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# **Efficiency of thermodynamic inhibitors for melting gas hydrates**

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## **Preface**

The research presented in this report is done as a finishing project of my Master of Technology education at the NTNU. It was performed at the multiphase lab of Sintef in Trondheim, with Roar Larsen and Jón Steinar Guðmundsson as supervisors.

The project work has consisted of low pressure laboratory experiments and analyzing the results. High pressure experiments were planned as well, but there was unfortunately not enough time to do these.

I would like to thank Roar for the opportunity and the support during this project.

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## Abstract

*Background:* Hydrate plugs have cost the oil companies billions of dollars in both lost production, ruined equipment and the loss of lives. Hydrate plugs can form both in wells, pipelines, risers and the production equipment. When plugs form in a riser, the water will separate out and form a column on top of the plug. One way of removing hydrate plugs, is with so-called thermodynamic inhibitors (antifreeze solution). The most common inhibitors in use today are methanol and glycols (MEG and TEG). A salt, HCOOK, which is already in use on drilling rigs as a high performance drilling fluid, has been suggested as a new, more efficient inhibitor.

*Objectives:* The major goal of this project was to compare the efficiency of the common inhibitors, methanol and TEG, with the new inhibitor HCOOK. In this comparison, the costs of using the different inhibitors were not taken into account.

*Methods:* Hydrate plugs were formed out of water and THF (Tetrahydrofuran) in a low pressure environment (atmospheric). The plugs were formed in test tubes in a water bath with a circulating cooling liquid. They were melted using the three inhibitors. Methanol and TEG were injected 100% pure, while different concentrations of HCOOK were used. The melting was measured through a decreasing plug-size; this decrease was than calculated to lost hydrate-plug-volume. To simulate the situation in risers, tests were also done with a water-column on top of the plugs.

*Results:* The results show that 100 % pure TEG is as efficient as a 20 wt% HCOOK-solution. Both of these are much more efficient than 100 % pure methanol. The 70 wt% HCOOK-solution is more efficient than the 60 wt% solution, which again is more efficient than a 50 wt% solution and so forth. The results from the experiments with a water-column on top show the same results: a high concentration of HCOOK is more efficient than a low concentration of HCOOK, but the melting slowed down compared to without a water column on top. With the water column the efficiency of TEG is in between the 10 and 30 wt% HCOOK-solution, even though the melting rate of TEG is not influenced by the water-column.

*Conclusions:* HCOOK is overall superior to both methanol and TEG as a hydrate plug remover. Even though more testing is necessary, HCOOK should absolutely be considered as an inhibitor for the nearest future.

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## Abbreviations

ID	Inner diameter of the test tube	dm
h	Height of the test tube	dm
A	Area of the cross section of the test tube	dm <sup>2</sup>
V	Volume of the test tube	ml
$\rho$	Density	g/ml
$\mu$	Viscosity	cP

TEG	Triethylene glycol
MEG	Monoethylene glycol
HCOOK	Potassium formate
MeOH	Methanol

In this report the term *inhibitor* is used both for “real” hydrate growth inhibitors and for hydrate plug removers. There is no difference between the two expressions; they only distinguish between the intended uses.

THF-solution refers to a solution with 21 vol% THF and 79 vol% water.

Throughout the report, *hydrate-to-inhibitor ratios* are mentioned; i.e. 1:2, 2:1 etcetera. In all cases the first number mentioned represents the volume of THF-solution and the second number represents the volume of the inhibitor.

# 1 Introduction

Hydrate plugs cause major problems for the oil industry world wide. A lot of money is spent on preventing and removing them. Hydrates are crystals with well-defined structures which occur when water encages gas molecules smaller than 1 nm at low temperatures and elevated pressures. The encaged gas molecules include mostly methane, but also ethane, propane and butane in addition to CO<sub>2</sub>, H<sub>2</sub>S and N<sub>2</sub>.

Hydrate plugs can form in wells, flow-lines, risers and other production equipment. When hydrate plugs form in a riser, a water column will form on top of the plug due to separation of the multiphase liquid. Different hydrate prevention methods are in use today; heating of the pipe, burial, insulation, bundling and injection of thermodynamic inhibitors. The most common hydrate inhibitors used today are methanol and glycols (MEG and TEG). A new inhibitor has been suggested; Potassium formate (HCOOK). A major disadvantage of the common inhibitors is low density; HCOOK forms a high density, low viscosity brine.

The objective of this project was to compare the efficiency of the common inhibitors, methanol and TEG, with the new inhibitor HCOOK. In this comparison, the costs of using the different inhibitors were not taken into account.

Hydrate plugs were formed in test tubes and melting by the different inhibitors was measured. To simulate possible situations in risers, experiments were also done with a column of water on top of the plugs. In this way the hydrate removing efficiency of the three inhibitors could be compared.

After this introduction, some background about hydrates and how and why they form is presented in chapter 2. Here common means of hydrate plug prevention and removal are explained. Finally some other research done in the nearest past is discussed. Chapter 3 shows the different physico-chemical properties of the different inhibitors and describes the methods used in this project. The results are presented in chapter 4 and discussed in chapter 5. The conclusions of this work are shown in chapter 6 and future work suggested in chapter 7.

## 2 Background

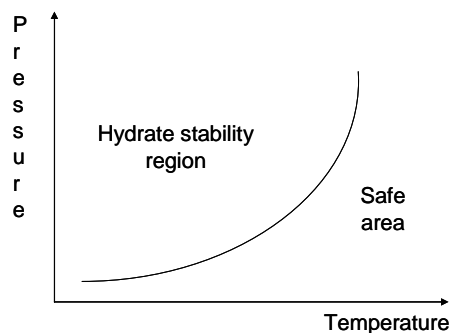
Since Hammerschmidt in 1934 found that hydrate plugs, not ice plugs, were plugging North American natural gas pipelines, a lot of research has been done to find a way to get rid of this problem. Hydrates are still a big problem for the oil companies and there is still a major effort to find out more about hydrates.

### 2.1 Hydrates

Natural gas hydrates are crystals with well-defined structures which occur when water encages gas molecules smaller than 1 nm at low temperatures and elevated pressures [Kelkar et al.]. At typical ocean temperature of 4 °C, 90 m of water depth provides the pressures required for hydrate formation [Sloan]. The encaged gas molecules include mostly methane, but also ethane, propane and butane in addition to CO<sub>2</sub>, H<sub>2</sub>S and N<sub>2</sub>. They occur naturally as surficial outcrops and as cementing agent in sediments. They are metastable and can easily dissociate, resulting in slumping or slides [Boatman].

### 2.2 Formation of hydrates

Hydrates can only exist within a certain range of temperature and pressure. The relationship between necessary pressure and temperature can be described by an equilibrium curve which can be seen in figure 1.



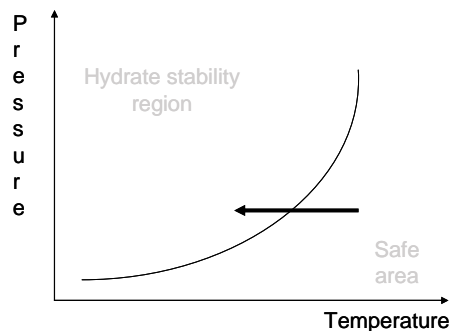
**Figure 1:** The hydrate stability curve

On the left-hand side of the curve, hydrates can exist (the hydrate stability region), on the right-hand side, they can not exist (the “safe” area). The curve describes the melting temperature of hydrates at varying pressures, not the formation temperature. For the initial formation of hydrates, a certain degree of subcooling is required. Subcooling can be defined as the temperature below the equilibrium temperature which enables hydrate formation. The degree of subcooling seems to be stochastic, which means that it is not possible to predict how large the necessary subcooling will be, and this subcooling will vary for the same mixture under equal conditions. It is dependent on contact area between the hydrate forming gas components and water, the rate of cool-down, impurities, velocity of flow and turbulence. Larsen states in his doctoral thesis: “There are numerous examples of systems which have been sitting well inside the hydrate forming region for

long periods of time (days and weeks) without having hydrates appear. The barrier against nucleation of the first hydrates is large enough to often require vigorous stirring, nucleation promoting surfaces or other “non-thermodynamic” factors to initialize the process of hydrate growth.” [Larsen, 1997]

Hydrates form in hydrocarbon processes in two fundamental ways: slow cooling of a fluid as in a pipeline and rapid cooling caused by depressurization across valves or through a turbo expander. [Sloan] In a gas/multiphase pipeline, hydrate particles first develop in the water phase without coalescing. When the amount of particles increases however, they will start clinging to each other and form lumps. At this stage, the danger of plug formation is biggest. The lumps might stick to the tube wall, or become large enough to plug the entire width of the tube. When the lumps are readily developed, the free water is embodied in the hydrate lumps and may act as glue between the particles [Cappelen].

In gas pipelines problems with hydrates often appear in connection to shut-ins. If the system is at a standstill long enough, the temperature of the fluid will decrease towards the ambient temperature. The system pressure stays the same, but the temperature will eventually sink below the equilibrium temperature described by the equilibrium curve (at that pressure) and hydrates will form. See figure 2 below.



**Figure 2:** What happens when the liquids in the pipe stand still

This problem will be the same in vertical risers, valves, separators and other processing equipment if the ambient temperature is low enough.

It is important to acknowledge the fact that hydrates do not need temperatures lower than 0 °C to be able to form. Even if hydrates are 85 mol% water, hydrates might form at temperatures as high as 21 °C if the system pressure is high enough. [Sloan]

### **2.3 Hydrate plug prevention**

To be able to avoid the formation of hydrate plugs, various measures are used: heating of the pipe, direct heating or induction heating, burial of the pipe, bundling, insulation and injection of thermodynamic inhibitors [Larsen, 2005].

The traditionally used hydrate inhibitors are chemicals that “use up” the water molecules. This means that the chemical bonds to the water molecules. In this way there is no free water left for the gas to bind to, and if enough inhibitor is injected no hydrates can be formed.

New means of hydrate inhibition are starting to become more popular because of the small injection rates required compared to the traditionally used chemicals. These new chemicals are kinetic inhibitors and antiagglomerants that will allow small hydrate particles to form, but prevents them from sticking together to form bigger particles that might block the pipeline. These new inhibitors can however not be used to melt already formed hydrate plugs [Sloan].

### **2.4 Removing hydrate plugs**

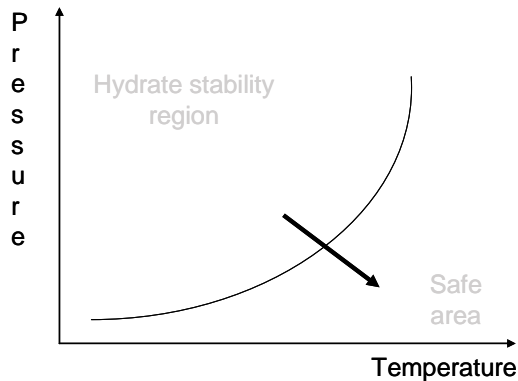
Even though prevention is done quite a lot; hydrates might still form and plug pipelines due to unforeseen events. In the case of hydrates plugging the pipe or riser, additional action has to be taken. This might include depressurization from one or both sides of the plug, external heating or injection of large quantities of inhibitors. If a two-sided depressurization is not an option, one sided pressure relief has to be done with care.

