MEG systems. In the concentration range from 0 to 5 wt% MeOH, he found that hydrate formation rate increased ten folds. The same was observed for MEG at 2 wt% concentration. The calculated water conversion

rates from the flow simulator (although not in the same concentration interval) do not show the same trend. Figure 9 shows the conversion rates during the fast hydrate growth period. At a rotational speed of 1 m/s, the uninhibited and 10 wt% MEG systems show similar water conversion rates, whereas the systems containing 20 and 30 wt% MEG show slower conversion rates. However, for the uninhibited system, the water conversion rate levels off and decreases at high sub-cooling, whereas for all of the underinhibited systems the water conversion rate increases monotonously with increasing subcooling. This may indicate that there are less mass transfer limitations in the uninhibited systems. In all the experiments performed in this study, the temperature increase during hydrate formation was very limited, indicating that heat transfer was not the limiting factor for hydrate growth. In the experimental setup by Yousif, there was no oil phase, so hydrates formed directly at the gas/water interface. In the flow simulator there is no or very little direct contact between the gas and water phase, except at very high rotational speed. Most of the hydrate formation will therefore take place at the oil/water interface. The hydrate formation will be limited by the accessibility of both hydrate formers and water. This will be seriously restricted when the hydrates agglomerate and form large lumps, with water and oil pockets enclosed within.

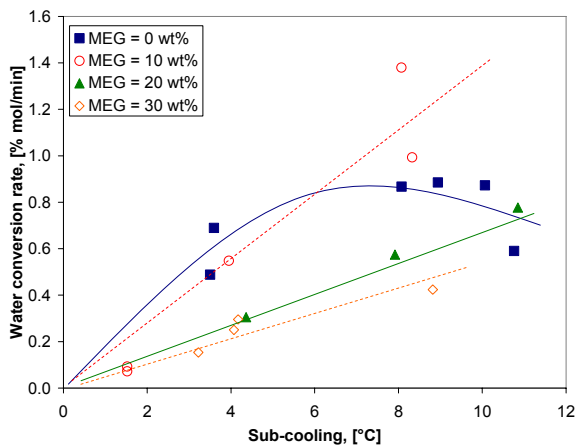


Figure 9. Water conversion rate as a function of sub-cooling for uninhibited and underinhibited Exxsol D60 systems at 70 bar. Trend lines drawn for easier interpretation. Dynamic cooling experiments. Rotational speed of flow simulator: 1 m/s.

Water to hydrate conversion

The fraction of water converted to hydrates for the uninhibited system increases first with increasing sub-cooling but starts to decrease at higher subcoolings (Figure 10). The initial increase is parallel to that observed for the underinhibited systems. At low subcoolings the conversion is relatively low for all the systems and no major difference exists between the systems. It is first at high degrees of subcooling that differences appear. At such conditions hydrate formation is so fast that large lumps can be easily formed when the particle characteristics have the tendency for agglomeration and there would not be enough inhibitor to slow down the further growth. This would be the case for the uninhibited system and would also be expected for systems with very low inhibitor concentrations. Figure 10 confirms this clearly for the 0% MEG case. The fast hydrate growth results in enclosure of water and oil pockets within hydrate lumps. This will also contribute to low degree of conversion.

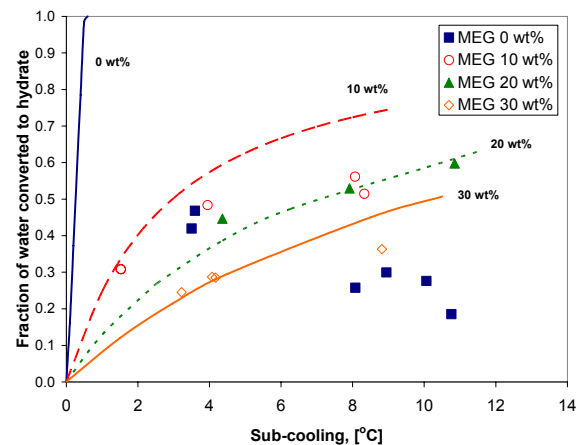


Figure 10. Fraction of water converted to hydrate at end of hydrate formation, as a function of sub-cooling for uninhibited and underinhibited Exxsol D60 systems at 70 bar. Experimental points and theoretical maximum conversion curves. Dynamic cooling experiments. Rotational speed of flow simulator: 1 m/s.