While decreasing pressure at only one side of the plug, two unwanted results may occur:

- 1) Joule–Thomson cooling may occur for very porous hydrate plugs. On the downstream side of the plug the plug may extend. Gas will seep through the porous plug and more hydrates might form due to the pressure on the other side.
- 2) If the hydrate plug releases from the pipeline wall, the upstream pressure causes this plug to become a pipeline projectile, sometimes with disastrous results at pipeline bends, elbows, etc. This might lead to very dangerous situations that in the past have taken lives [Sloan].

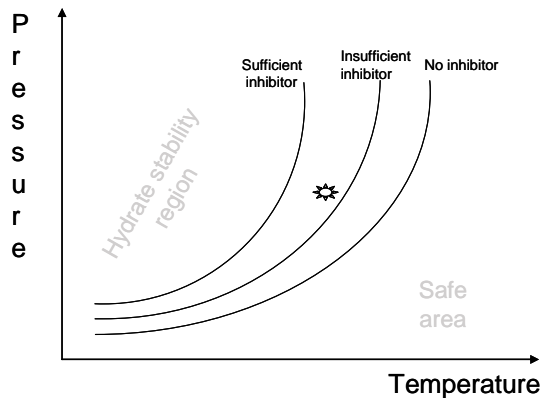
Melting of a hydrate plug with direct heat is not totally without risk either. Hydrates contain as much as 180 volumes of gas at standard temperature and pressure per volume of hydrate. When hydrate plugs are dissociated by heating, the gas is released and the pressure increases. If the pressure is confined the pipeline might rupture. [Sloan]

When the temperature increase and/or pressure decrease has been done correctly (slowly) the system will be outside the hydrate stability region.



**Figure 3:** Removing the system from the hydrate stability region. This is achieved by increasing the temperature and decreasing the pressure

It is also possible to decrease the hydrate stability region. This can be done with chemicals that will reduce the equilibrium temperature of the hydrates thus taking the multiphase flow/hydrates out of the stability region. These chemicals act as thermodynamic inhibitors. Today, the most usual thermodynamic inhibitors are methanol and glycols. [Fadnes]



**Figure 4:** Decreasing the hydrate stability region. The star represents the system temperature and pressure.

If the plug is in a landline, it is mostly not very difficult to locate it and in that case apply external heating. If it is not in a landline, locating the plug might not be that easy. In the first place it might not be easy to find the plug, and when it has been located, it might turn out to be difficult to get the inhibitor next to the plug for melting. If the plug is located in a riser, the operator is dependent on gravity to get the inhibitor next to the plug, if injecting from above. Even though risers are easiest accessible for applying inhibitors, a major disadvantage arises there. When a plug is formed the multiphase (two- or three-phase) liquid is separated. Water has the highest density of the liquids present and will therefore sink down. This might form a column of water directly on top of the plug. Because there most likely is a column of water on top of the hydrate plug in a riser, methanol might not be a good inhibitor to use. The low density of this chemical will

hinder it from getting through this layer of water. Even though the densities of glycols are higher than that of water, it might be advantageous to use a substance with an even higher density. To overcome the problem with low density, for instance methanol weighted with brine has been utilized in the field [Li , 2002]

Even if there is no water-column on top of the hydrate plug, water can be a problem for inhibitors. When a hydrate plug is melted in a riser, the freed water will lay on top of the plug. If the inhibitor has lower density than water, it will stay on top of this layer and not be in direct contact with the plug. Naturally, there will be circulation and mixing will occur, but the water will also dilute the inhibitor, in addition to hindering its path. This dilution will thereby decrease the effect of the inhibitor.

If the inhibitor has a higher density than water, it will displace the water, and if heavy enough when given time, the concentration will be close to 100% close to the plug. However, if the dense inhibitor is highly soluble in water, it might dissolve, and therefore a diluted inhibitor acts on the plug. If the inhibitor, due to its solubility, mixed totally with the freed water and gas, a concentration of the inhibitor in the liquid on top of the plug could be estimated. In that case, looking at the hydrate stability curve would give the necessary concentration of inhibitor needed to melt the plug. Then an estimate can easily be made of the amount of inhibitor necessary to reach that specific concentration.

The rate of mixing does not only depend on the densities of the mixing components (inhibitor and water in this case), but also on the viscosity. Viscous forces are frictional forces that attempt to make all parts of a fluid move at the same velocity. When the viscosity of a fluid is high, its ability to mix into another medium is low. [Li, 2000] Assuming this; a high density, low viscous fluid will be a better substance for hydrate plug removing in a riser with a water column on top of the plug.

If a hydrate plug is detached from the sides of the gas pipe/riser while being melted, it will float up if the liquids on top of the plug are heavy enough. The buoyancy of the plug will increase when the density of the liquids on top of the plug increases. That is; the heavier the inhibitor is, the more mass it can “lift”. According to this, a high density inhibitor might need to melt less of the plug before it floats, than a low density inhibitor, if viscosity, and other physico-chemical properties, are the same.

The properties of the hydrates are likely to change at high pressures (> 100 bar) compared to low pressures. At high pressures the hydrates will most likely be more stable than at low pressures.

## 2.5 Other research

A lot of research has been done on hydrates since Hammerschmidt discovery. It is outside the scope of this report to review all the research. Only some research done on the promising new inhibitor potassium formate is presented here.

The last couple of decades, methanol and MEG have been used extensively as thermodynamic inhibitors. They have been used both for inhibiting hydrate growth and for melting plugs. The problem with these is not only their relatively low density: While most of the methanol dissolves in the water phase, a significant amount of methanol either goes to the vapour phase or dissolves into any liquid hydrocarbon phase present. [Sloan] This is also the case with MEG. The problem is that both methanol and MEG has to be in contact with the water to be able to “use it up”, and act as hydrate inhibitors. When the chemicals are dissolved in the hydrocarbon phase, they are naturally prevented from contact with the water. Because of this, a substantially higher amount of methanol and MEG has to be injected than a chemical that did not dissolve in the hydrocarbon phase. [Sloan] When melting hydrate plugs in risers, it is of great advantage to use a substance substantially heavier than water. Potassium formate (HCOOK) is a salt that might prove to be this heavier substance. The salt is readily available as it today is used as an additive in high performance drilling and completion fluids. HCOOK-solutions have a high density and are non-corrosive towards metals. Compared to methanol and glycol its losses to the hydrocarbon phase will be minimal as it has low solubility in hydrocarbons, and it is non-volatile. The recovery and regeneration of HCOOK should also in principle be a simple process. A 50 wt% solution of HCOOK in water has a freezing point of around -60 °C, which compares well with methanol and glycols. [Fadnes et al.] A 75 wt% solution of HCOOK is nearly two times as dense [Fadnes, calculated here; see appendix B] as methanol [supplier] and 1.3 times as dense as TEG [supplier].

In 1998 Fadnes et al. did a study where they compared the properties of conventional inhibitors with the performance of potassium formate in high pressure cells. Fadnes compared his results with HCOOK as a gas hydrate formation inhibitor with the inhibitory effects of NaCl, methanol and MEG derived from the PVTsim simulation software. The experiments and simulations Fadnes went through were with methane hydrates in a simulated flowing environment. He found that on mass basis HCOOK is slightly less effective as a gas hydrate inhibitor than methanol but slightly better than MEG. Fadnes also found that 10, 20 and 30 wt% HCOOK-solutions would lower the gas hydrate equilibrium temperature with respectively 2.5, 7.1 and 12.9 °C for high pressure methane hydrates. He investigated the hydrate equilibrium temperature at hydrate formation.

Cappelen did some experiments to verify the lowered equilibrium temperatures that Fadnes found. Cappelen found these “*shiftings*” for low pressure THF-hydrates: 7.4, 10.3 and 16.7 °C respectively at 10, 20 and 30 wt% HCOOK. However, while Fadnes et al. did the experiments in a high pressure cell with methane-hydrates, Cappelen did her experiments with THF (Tetrahydrofuran) -hydrates in a low pressure environment. Another large difference was that she found the hydrate equilibrium temperature by looking for melting point, while Fadnes looked at the hydrate formation point. Cappelen also investigated the rate of melting of the vertical hydrate plugs. Larsen found the hydrate equilibrium temperature of THF-hydrates to be 4.4 °C while Cappelen found it to be 4.6 °C. The reason for this difference might be presence of air during hydrate formation. Nitrogen and oxygen will enter the small cavities and strengthen the bonds, which again will increase equilibrium temperature. [Larsen, 1997]

The experiments Cappelen conducted were at the equilibrium temperature for each of the HCOOK-concentrations that were found by Fadnes, and one and two degrees below each of these. She found that the hydrates would melt better with a low concentration of potassium formate at a high temperature than with a high HCOOK-concentration at a low temperature (< 0 °C). She also found bigger equilibrium temperature shiftings for THF-hydrates at atmospheric pressure compared to Fadnes’ results.

She concluded that potassium formate seems to have a better effect on THF-hydrates at atmospheric pressure than on methane-hydrates at high pressure. As her experiments were conducted at shifted equilibrium temperatures, the hydrate plugs should not have melted at all if the melting effect Fadnes found was applicable to a low pressure THF-hydrate system.[Cappelen; Fadnes]

The physical properties of methanol and MEG make the chemicals unsuitable for use in certain situations. Potassium formate might just have those physical properties that methanol and MEG lack. Both Fadnes’ and Cappelen’s experiments confirm that this might be true. More research should therefore be done on this new hydrate inhibitor. Some research is presented in this report.

## 3 Materials and methods

### 3.1 Chemicals

The purity of all chemicals was assumed 100%.

**Methanol (MeOH)**

Producer: Merck  
Purity:  $\geq 99.8\%$   
Chemical formula:  $\text{CH}_3\text{OH}$   
Density: 0.79 g/ml  
Melting point:  $-98\text{ }^\circ\text{C}$   
Viscosity: 0.52 cP

**Triethylene Glycol (TEG)**

Producer: MI Production Chemicals  
Purity:  $\sim 100\%$   
Chemical formula:  $\text{C}_6\text{H}_{14}\text{O}_4$   
Density: 1.12 g/ml  
Melting point:  $-4.6\text{ }^\circ\text{C}$   
Viscosity: 49.4 cP

**Tetrahydrofuran (THF)**

Producer: Merck  
Purity:  $\geq 99.8\%$   
Chemical formula:  $\text{C}_4\text{H}_8\text{O}$   
Density: 0.89 g/ml

**Potassium Formate (HCOOK)**

Producer: Fluka  
Purity:  $\geq 99\%$   
Chemical Formula: HCOOK  
Density: 50 wt% = 1.32 g/ml \*

The potassium formate was delivered as a crystalline compound, and was diluted in tap water. The density of potassium formate was not provided by the producer (\*), so it had to be measured. Data was collected for 10, 50, 60, 70 and 75 wt% solutions, where both weight and volume were measured. Viscosity of a 60 wt% HCOOK-solution is according to Fadnes 2 cP. This could not be verified. A homogeneous solution could not be made for a heavier solution than 75 wt%. From this data the density of all concentrations was derived, this is shown in appendix B.