The uninhibited systems, however, show increasing water to hydrate conversion with increasing sub-cooling and flatten out at the highest subcoolings tested. The underinhibited systems follow quite closely the curves for maximum possible water to hydrate conversion achievable at equilibrium. This suggests that mass transfer limitations are more or less absent, which again means a good contact between the water

phase and the hydrate formers. Since the adhesion between hydrate particles decreases with increasing MEG concentration, the occlusion of water and oil within hydrate lumps is less likely to happen. This would mean increased contact area between the growing hydrate particles and the reactants. At higher degree of sub-cooling this makes the underinhibited system to convert more of the water to hydrates.

Hydrate agglomeration: capillary adhesion forces

Hydrate nucleation and initial growth depend upon the mass transfer characteristics and the thermodynamic properties of the systems, such as equilibrium temperature, pressure and composition. The kinetic driving forces will accordingly increase along with increased thermodynamic forces. This is why in general the induction time decreases and water conversion rate increases with increasing degree of sub-cooling. The aggregation of hydrate particles, on the other hand, depends upon physical and mechanical properties such as the fluid dynamics of the system, particle size and the interparticle adhesion force. Camargo and Palermo [9] suggested that hydrate agglomeration in black oil systems was dominated by capillary attractive forces. The hydrate particles would then start to agglomerate, held together by liquid bridges between the particles. The adhesion force between the particles is caused by capillary condensation of liquid bridges either from a vapour atmosphere or through the drainage of liquid from adjacent adsorbed fluid layers, see Figure 11.

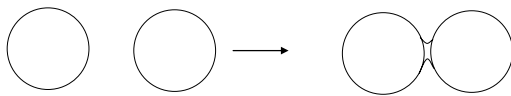


Figure 11. Capillary condensation of liquid between contacting spheres.

The concept of capillary adhesion forces between hydrate particles has been experimentally investigated by Sloan and co-workers [10, 11]. They have shown that the adherence force decreases with increasing degree of sub-cooling, due to the loss of liquid water film on the particle surface [10]. This is in analogy to making snowballs with wet snow (easy process) versus using dry, powder snow (very difficult process!).

This is also the initial concept of SINTEF's Cold Flow project [12], where all water is thought to be converted to small sized, dry hydrate particles, removing the capillary adhesion forces. Sloan et al [11] also showed that the adhesion forces between hydrate particles decrease when the interfacial tension decreases.

Adhesion of particles through capillary forces is a well known mechanism in fields such as powder technology, granular media and tribology. For instance in the field of granulation, many of the physical descriptions apply directly to hydrate systems. Granulation is a process to enlarge fine powders into larger particles, or granules. One way of doing this is by adding liquid which sticks the constituent particles together. The liquid binds the particles together by a combination of capillary and viscous forces until more permanent bonds are formed by subsequent drying or sintering. In order to control and optimize the process, granulation has been a subject of research for almost 50 years.

The current view of the granulation process is that it is a combination of three rate processes [13]:

1. Wetting and nucleation. Here the liquid binder is distributed to the dry powder to give a distribution of nuclei granules.
2. Consolidation and growth. The granules grow and compact as a result of collisions in granulator.
3. Attrition and breakage. The granules break due to impact and wear in the granulator.

Depending on the liquid to solid ratio, granules can exist in different states of liquid saturation [14], see Figure 12.

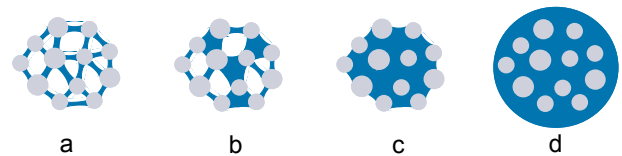


Figure 12. Different states of liquid saturation in granules: a. pendular; b. funicular; c. capillary; d. droplet.

In the pendular state the particles are held together by liquid bridges only present at the contact points. The funicular state is a transition between the pendular and capillary state where the granule is not fully saturated with liquid. The capillary state occurs when all the voids in the granule is

saturated with liquid, which provides the strongest granule. At the surface, the liquid is drawn back into the pores under capillary action, and inside the granules, the particles are completely surrounded with liquid. If more liquid is added, the strength of the granule decreases rapidly, and the granule will be converted into a system with particles suspended into the liquid or a paste. This is called the droplet stage.

The strength of the liquid bridge is mainly controlled by two forces: capillary and viscous. The low viscosity of water makes capillary forces dominant over viscous ones for water bridges. We will therefore only consider capillary forces for hydrate systems in the following discussion. The capillary force arises as a consequence of the suction pressure caused by the curvature of the liquid interface between water and oil (or gas). This capillary suction pressure is given by the Young-Laplace equation:

$$\Delta P_{cap} = \gamma_{LL} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1)$$

where γ_{LL} is the interfacial tension between water and oil. r_1 and r_2 are the two principal radii of curvature of the surface, as shown in Figure 13.

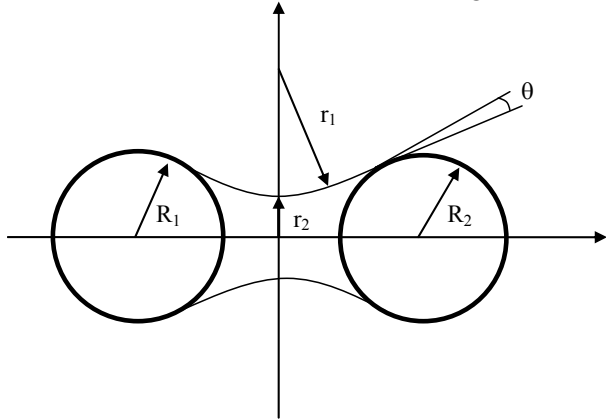


Figure 13. Schematic of liquid bridge between two spheres.

The liquid bridge profile cannot in general be solved analytically. Hence, numerous approximations exist for the capillary force [15, 16]. A simple estimate of the maximum capillary force between two smooth, rigid surfaces at contact is given by [17]:

$$F_{cap} = 2\pi R^* \gamma_{ll} \cos \theta \quad (2)$$

where R^* is the harmonic mean radius of the two particles ($1/R^* = 1/R_1 + 1/R_2$) and θ is the contact

angle of the liquid forming the bridge on the solid surface. For rough surfaces, the contact area will be smaller, giving a lower capillary force than that given by Eq. (2).

A widely quoted model for predicting the static tensile strength of granules was developed by Rumpf [18]. He suggested that the theoretical strength of a granule is the summation of all the interparticle forces across the fracture surface. For a granule in the funicular and capillary states, the tensile strength is given by:

$$\sigma_t = SC \frac{1 - \varepsilon}{\varepsilon} \frac{\gamma_{LL} \cos \theta}{d_p} \quad (3)$$

where S is the liquid pore saturation, C is a material constant (equal to 6 for uniform spheres), ε is granule porosity and d_p is the surface-average particle diameter. As shown by Schubert [19], the tensile strength is expected to increase with increasing saturation in the funicular state, up to a maximum as the granule is fully saturated in the capillary state. Any increase of the binder liquid above saturation level will cause the tensile strength to rapidly decrease, as shown in Figure 14.

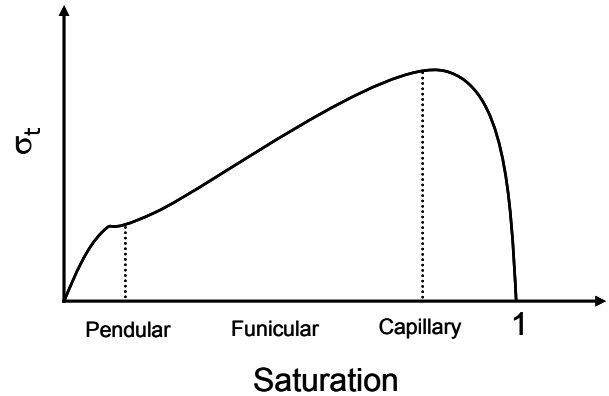


Figure 14. Relationship between tensile strength and wet granule saturation.