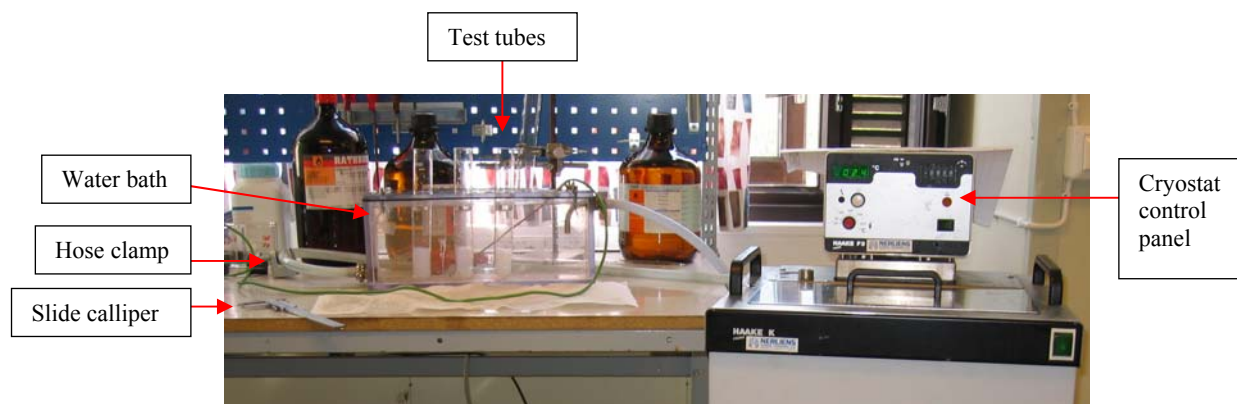
In this project, TEG was used in stead of MEG, even though MEG is most common used. TEG has a slightly higher density, and is better visible in water, which makes it easier in use. Otherwise TEG has about the same properties as MEG.

The THF did not make a clear solution when it was mixed with tap water, but rather a milky white solution. This made it easy to distinguish the melted hydrate from the inhibitors. THF is a volatile compound.

### 3.2 Equipment

A Haake K cryostat bath and a Haake F3 cryostat control panel from Fisons were used to cool the cooling liquid. The bath contains heat exchanger tubes and a pump. The pump delivers cooling liquid to the water bath through (flexible) tubes. The cooling liquid is a mixture of water and TEG (unknown concentration of TEG) to avoid freezing when subzero temperatures are required. The pump has one specific rate that can not be changed, and the cooling rate of the cryostat is around 20 °C per hour dependent on the ambient temperature. A hose clamp was used to regulate the volume of cooling liquid in the water bath. See figure 5 for the experimental set up.

The water bath is a container made in Plexiglas. The container measures 32.5 x 10 x 12.5 cm (l, w, h). The lid contains four holes for the test tubes, each of them with a diameter of 30 mm. This made the test-tubes fit precisely (see figure 6).



**Figure 5:** Picture of the experimental set up

The test tubes are 200 mm tall, with an inner diameter of 27 mm. A simplified calculation gave a total volume of 114.5 ml. Calculations of test tube-volume are shown in appendix A. The volume was calculated (not only measured), based on cross sectional area, because melting volume had to be calculated in the same way later on.



**Figure 6:** The test tubes fit precisely in the holes in the lid of the water bath

### 3.3 Methods

#### 3.3.1 ice

Ice was made in regular ice cube bags from the supermarket. The ice cubes were smashed up as fine as possible with a hammer and mixed with water in the test tubes. With the cryostat temperature set to  $-4\text{ }^{\circ}\text{C}$ , 20-30 minutes were required for making solid ice. In the experiment 8 cm of ice was made.

#### 3.3.2 THF-hydrates

For low pressure experiments, THF-hydrates were formed. Stoichiometric THF-hydrates consist of 21 vol% THF and 79 vol% water. This mixture is from here on called THF-solution and it was mixed by swirling the tubes. When the solution was milky white, total mixing was assumed. The tubes were put in the water bath, when the temperature there was on its way down to  $-8\text{ }^{\circ}\text{C}$ . The temperature at which hydrates were formed was not always the same from experiment to experiment.

A temperature below the equilibrium temperature was however not enough to make hydrates of the THF-solution. A nucleation-promoting surface also needed to be present. This could be the sensor from the thermometer, or just a string of metal. The reason for this is explained in chapter 2.2 page 2. Dependent on the exact temperature in the water bath and the amount of solution, everything from half an hour to an hour were necessary for the hydrates to form. The amount of THF-solution varied in the first experiments. A standard was established after these first experiments. In experiments with 1:x hydrate-to-inhibitor ratio, 15 ml was used. In experiments with 2:1 ratios, 30 ml was used.

#### 3.3.3 melting

Before melting with the different inhibitors, the top of the ice/hydrate plug was marked. Then the inhibitor was poured over the plug from a beaker or injected with a syringe. Measurements of melting were at first done with a ruler and later with a slide calliper. All the tubes had to be lifted out of the water bath to get somewhat precise measurements. With methanol as inhibitor, 30 minute intervals were used between each measure, with TEG and HCOOK, a 10 minute interval was necessary.

The ice was melted only with 100% pure methanol. The plugs were melted with 20 ml of methanol. The first tube was stirred while the other one was not.

The THF-hydrates were melted with methanol, TEG and HCOOK at  $+2.4\text{ }^{\circ}\text{C}$ . Methanol and TEG were injected pure, while the HCOOK was injected in different concentrations. Different hydrate-to-inhibitor ratios were also used. Ranging from 2:1 to 1:3.

The measurements were stopped when a plug had floated up or if it was totally hollowed out by the inhibitor. In some cases experiments lasted more than 24 hours. In those cases, the experiments were stopped when no melting had been observed for a couple of hours.

A source of different rate of melting might have been the different temperatures of the cooling liquid at which the THF-solution was mixed. Sometimes, the THF-solution was mixed when the cryostat had been off for instance over the night, and the temperature of the cooling liquid would be around 18 °C. Other times, the solution was mixed just after use, and the temperature of the cooling liquid could be around 0 °C. The different temperature at which the THF-solution would be cooled from might have given different values of porosity and permeability. It is conceivable that when a liquid is slowly cooled and frozen, it might freeze more equally all over than it would if it was suddenly cooled from 17 °C to below freezing point.

A test experiment was done. The THF-solution was put into the cooling liquid with a falling temperature of around 0 °C, when the test-tube was put into the Plexiglas container. The lowest temperature was as usual around -8 °C. After around an hour, dyed water was poured over the plug. As can be seen in figure 7 the plug was not visibly permeable.



**Figure 7:** Dyed water on top of the plug shows that it is visibly impermeable. The presence of colour in the middle is where the nucleation promoting surface was removed. It can be seen that the colour does not penetrate the plug elsewhere. This test has been performed several times with the same results.

The picture was taken some hours after injection of the dyed water. The plug did not seem to be permeable, but it might still be porous, which would probably increase the rate of melting a bit compared to a non-porous plug.

The following experiments were conducted both with and without a column of water on top of the hydrate plugs. All the experiments conducted with the water column were done with 30 ml of hydrates, 15 ml of water and 15 ml of inhibitor. When hydrate formation was complete, the water was poured over the plug. Then the inhibitor was carefully poured on top of water.

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## 4 Results

### 4.1 Start-up problems

As is mostly the case when using an experimental set-up for the first time, a period of trial and error is necessary before finding *the* way to do it.

#### 4.1.1 level of cooling liquid

Keeping a constant level of cooling liquid in the water bath was not easy. As mentioned before, this was regulated with a hose clamp. By changing the tightness of the hose clamp the level would change, but this change happened very slowly. When leaving the laboratory in the belief that the cooling liquid is at an ok level, one might come back and find the lab “flooded” just an hour later. Also when leaving an experiment overnight, sometimes the cryostat pump had started sucking air instead of cooling liquid, because the cooling liquid was on the floor. Experiments had to be repeated because of this. This was an often occurring problem, especially in the start, but some kind of balance was found shortly afterwards.

#### 4.1.2 finding the amount of THF-solution

Where to start when starting a new experiment? Especially without any previous experiments to base a starting point on, this of course led to some problems. The amounts of THF-solution and methanol varied quite a bit in the first experiments. This is shown in table 1 page 15 and will also influence the presentation of the first results. After these start up experiments the standard of 15 or 30 ml THF-solution was found.

#### 4.1.3 nucleation

As mentioned earlier there is a barrier against the first nucleation of hydrates. (See chapter 2.2) This was experienced in the start. 30 ml of THF-solution was mixed in two test-tubes. The test-tubes were left alone for hydrate formation overnight with the cryostat temperature at  $-5^{\circ}\text{C}$ . The following morning there were no visible signs of hydrates. The temperature of the cooling liquid was  $-5^{\circ}\text{C}$ , but the temperature of the THF-solution was found to be around  $+4^{\circ}\text{C}$ . So a low surrounding temperature was not enough for hydrates to form. Instant nucleation was however observed when the sensor of the thermometer was put into the solution. The crystals can be seen in figure 8.



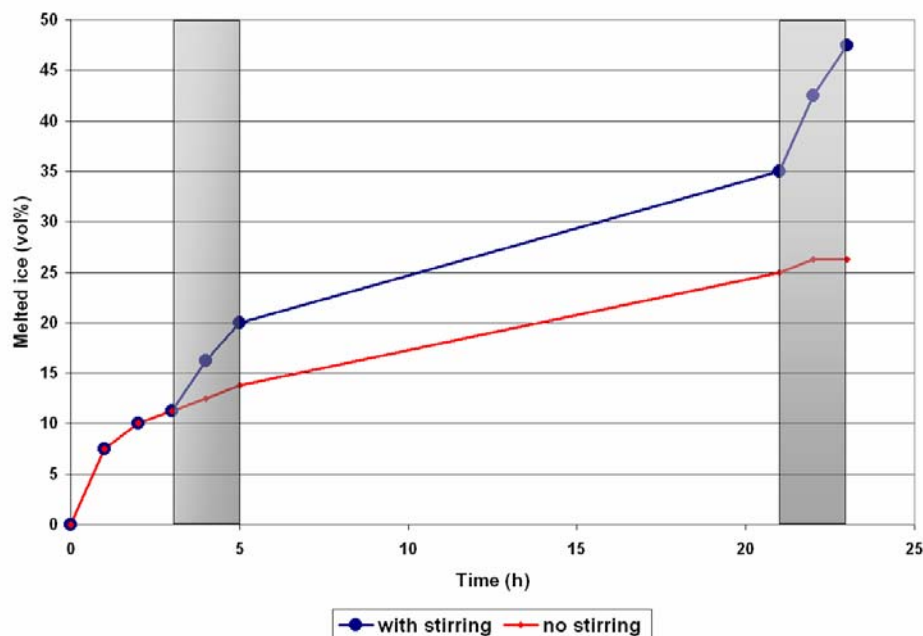
**Figure 8:** Hydrate crystals on the sensor of the thermometer

After the initial nucleation, with help from a nucleation surface, the rest of the hydrate forming process went rather fast. After about 40 minutes both of the test tubes contained a seemingly solid hydrate plug. Through the hydrate forming process, the liquid THF-solution that was still present had a temperature of +4°C. Because of this, it is safe to say that no water was freezing to ice, and all the solids in the tubes were in fact hydrates. The sensor that had been used as a hydrate promoting surface was in the first experiments cooled, but it was experienced later, that only a nucleation promoting surface was needed.