It is important to point out that there are normally no chemical reactions involved in a granulation process; this is perhaps the main difference from a hydrate system, where hydrate formation complicates the overall picture. However, it is easy to see that many of the same principles apply to the hydrate process. In the same way as the granules are held together by adhesion forces arising from interfacial tension forces at the liquid/air interface, the hydrate agglomerates are held together by the surface tension forces at the water/oil or water/gas interfaces. As already

mentioned, this has already been suggested by several authors [9-11, 20] and is generally accepted as the main cause for hydrate agglomeration. However, models for hydrate agglomeration have been mostly investigated as part of hydrate slurry models, where the primary hydrate particles are formed from emulsified water droplets [21-23]. For fluid systems with a free bulk water phase, typically for gas-condensate and high water cut systems, hydrates start to form in the bulk oil/water interface. Once aqueous bridges between hydrate particles have been formed, they have the potential to be converted to solid hydrate bridges depending on the liquid bridge composition and the availability of hydrate formers in the surrounding gas or oil phase. Such a conversion of liquid bridges to solid bridges will make the agglomerates more sustainable to high shear forces. In addition, entrapped oil and gas within the agglomerate will also support the capillary suction pressure of the liquid bridges.

Based on the lessons learned from granulation theory, there are basically four ways of avoiding hydrates to agglomerate through capillary liquid bridges:

1. *Reducing the interfacial tension between oil and water.* This will directly reduce the strength of the aqueous bridge. Well dispersed low water cut systems may be easily transported both during and after hydrate formation. However, oil and water may separate in such systems during shut-ins and plugs may form soon after the start-up.
2. *Increasing the contact angle between the liquid forming the bridge and the hydrate particles.* This will prevent water to wet the hydrate surfaces and the hydrate particles will disperse into the oil phase. This is the basic mechanism for anti-agglomerant additives [24]. It is also the main mechanism for oils showing natural hydrate transportability [25].
3. *Reducing the liquid binder content to a minimum.* This is the basic for one of the cold flow concepts [12], where all water is supposed to be converted to small sized, dry hydrate particles, removing the capillary adhesion forces.
4. *Increasing the liquid binder content above the maximum saturation level.* If fine sized hydrate slurry particles can be formed, the slurry can be transported by using water as the carrier medium [26].

Common to all the above approaches is the potential of forming agglomerates or deposits during the hydrate formation process. Avoiding the formation of strong capillary bridges and conversion of such liquid bridges to solid ones is essential during hydrate growth to prevent hydrate deposition and plug formation.

Based on the above analysis, we propose the following mechanism for agglomeration during hydrate formation.

1. Primary hydrate particles stick to each other or pipe wall by capillary adhesion forces (aqueous bridges).
2. Hydrate growth in some of the aqueous bridges makes the particles grow together or on the pipe wall. The hydrate bridge growth rate will depend on the availability of hydrate formers and the thermodynamic driving force around the growth sites. The total strength of the hydrate bridges will be determined by the thickness and length of the solid bridges. The combined strength of aqueous and hydrate bridges will be balanced by the shear forces and determine the sizes of the agglomerates or deposits.

These results allow now a framework to explain the relationship between the hydrate plugging potential and the MEG concentration as outlined in Figure 6. Without thermodynamic inhibitor, all of the water has the potential to be converted to hydrates (assuming excess of hydrate formers). After nucleation, hydrates will form at the oil/water interface. These hydrate particles will be water wetted, and the local hydrate to aqueous ratio will be high and preferable for formation of capillary bridges. The hydrate particles will agglomerate to large lumps with both water and oil/gas entrapped. Some hydrates may continue to form within the aqueous bridges, making harder and stronger lumps/deposits. The water phase wetting the outside of the lumps will continue to react to form more hydrates, resulting in larger lumps with a dry surface. These lumps would still contain much liquid inside. The formation of a dry skin on the outside of such hydrate lumps will seriously limit further hydrate growth. However, as such lumps contain a lot of unreacted water they have a high potential for plugging. As these lumps collide with each other or the pipewall in bends or other restrictions, the encapsulated water may be freed. The free water can then rapidly convert and

bind lumps together or depositing on pipe walls, jamming the pipeline.