## 4.2 Melting ice

Ice was melted as a low-cost, simple introduction to melting hydrates. Ice plugs were formed as described in methods. The melting started immediately after the methanol was poured over the ice plugs, but the melting seemed slow. Even if both methanol and water are clear fluids, the interface between methanol and the melt water could quickly be seen. This was a visible effect due to different refraction of light. Since the columns of water and methanol were seen separately, it was clear that methanol mixed badly with melt water. The melt water formed a barrier between the ice plug and methanol, since the methanol has a low density. Due to this effect, the concentration of methanol was low close to the ice plug and melting was slow.

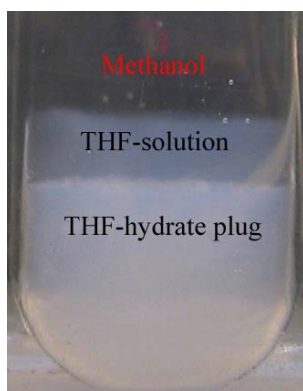
To test the importance of density difference, an experiment with stirring was compared to one without. Stirring was performed in one of the tubes, while the other tube was left alone. Stirring was done somewhat continuously between three and five hours after experiment start and then again somewhat continuously between 21 and 23 hours after the methanol was poured over the ice plug. The results of this are shown in figure 9. A faster rate of melting was seen in the tube with stirring.



**Figure 9:** Melting ice with methanol, with and without stirring. The periods with stirring are marked grey.

### 4.3 Melting hydrates with methanol

After the introduction experiments with ice, the experiments with THF-hydrates were started. The inhibitor used in the first experiments with THF-hydrates was methanol. When this particular THF is mixed with water, the solution becomes milky white. The colour of melted THF-hydrate is also milky white. The effect of melting by inhibitors can be seen easily because of this. Figure 10 shows both the milky white colour of the melted THF-hydrate and the smooth melting surface of the plug when melted with methanol.



**Figure 10:** Melting a hydrate plug with methanol. The picture is taken with a black background.

The THF-solution is heavier than the methanol; it thereby creates a column of fluid that the methanol has to penetrate to be able to melt more hydrate. The data from melting with methanol are shown in appendix C.

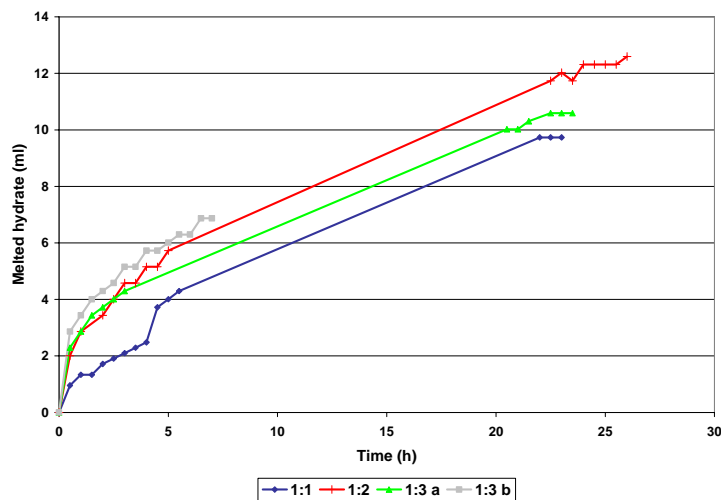
#### 4.3.1 without a column of water

As explained earlier, the volume of hydrate varied some in the first experiments. Because of this, the degree of melting between the experiments is shown in ml, not in % melted hydrate as will be done later. The volumes used are shown in Table 1.

**Table 1:** The different volumes of hydrate and methanol used. The corresponding hydrate-to-inhibitor ratios are also shown.

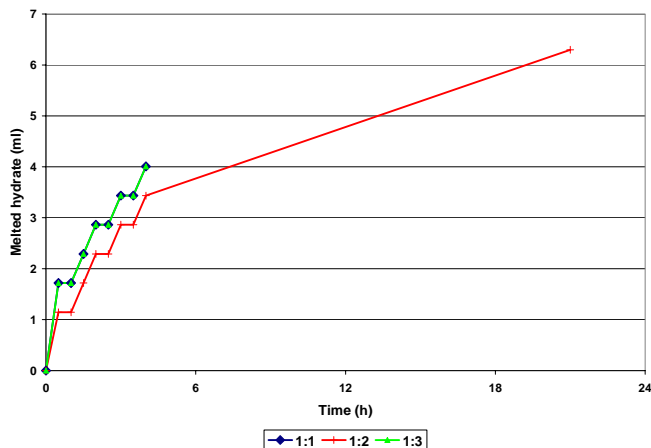
volume THF-solution (ml)	volume methanol (ml)	hydrate-to-inhibitor ratio
30	30	1:1
15	30	1:2
20	40	1:2
20	60	1:3
14	42	1:3
15	15	1:1
15	30	1:2
15	45	1:3
30	15	2:1

Melting of THF-hydrates with methanol was performed with three different hydrate-to-inhibitor ratios. The rate of melting is shown in figure 11. This figure shows some deviations between experiments with the same ratios. This might give the impression of bad experimental standard, but it will be shown later that this deviation is small, so small that it is insignificant.



**Figure 11:** Melting hydrate plugs with different hydrate to methanol ratios. In 1:3 a was 20 ml THF-solution with 60 ml MeOH was used and in 1:3 b 14 ml THF-solution with 42 ml MeOH was used.

The results presented in figure 11 are results found in the initial experiments where hydrate amounts varied constantly. After these the standard of 15 ml THF-solution in 1:x ratios was found and used. In figure 12 the results of hydrate melting with methanol without a column of water are shown. These results are later compared with TEG results, as opposed to the results in figure 11.



**Figure 12:** Melting hydrate plugs with methanol. Here 15 ml of THF-solution was used in each experiment, together with 15, 30 and 45 ml of MeOH. Note the overlap of the 1:1 and the 1:3 graphs.

One might expect that a larger amount of inhibitor with respect to hydrate will increase the rate of melting. Figure 11 and 12 do not show this logical increase conclusively. It is almost contradicting, but the differences are insignificant as will be shown when comparing to other inhibitors.

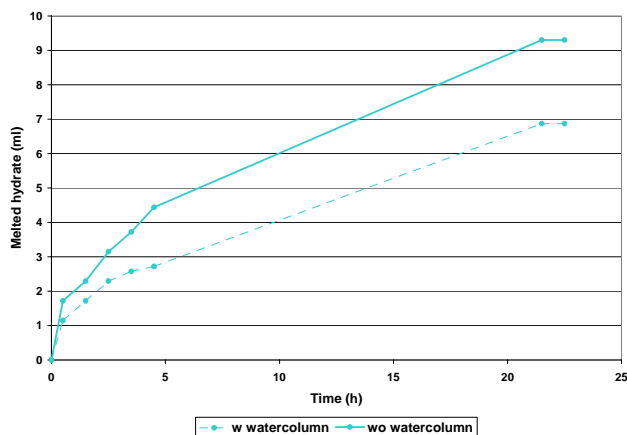
A 1:3 ratio with methanol still give a slow melting rate. With the other inhibitors the hydrate-to-inhibitor ratio was also increased to 2:1. Here 30 ml of THF-solution was used. For comparison, some experiments with methanol were also done with this ratio. The results of these are shown in figure 13.

### 4.3.2 with a column of water

When a hydrate plug forms in a riser, a column of water on top of this plug will be expected. To account for this fact, experiments were conducted with a column of water on top of the hydrate plugs. The hydrate plugs were formed first, then 15 ml of water was poured on top. By pouring water on top of the plug, some melting was observed but this is not taken into account in the results shown. This effect is assumed to be the same for all experiments done with a column of water on top, and can therefore be neglected when comparing the effect of inhibitors.

Some mixing occurred as an effect of the pouring of methanol on top of the column of water. This mixing is assumed to occur also in risers when injecting the inhibitor, when performed in the field. In every case the mixing will increase the effect of the inhibitors, but the amount of mixing is assumed to be equal in these experiments.

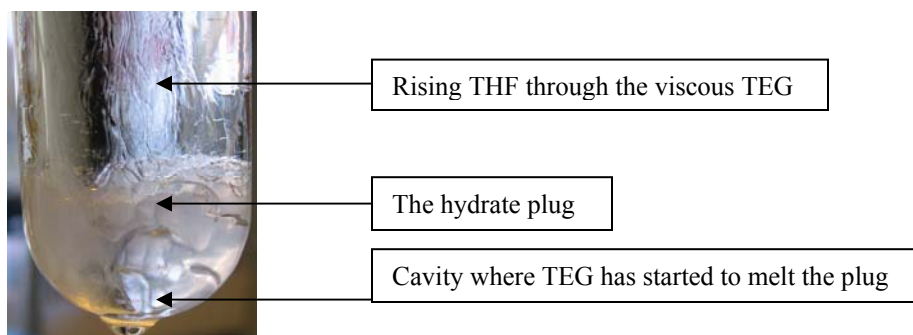
The melting of THF-hydrates with methanol, with a column of water on top of the hydrate plugs was measured. These experiments were done with a 2:1 hydrate-to-inhibitor ratio, and are shown in figure 13. In this figure results with water on top are compared to results without water. In both cases the same ratio was used. The experiments were stopped after a 24-hour period.



**Figure 13:** With and without a column of water using methanol as inhibitor.

#### 4.4 Melting hydrates with TEG

TEG was used as an alternative inhibitor. The melting surface of the hydrate plugs was much more uneven than the melting surface of the plugs when methanol was used as an inhibitor. (See figure 10). This made it more difficult to measure the melting. The TEG also seemed to melt along the sides of the plug. In some cases TEG melted its way along the sides of the plug and started melting the plug from beneath as well. Some of the plugs even melted from underneath the plug. An example of all this is shown in figure 14.



**Figure 14:** Melting a hydrate plug with TEG

The rate of measuring had to be increased to once every ten minutes because the rate of melting increased substantially compared to melting with methanol. The data from melting with TEG are shown in appendix D.

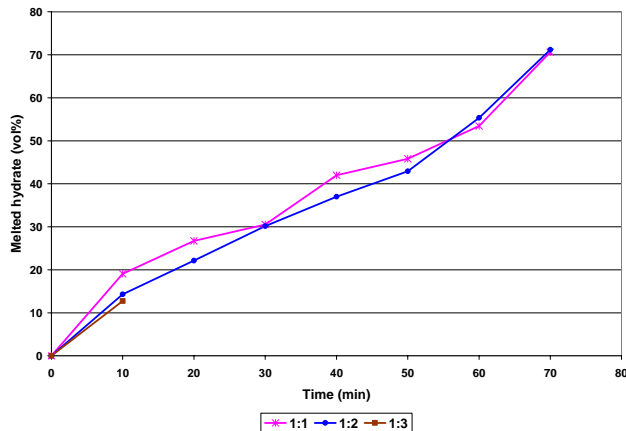
##### 4.4.1 without a column of water

As with methanol the first experiments were done without a column of water on top of the plugs. To be able to compare the melting performance of TEG with both methanol and HCOOK, experiments with both 1:x and 2:1 hydrate-to-inhibitor ratios were performed. See Table 2 for the different amounts used. Here the standard of 15 and 30 ml was constantly used.

**Table 2:** The different amounts of THF-solution and TEG used to melt the plugs

volume THF-solution (ml)	volume TEG (ml)	hydrate-to-inhibitor ratio
15	15	1:1
15	30	1:2
15	45	1:3
30	15	2:1

In figure 15 the first experiments with a 1:x ratio are presented. Note that the time scale with TEG experiments is in minutes compared to hours with methanol. This implies a faster rate of melting than with methanol. It can be seen in the figure that a 1:3 ratio does not melt the plug faster than with a 1:1 ratio. This might again contradict expectations.



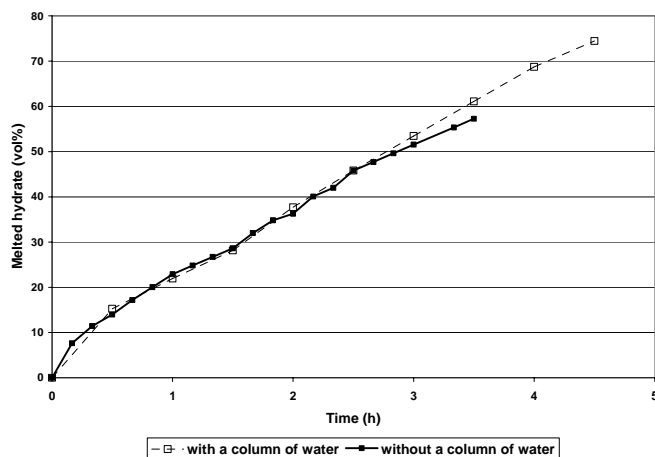
**Figure 15:** Melting hydrate plugs with different hydrate-to-TEG ratios. Note the time axis; minutes, not hours.

#### 4.4.2 with a column of water

To simulate the situation in a riser, also TEG experiments were done with a column of water on top of the plug. With TEG as the inhibitor it was easy to spot the interface between water and TEG, and the extent of mixing was observed. (This is seen at the top of figure 14)

Two plugs were melted with TEG with a column of water on top. (See figure 16) The plugs melted with fairly much the same rate; after 2 hours both had melted 38%. The floating times (the time when plugs floated up) were not the same. This will be discussed later.

Figure 16 compares melting with TEG with and without a column of water on top of the plugs. In both cases a 2:1 hydrate-to-inhibitor ratio was used. As can be seen in the figure, melting with a column of water does not seem to be slower than melting without a column of water.



**Figure 16:** With and without a column of water on top using TEG as inhibitor. Where possible, average values are used.

### 4.5 Melting hydrates with HCOOK

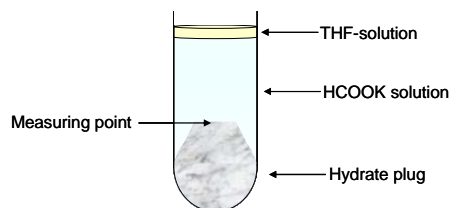
A major goal of this project was to compare the efficiency of the “new” inhibitor HCOOK to the more common inhibitors methanol and TEG. The results of these experiments will be presented here. The data from melting with HCOOK are shown in appendix E.

The first experiment with HCOOK was enough to prove the power of HCOOK as an inhibitor. Three plugs were prepared with 1:1, 1:2 and 1:3 hydrate-to-inhibitor ratio. All three plugs were floating within ten minutes. Of course this was a promising result, but it could not easily be quantified. To be able to make a comparison, 2:1 ratios were used in all experiments with HCOOK.

The melting surface of the plugs when melting with HCOOK was smoother than when they were melted with TEG, but not as smooth as when they were melted with methanol. The melting surface was cone shaped, as shown in this picture:



**Figure 17:** Melting with HCOOK



**Figure 18:** illustration of melting with HCOOK  
The measuring point is also shown

Since the plug melted into a cone shape, the plug would not melt as much on the top as on the sides, and not always equal on all the sides. The top of the plug was however chosen as the measuring point. (see figure 18). This will of course influence the accuracy of measurement and will be discussed later.

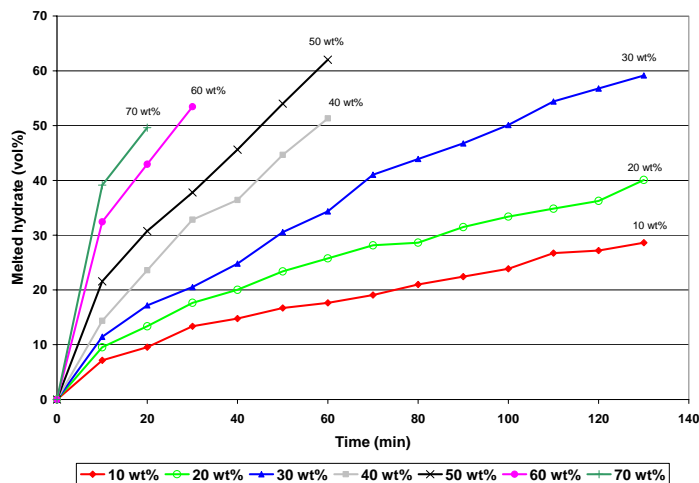
The densities of the HCOOK solutions are higher than that of the THF-solution. This means that the melted hydrate will migrate to the top of the HCOOK column; the HCOOK solution will always be directly on top of the plug. (See figure 18) Different concentrations of HCOOK were used and the densities of these are shown in table 3. It was found impossible to dilute more than 75 wt% in water.

**Table 3:** The measured densities of the different concentrations of HCOOK used. Calculations of densities are shown in appendix B

HCOOK-concentration (wt%)	Density (g/ml)
10	1.06
20	1.12
30	1.19
40	1.25
50	1.31
60	1.38
70	1.44

### 4.5.1 without a column of water

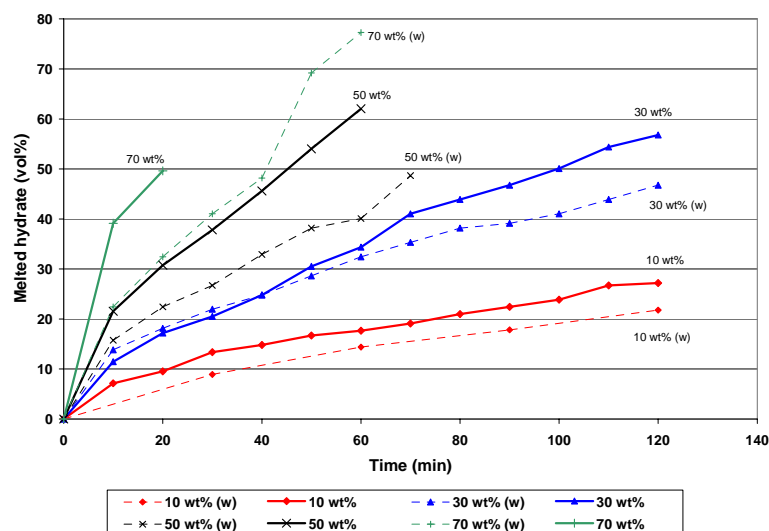
Again experiments without water on top were done first to determine the efficiency of the inhibitor. 30 ml of THF-solution and a hydrate-to-inhibitor ratio of 2:1 were used in these experiments. HCOOK-concentrations from 10 wt% to 70 wt% with increments of 10 wt% were used to melt the plugs. The results are shown in figure 19. It can be seen that 70 wt% is more efficient than 60 wt% and so on. Most experiments were repeated several times, and an average is presented where possible.



**Figure 19:** Melting hydrates with different HCOOK-concentrations. This figure shows the average rate of the melting, and is not representative for when the plugs floated.

### 4.5.2 with a column of water

Again to simulate the situation in a riser, experiments with a column of water on top of the plugs were conducted. The mixing as observed with methanol and TEG was also observed here. 10, 30, 50 and 70 wt% HCOOK-solutions were used. The results are shown in figure 20. As in the experiments without a water column, the higher the concentration is, the higher the melting performance is.



**Figure 20:** With and without a water column on top using HCOOK as inhibitor. As well as in figure 19 the endpoints of the graphs are not representative for when the plugs started to float.

## 4.6 Comparing results

The goal of this project is to compare the performance of the different inhibitors. Even though the results presented above give a fairly good impression, the results will be compared here. Both inhibitor efficiency and the difference in floating time will be shown.

### 4.6.1 rates of melting

It was clear already in the first minutes of the first TEG experiment that TEG is superior to methanol as a hydrate plug remover. It should also become clear from figure 21 that the hydrate-to-inhibitor ratio has a very small influence on the rate of melting, for both methanol and TEG. It is very clear that TEG is much more efficient than methanol.