When water is converted to hydrates in an uninhibited system, the inhibitor concentration in the aqueous phase will increase. This will change the hydrate equilibrium temperature of the remaining water phase so that at some point during hydrate formation, this aqueous phase will be inhibited at the given temperature and pressure. Assuming no natural hydrate transportable compounds, which are the general case for gas-condensates and most light oils, the surface of the hydrate particles will be hydrophilic, so the remaining aqueous phase will wet the hydrate surfaces. Such wetted particles can now attach themselves to the pipe wall or to each other through liquid bridges and thus forming larger agglomerates or lumps. During the hydrate formation period, there is also a probability that some of the liquid bridges are converted to solid ones, strengthening the agglomerates. This will limit the water conversion as some un-reacted water may be enclosed within the agglomerate. The experimental water to hydrate conversion for the 10 wt% MEG system was not as high as the theoretical, indicating some mass transfer limitations due to formation of solid bridges. The combination of both solid and liquid bridges, in addition to wetted hydrate surface, explains the high plugging potential for that system.

At higher MEG concentrations, the liquid to hydrate ratio will at some point cross the maximum saturation point, causing the capillary forces to diminish. Conversion to solid bridges is then avoided and the formed hydrates can be more or less transported as water-wet slurry.

The observations of MeOH and MEG uninhibited systems show that there is an increase in the deposition of hydrate particles at concentrations up to around 10 wt% of inhibitor, with a decrease at higher concentrations (around 20 wt%) and no deposition at concentrations from 30 wt% and higher. This corresponds, using granulation terms, to a transition from the funicular and capillary states to a droplet state. Figure 15 shows the overall results with different states for the three regions.

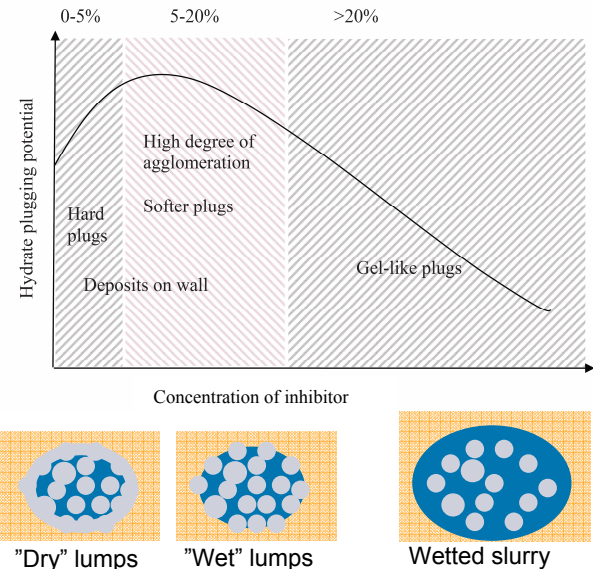


Figure 15. Conceptual picture of hydrate behaviour at different inhibitor concentrations.

Apart from the effect of thermodynamic inhibitors on hydrate formation and plugging risk, the results presented here also show that plugs form more easily at lower flow rates, higher water cuts, and smaller inner diameter of the pipe. The diameter effect was also reported by Kinnari et al [27], which experienced that a 2" model template plugged easily in tests with low gas rates, while a 6" model template hardly plugged at all.

CONCLUSIONS

The hydrate plugging potential of MEG or MeOH uninhibited systems increases to a maximum at inhibitor concentrations about 10-15 wt% and then decreases at higher concentrations compared to the uninhibited system. In the uninhibited system all water in contact with hydrate formers can be converted to hydrates. This results in formation of large hydrate lumps with water and oil pockets trapped inside but with relatively dry surface outside. The dry surfaces will limit the further growth and agglomeration of the system. The inhibitor concentration in an uninhibited system will increase during hydrate formation, until the remaining aqueous phase is inhibited. This self-inhibited aqueous phase will wet the hydrate particles, giving extra agglomeration due to capillary forces. During the hydrate formation period, there is also a possibility that some of the liquid bridges are converted to solid ones, strengthening the agglomerates. This results in a maximum hydrate plugging potential around 10-15

wt% inhibitor concentration. At higher inhibitor concentrations, above 20-30 wt%, the liquid to hydrate ratio is above the maximum saturation point, causing the capillary forces to diminish. The formed hydrates can then be more or less transported as water-wet slurry.

The inhibitor concentration ranges given above are only meant to be indicative, and will depend on for example the degree of sub-cooling, water cut and the fluid dynamics of the system. The understanding of how shear forces affect the hydrate formation, agglomeration and plugging is poor and will be addressed in future work on underinhibited systems.

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