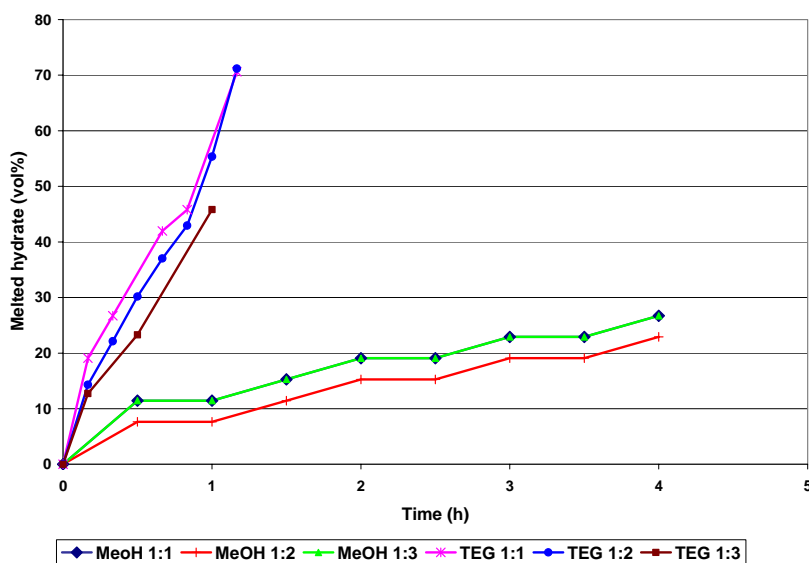
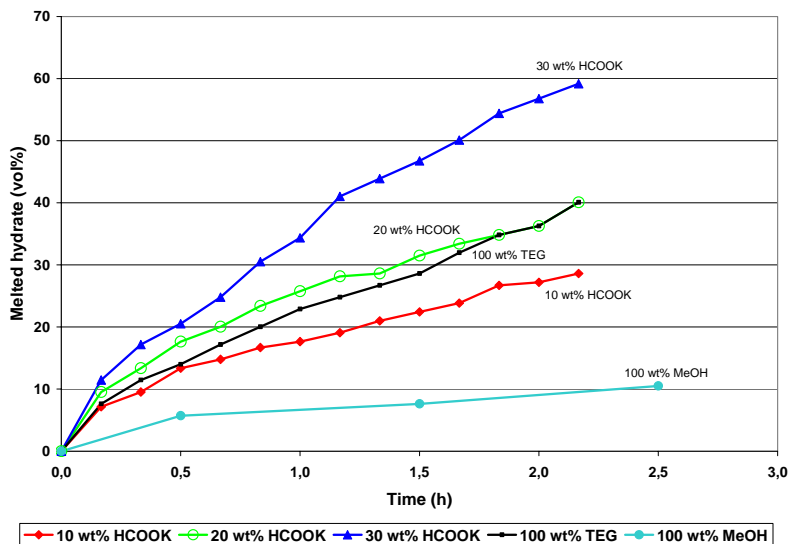


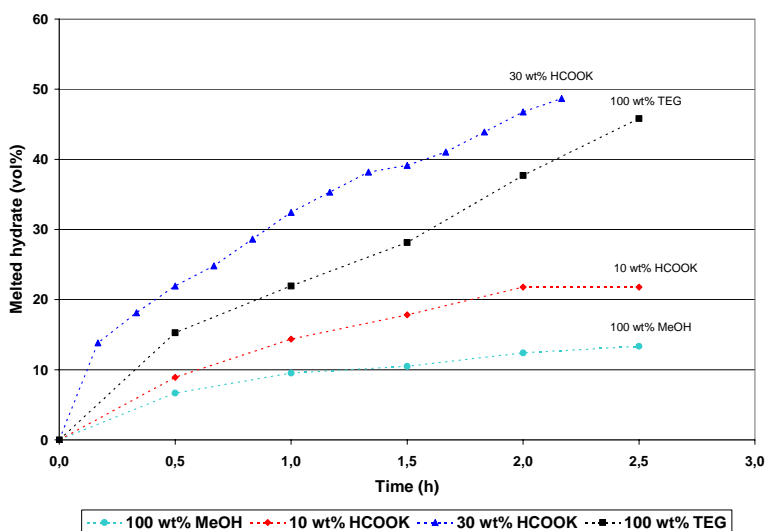
Figure 21: Comparing the melting efficiency of methanol and TEG

The results presented before should give the impression that HCOOK is the absolute best hydrate plug remover of the three presented. Figure 22 leaves no doubt. 100 wt% TEG is only as good as around a 20 wt% HCOOK-solution for melting THF-hydrate plugs at low pressures. The higher concentrations of HCOOK are not in this figure, as they all lay well above the 30 wt% solution. (See figure 19 page 21).



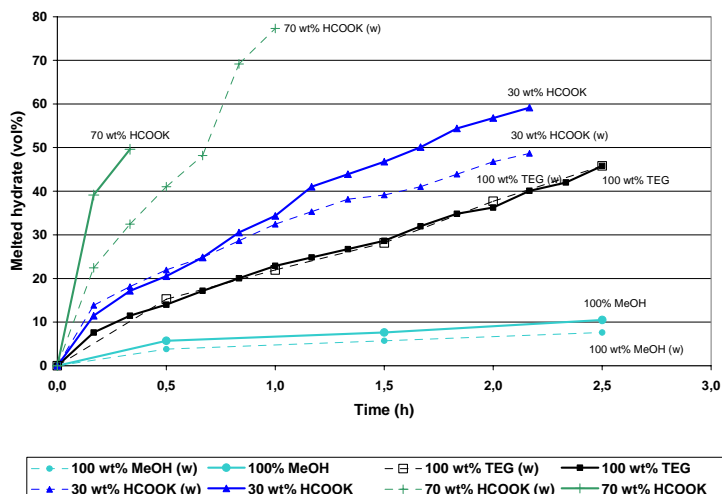
**Figure 22:** Comparing the efficiency of methanol with TEG and HCOOK without a column of water

The same trend can be seen when melting with a column of water on top of the plugs: methanol is the absolute least efficient inhibitor, while 100 wt% TEG is as efficient as between a 10 and 30 wt% HCOOK-solution. (see figure 23) Again HCOOK is superior to both TEG and methanol.



**Figure 23:** Comparing the efficiency of methanol with TEG, and HCOOK with a column of water

The effect of a water column on top of the hydrate plugs is shown in figure 24. Only with TEG it seems to make no difference, while with both methanol and HCOOK the presence of water seems to slow down the melting process.



**Figure 24:** Comparing results of the different inhibitors with and without water

When presenting the results for methanol it was commented that the observed differences were insignificant. In figure 24 this insignificance is shown clearly. While the melting efficiency in figure 13 seemed quite different, figure 24 shows that it is almost negligible compared to the efficiencies of both TEG and HCOOK.

#### 4.6.2 differences in floating time

It was observed that there were differences in floating time. Different plugs that had the exact same conditions and were treated with the same inhibitor did not necessarily float at the same time. Two extremes as an example: plugs melting with a 50 wt% HCOOK-solution; one floated up before 10 minutes had passed; another was not floating before 60 minutes had passed. These are two extremes, the rest of them floated up in an average of 38 minutes. There is however a clear relation between the efficiency of the inhibitor and the time it takes to make the plug float. The faster the plug melts, the faster it will float. The methanol experiments were ended long before the plugs would be able to float. These experiments will therefore not be discussed here.

The plugs melted with a higher concentration of HCOOK (40-70 wt%), without a column of water on top, floated up before they could melt 100%. The experiments were stopped before the plugs floated when they were melted with 10, 20 and 30 wt% solutions, because this would take too much time. As can be seen in table 4 the plugs melted with 70 wt% HCOOK solution floated up earlier than the plugs melted with 60 wt% and so on. The same trend can be seen on the plugs melted *with* a column of water on top. The table shows average times. The experiments with 10 wt% HCOOK and water was done together with a methanol and water experiment. That is the only reason those plugs were allowed to melt for such a long time. It can be seen that the plugs melting without a water-column is floating up much faster than the plugs melting with water.

**Table 4:** Average times of floating for plugs melted with HCOOK. Times for both with and without water on top of the plugs are shown. The hydrate-to-HCOOK ratio is 2:1. \*<sup>1</sup> experiments stopped after 2 hours.

HCOOK-concentration (wt%)	Time of floating (min)	
	Without water	With water
10	* <sup>1</sup>	1350 (22.5 h)
20	* <sup>1</sup>	-
30	* <sup>1</sup>	130
40	75	-
50	38	65
60	35	-
70	20	60

As there was no clear relation between the hydrate-to-TEG ratio and melting-efficiency, it does not seem to be any clear relation between the hydrate-to-TEG ratio and the time it takes to make the plugs float either. This can be seen in table 5. The only conclusion that can be drawn from this table is that it takes more time to make a plug covered with water float, than it takes to make a plug not covered with water float.

**Table 5:** Average time of floating for plugs melted with TEG. The different ratios are shown for both with and without a water column on top of the plug. The concentration of injected TEG is 100 %.

Hydrate-to-TEG ratio	Time of floating (min)	
	Without water	With water
1:1	47	-
1:2	57	-
1:3	27	-
2:1	177	195

## 5 Discussion

In the experiments done, several sources of error can be recognized. The different properties of the inhibitors have also influenced the results. Here some of these points will be discussed.

### 5.1 Experimental setup

The temperatures in the water bath are set in the cryostat control panel. The temperature of the cooling liquid will always be lower than the ambient temperature. On the way from the cryostat to the water bath, some heat exchange will occur. With higher ambient temperatures the cooling liquid in the water bath has been warmed more than with lower ambient temperatures. The difference in ambient temperature from day to day might cause some deviation in the forming and melting of the hydrate plugs. It might cause slower forming and faster melting as the temperature has become higher. Since so many experiments are done, this factor is thought to average out.

Volumes were mostly measured in 60 and 20 ml syringes and a 10 ml pipette. The low resolution on the scale of the syringes will give less accuracy. But this is the same for all the experiments and does not have much to say for the results obtained.

Even though the THF-to-water ratios might not have been exactly stoichiometric due to volume inaccuracy, the temperature secured that no ice was formed, only hydrates. If ice was present, it might have taken more time to melt the plugs due to a lower equilibrium temperature. The temperature in the THF-solution (that was still liquid) was however never below +4 °C, so ice could not have formed.

The accuracy of measurements was increased when a slide calliper was used in stead of a regular ruler. As will be discussed a bit later, it was mostly the different melting surfaces that decreased the accuracy. To be able to measure, the tubes had to be lifted out of the water bath. The exposure to higher ambient temperature might increase the melting rate somewhat, but this effect is assumed insignificant because of short exposure time (~20 seconds).

The results of Cappelen and Fadnes were quite different from each other and also quite different from the results presented here. It is important to note the differences in experimental setup between them. Cappelen used THF-hydrates at a low pressure; Fadnes used methane hydrates in high pressure environments. [Cappelen, Fadnes] The results presented here were obtained in a low pressure environment with THF-hydrates. The fact that Cappelen's results were different from Fadnes' might be due to that they used different types of hydrates and tested in different pressure environments. The difference between the results presented here and Fadnes' (a major difference in efficiency of HCOOK) might also be due to the use of different types of hydrates and different pressure environments. When comparing the results of the new inhibitor HCOOK, it is important to keep these experimental setup differences in mind.

The melting experiments presented here have all been done at +2.4 °C. Fadnes and Cappelen were researching the different equilibrium temperatures that different concentrations of HCOOK would give. Cappelen found that HCOOK lowers the equilibrium temperature the hydrate plugs more effectively than Fadnes did. [Cappelen, Fadnes] Why there might be differences between their results is discussed above. When an inhibitor lowers the equilibrium temperature, the rate of melting will increase. In this project the efficiency of different inhibitors is compared, and the importance of change in equilibrium temperature is therefore not considered.

## **5.2 Hydrates**

During hydrate formation none of the tubes were capped. This might have an influence on the stability of the hydrates as discussed in chapter 2.5 page 8. The hydrates may have become more stable, as nitrogen and oxygen would have entered the small cavities and strengthen the bonds, without a cap. This effect will only increase the melting time compared to the situation with a cap. The efficiency of melting presented here, has been performed on very stable hydrate plugs, and might even be better in environments with less access to oxygen and nitrogen. As THF is a volatile compound, some might evaporate when mixing with water, making the THF-solution non-stoichiometric. This might also have an influence on the rate of melting

In the first experiments the sensor of the thermometer was used as a nucleation promoting surface. As shown in figure 7 this created a small cavity in the hydrate plug after its removal. Later on, a thin metal string was used as a nucleation promoting surface, and the cavity left was therefore much smaller. Even though the rate of melting might have increased due to this little extra surface area, the effect is thought to be negligible.

Hydrate formation has been done at different temperatures. Quick cooling might produce porous plugs. Different temperatures from experiment to experiment might therefore influence the strength of the hydrate plugs. Figure 7 shows that the plugs were visually impermeable. The effect of different temperatures through hydrate formation is thought to be small.

Plugs melted with the different HCOOK-solutions melted into a cone-shape (figure 17). Melting was not necessarily equal on all sides. The top of the plug was always chosen as the measuring point. This ensured that the same measuring point was chosen at each experiment. However, measuring in this way does not represent the total melting correctly, since the sides did not melt equally. Total melting due to this is underestimated since the melting on the sides is not accounted for. This source of error is assumed to be the same for all HCOOK-experiments.

Some of the results seem to indicate that there is no relationship between the rate of melting and the hydrate-to-inhibitor ratios used (see figures 11, 12, 15 and 21). As mentioned before, this deviation is insignificant for the methanol experiments when comparing with TEG and HCOOK-results.

Even though the hydrate-to-TEG ratios differ, the melting rates of these do not; they are very similar (see figure 15). It therefore seems insignificant how much TEG is injected compared to the size of the plug. Due to the density of TEG it is very likely (and somewhat observed) that TEG will sink to the surface of the plug (when the plug melts and THF-solution is freed). It does not matter what the ratio is, since a concentration of about 100 % has contact with the plug at all times.

It has to be mentioned that in the field it might be difficult to measure the exact size of the plug and talking in hydrate-to-inhibitor ratios might be somewhat irrelevant. But the results show that the ratio is not that important, but concentration at the top of the plug is.

## **5.3 Inhibitors**

### **5.3.1 mixing**

The experiments that were done with ice showed that if possible, stirring should be done when melting ice-plugs with methanol. The stirring is efficient because methanol has a lower density than water. The migration through water will therefore be very slow, and stirring will increase the concentration of methanol close to the ice plug.

As mentioned in the results, there was a clear interface between the melted hydrate and the methanol. This is most likely because the methanol mixes poorly with the THF-solution. When a hydrate plug melts, water will be freed, together with THF. This solution will, because of its higher density, not float up, but stay on top of the hydrate plug. In stead of mixing with the methanol, the solution will just displace the methanol and create an almost impenetrable layer for the methanol. The concentration of methanol at the plug will thus decrease, and so will the rate of hydrate plug melting. This effect can be seen in all figures regarding methanol melting (figures 11, 12 and 13), since the curve is steep at first and then levels off.

In the experiments with a column of water on top of the plug, the melting did not go very much slower (figure 13) than without. It is conceivable that a column of water would hinder the methanol from gaining contact with the hydrate plug, and thereby hinder melting. But this does not seem to be so, even though melting is slower.

In all the experiments with a column of water on top mixing was observed when pouring/injecting inhibitors on top of the water. The mixing due to pouring was quite extensive compared to the mixing at the interface between two liquids with different densities. The mixing due to pouring is assumed to also occur in risers, the effect of it in these experiments, will therefore not influence the results negatively.

### **5.3.2 physico-chemical properties**

The physico-chemical properties of the different inhibitors make a difference in how efficient they are. The influence of some physico-chemical properties on the results are discussed here.

In this project, TEG was used in stead of MEG, even though MEG is most common used. The fact that TEG has a slightly higher density might give slightly different results than with MEG, and this should be taken into account when comparing MEG with TEG results.

In paragraph 5.3.1, the disadvantage of methanol's low density was discussed. The effect of density on the rate of melting of the other inhibitors will be discussed here.

As the density of TEG is only 1.12 g/ml and the 30 wt% HCOOK solution is ~1.19 g/ml and the 70 wt% HCOOK-solution is ~1.44 g/ml (see table 3), other factors than density seem to be important when these inhibitors have to penetrate a column of water. Li (2000) states that a solution with a high viscosity will have more problems to mix in another medium then a solution with a low viscosity. Keeping this statement in mind and the findings shown above, it would be tempting to say that the HCOOK-solutions are more viscous than TEG. This is not true, however, because a 60 wt% HCOOK-solution in water has a viscosity of 2 cP [Fadnes] and TEG has a viscosity of 50 cP [supplier].

Another physico-chemical property that is important in this context is miscibility (the ability to mix). As Li's statement shown above, miscibility is affected by viscosity. At the same time, the ability to penetrate a column of water will also be affected by these two properties. Density will affect the ability to penetrate, while viscosity will affect the miscibility. HCOOK probably mixes somewhat faster, while glycols, i.e. TEG, mix somewhat slower due to its viscosity and miscibility.

It might seem like TEG is able to penetrate water better than HCOOK, as the column of water does not seem to affect the rate of melting with TEG much. With HCOOK, the effect of the water column is absolutely there. After half an hour the difference in amount of melted hydrate is almost 12 vol% for the 70 wt% HCOOK-solution (see figure 20). After an hour the difference is around 10 vol% for the 30 wt% HCOOK-solution. In both of these examples, the fastest melting plug is the one without a column of water. When a water column is present, TEG would use longer time to mix; it therefore might sink slowly through, due to its density, and has a concentration of close to 100% at the top of the plug. Due to this, there is no difference in effect with or without a water column on top, as was observed.

In the case of HCOOK, some mixing will occur. The concentration at the top of the plug will therefore be lower than applied at the start of the experiment. This could explain the difference in effect that was observed with and without a column of water.

Another effect of the low miscibility of TEG was observed in figure 14. The hydrate plug is releasing THF-solution due to melting; these open spaces create a possibility for inhibitors to penetrate into the plug. Since TEG mixes badly, it is being dispersed by the THF-liquid; this forms small drops of TEG. These small drops can sneak into the small cavities that arose due to melting. This could be a reason why TEG could be seen underneath the hydrate plug in figure 14.

### 5.3.3 efficiency

Of course the most interesting part of this project is comparing the efficiencies of the different inhibitors.

Fadnes found that the hydrate inhibitory effect of 10 wt% HCOOK is about the same as the effect of 7.5 wt% methanol or 12.5 wt% MEG. And the effect of 30 wt% HCOOK is similar to the effect of 25.5 wt% methanol or 37.1 wt% MEG. [Fadnes]

The results presented here show totally different inhibitor efficiencies. 20 wt% of HCOOK gives about the same results as 100 wt% TEG, and all HCOOK concentrations above this perform better. 100 wt% methanol can not compete with any of these. It might be so that high pressure changes the efficiency of the inhibitors, this has to be tested.

Another factor might be the different hydrates used in Fadnes' research compared to this one. It is also important to note that Fadnes obtained his results while inhibiting hydrate formation (hence, uses the inhibitor as a hydrate-prevention method), while the results in this report is obtained while removing hydrate plugs.

The efficiency of TEG is not hindered by the presence of water, released from or on top of the plug. The results show no clear difference between with and without the water column (see figure 15). Some part of this is probably due to the high density of TEG compared to that of water, which creates a ~100 % concentration of TEG at the top of the plug.

The efficiency of HCOOK is probably also partly due to its higher density. The fact that the higher concentrations make plugs float faster also is a positive effect. The faster hydrate plugs are removed from risers the better; the minimized time before floating by higher concentrations support fast removal.

## 6 Conclusions

- A water column on top of the hydrate plug hinders different HCOOK-solutions more than it hinders TEG from penetrating through to the plug. Even a 30 wt% HCOOK-solution with a column of water to penetrate is still melting the plug faster than 100 % pure TEG without a column of water.
- A higher concentration of HCOOK works better as a hydrate plug remover than a lower concentration of HCOOK. Not only does it work better because the plugs melt faster, but also because it takes less time to melt the plugs enough to make them float.
- Pure methanol is not a very effective THF-hydrate plug remover in a low pressure environment.
- Pure TEG is not as efficient as HCOOK as a THF-hydrate plug remover under low pressure circumstances, but it will still melt the plugs faster than methanol.
- Whether or not there is a water column on top of the plug, HCOOK is the absolutely most efficient hydrate plug remover of the three compounds tested.

## 7 Future work

An equally thorough array of experiments should be conducted in a high pressure cell, with methane or other hydrocarbon-hydrates. The experiments should be conducted with methanol, TEG and different concentrations of HCOOK at the same temperature (+2.4 °C) to verify the results in this report. They should also be done at other temperature levels to increase the usefulness of the results.

If such tests are successful, i.e. shows the same promising results as in this report, a large scale test of both melting plugs in risers and as a hydrate growth inhibitor in regular gas pipelines might be the way to go for further testing and qualification of the “new” inhibitor HCOOK.

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## Appendix A - Different calculations

Volume in the test tubes calculated as if they were not round in the bottom:

$$\text{ID} = 2,70 \text{ cm} = 0.27 \text{ dm}$$

$$h = 20.0 \text{ cm} = 2.00 \text{ dm}$$

$$A = \pi r^2 = \pi \frac{\text{ID}^2}{4} = \pi * \frac{0.27^2}{4} = 0.057 \text{ dm}^2$$

$$\underline{V} = A * h = 0.057 * 2 = 0.1145 \text{ dm}^3 = \underline{114.5 \text{ ml}}$$

The amount of THF necessary to make a stoichiometric THF-solution with an example of 30 ml total THF-solution:

$$\text{vol\% THF: } 21\%$$

$$\text{vol\% water: } 79\%$$

$$V_{\text{tot}} = 30 \text{ ml}$$

$$V_{\text{THF}} = 0.21 * 30 = 6.3 \text{ ml}$$

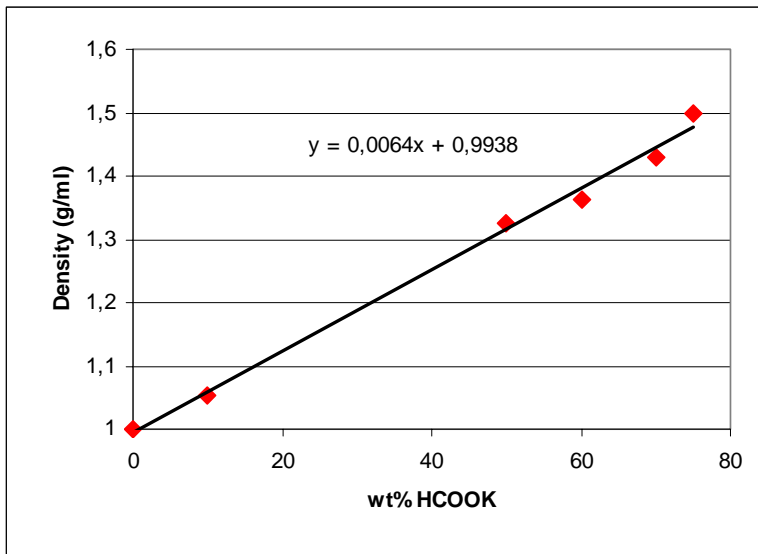
$$V_{\text{H}_2\text{O}} = 0.79 * 30 = 23.7 \text{ ml}$$

## Appendix B - Density calculations for HCOOK

Some densities were found by comparing weight and volume (measured values in red, calculated values in blue).

Concentration (%)	Mass (g)	Volume (ml)	Density (g/ml)
10	40.0	38.0	1,05
50	45,5	60.0	1,32
60	15.0	11.0	1,36
70	15.0	10,5	1,43
75	15.0	10.0	1,50

From these values a linear regression line was made. The formula for this line is:  $y = 0.0064x + 0.9938$ . From this formula, an estimate of the remaining densities of concentrations was made.



Estimated densities from the regression line formula

Concentration (%)	$\rho$ (g/ml)
0	0,99
10	1,06
20	1,12
30	1,19
40	1,25
50	1,31
60	1,38
70	1,44
75	1,47
80	1,51
85	1,54
87	1,55
90	1,57
94	1,60
100	1,63

**Figur A-1:** Regression curve used in estimating densities of HCOOK-concentrations

# Appendix C - Data from melting with methanol

The values shown are average values calculated from the different parallel experiments performed. Standard deviations of the melted hydrate values were below 6%.

Without a water-column					Without a water-column		
$V_{ice} = 45 \text{ ml}$					$V_{hydrate} = 30 \text{ ml}$		
$V_{methanol} = 45 \text{ ml}$					$V_{methanol} = 30 \text{ ml}$		
Ice-to-methanol ratio = 1:1					hydrate-to-methanol ratio = 1:1		
Time (h)	Tube 1 (stirring)		Tube 2 (no stirring)		Time (h)	melted hydrate (ml)	melted hydrate (%)
	melted ice (ml)	melted ice (%)	melted ice (ml)	melted ice (%)			
0	0	0	0	0	0,0	0	0,00
1	3	8	3	8	0,5	1	4,77
2	5	10	5	10	1,0	1	6,68
3	5	11	5	11	1,5	1	6,68
4	7	16	6	13	2,0	2	8,59
5	9	20	6	14	2,5	2	9,54
21	16	35	11	25	3,0	2	10,50
22	19	43	12	26	3,5	2	11,45
23	22	48	12	26	4,0	2	12,41
					4,5	4	12,41
					5,0	4	13,36
					5,5	4	14,31
					22,0	10	32,44
					22,5	10	32,44
					23,0	10	32,44

Without a water-column			Without a water-column		
$V_{hydrate} = 20 \text{ ml}$			$V_{hydrate} = 20 \text{ ml}$		
$V_{methanol} = 40 \text{ ml}$			$V_{methanol} = 60 \text{ ml}$		
hydrate-to-methanol ratio = 1:2			hydrate-to-methanol ratio = 1:2		
Time (h)	melted hydrate		Time (h)	melted hydrate	
	(ml)	(%)		(ml)	(%)
0,0	0,00	0,00	0,0	0,00	0,00
0,5	2,00	10,02	0,5	2,29	11,45
1,0	2,86	14,31	1,0	2,86	14,31
2,0	3,44	17,18	1,5	3,44	17,18
2,5	4,01	20,04	2,0	3,72	18,61
3,0	4,58	22,90	2,5	4,01	20,04
3,5	4,58	22,90	3,0	4,29	21,47
4,0	5,15	25,76	20,5	10,02	50,10
4,5	5,15	25,76	21,0	10,02	50,10
5,0	5,73	28,63	21,5	10,31	51,53
22,5	11,74	58,69	22,5	10,59	52,96
23,0	12,02	60,12	23,0	10,59	52,96
23,5	11,74	58,69	23,5	10,59	52,96
24,0	12,31	61,55			
24,5	12,31	61,55			
25,0	12,31	61,55			
25,5	12,31	61,55			
26,0	12,60	62,98			

Without a water-column			Without a water-column		
$V_{hydrate} = 14 \text{ ml}$			$V_{hydrate} = 15 \text{ ml}$		
$V_{methanol} = 42 \text{ ml}$			$V_{methanol} = 15 \text{ ml}$		
hydrate-to-methanol ratio = 1:3			hydrate-to-methanol ratio = 1:1		
Time (h)	melted hydrate		Time (h)	melted hydrate	
	(ml)	(%)		(ml)	(%)
0,0	0	0	0,0	0,00	0,00
0,5	3	20	0,5	1,72	11,45
1,0	3	25	1,0	1,72	11,45
1,5	4	29	1,5	2,29	15,27
2,0	4	31	2,0	2,86	19,09
2,5	5	33	2,5	2,86	19,09
3,0	5	37	3,0	3,44	22,90
3,5	5	37	3,5	3,44	22,90
4,0	6	41	4,0	4,01	26,72
4,5	6	41			
5,0	6	43			
5,5	6	45			
6,0	6	45			
6,5	7	49			
7,0	7	49			

**Without a water-column**  
 V<sub>hydrate</sub> = 15 ml  
 V<sub>methanol</sub> = 30 ml  
 hydrate-to-methanol ratio = 1:2

Time (h)	melted hydrate (ml)	melted hydrate (%)
0,0	0,00	0,00
0,5	1,15	7,63
1,0	1,15	7,63
1,5	1,72	11,45
2,0	2,29	15,27
2,5	2,29	15,27
3,0	2,86	19,09
3,5	2,86	19,09
4,0	3,44	22,90
21,0	6,30	41,99

**Without a water-column**  
 V<sub>hydrate</sub> = 15 ml  
 V<sub>methanol</sub> = 45 ml  
 hydrate-to-methanol ratio = 1:3

Time (h)	melted hydrate (ml)	melted hydrate (%)
0,0	0,00	0,00
0,5	1,72	11,45
1,0	1,72	11,45
1,5	2,29	15,27
2,0	2,86	19,09
2,5	2,86	19,09
3,0	3,44	22,90
3,5	3,44	22,90
4,0	4,01	26,72

**Without a water-column**  
 V<sub>hydrate</sub> = 30 ml  
 V<sub>methanol</sub> = 15 ml  
 hydrate-to-methanol ratio = 2:1

Time (h)	melted hydrate (ml)	melted hydrate (%)
0,0	0	0
0,5	2	6
1,5	2	8
2,5	3	10
3,5	4	12
4,5	4	15
21,5	9	31
22,5	9	31

**With a water-column**  
 V<sub>hydrate</sub> = 30 ml  
 V<sub>methanol</sub> = 15 ml  
 hydrate-to-methanol ratio = 2:1

Time (h)	melted hydrate (ml)	melted hydrate (%)
0,0	0	0
0,5	1	4
1,5	2	6
2,5	2	8
3,5	3	9
4,5	3	9
21,5	7	23
22,5	7	23

## Appendix D - Data from melting with TEG

The values shown are average values calculated from the different parallel experiments performed. Standard deviations of the melted hydrate values in the 2:1 experiments were below 2.5%.

In the experiments with the 1:1 ratio, standard deviation was maximum 14%, in 1:2 they were maximum 9%, in the 1:3 they were maximum 1%.

Without a water-column  
 $V_{\text{hydrate}} = 15 \text{ ml}$   
 $V_{\text{TEG}} = 15 \text{ ml}$       hydrate-to-TEG ratio = 1:1

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,0	0
10	1,9	19
20	4,0	27
30	3,9	31
40	6,3	42
50	6,9	46
60	6,6	53
70	10,6	71

Without a water-column  
 $V_{\text{hydrate}} = 15 \text{ ml}$   
 $V_{\text{TEG}} = 30 \text{ ml}$       hydrate-to-TEG ratio = 1:2

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0	0
10	2	14
20	3	22
30	4	30
40	6	37
50	6	43
60	8	55
70	11	71

Without a water-column  
 $V_{\text{hydrate}} = 15 \text{ ml}$   
 $V_{\text{TEG}} = 45 \text{ ml}$       hydrate-to-TEG ratio = 1:3

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0	0
10	2	13
20	-	-
30	3	23
40	-	-
50	-	-
60	7	46

Without a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{TEG}} = 15 \text{ ml}$       hydrate-to-TEG ratio = 2:1

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0	0
10	2	8
20	3	11
30	4	14
40	5	17
50	6	20
60	7	23
70	7	25
80	8	27
90	9	29
100	10	32
110	10	35
120	11	36
130	12	40
140	13	42
150	14	46
160	14	48
170	15	50
180	15	52
190	15	52
200	17	55
210	17	57

With a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{TEG}} = 15 \text{ ml}$       hydrate-to-TEG ratio = 2:1

Time (h)	melted hydrate (ml)	melted hydrate (%)
0,0	0	0
0,5	5	15
1,0	7	22
1,5	8	28
2,0	11	38
2,5	14	46
3,0	16	53
3,5	18	61
4,0	21	69
4,5	22	74

# Appendix E - Data from melting with HCOOK

The values shown are average values calculated from the different parallel experiments performed. Standard deviations of the melted hydrate values were below 7%.

Without a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 10 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,00	0,00
10	2,15	7,16
20	2,86	9,54
30	4,01	13,36
40	4,44	14,79
50	5,01	16,70
60	5,30	17,65
70	5,73	19,09
80	6,30	20,99
90	6,73	22,43
100	7,16	23,86
110	8,02	26,72
120	8,16	27,20
130	8,59	28,63

Without a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 20 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,00	0,00
10	2,86	9,54
20	4,01	13,36
30	5,30	17,65
40	6,01	20,04
50	7,01	23,38
60	7,73	25,76
70	8,45	28,15
80	8,59	28,63
90	9,45	31,49
100	10,02	33,40
110	10,45	34,83
120	10,88	36,26
130	12,02	40,08

Without a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 30 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,00	0,00
10	3,44	11,45
20	5,15	17,18
30	6,15	20,52
40	7,44	24,81
50	9,16	30,54
60	10,31	34,35
70	12,31	41,03
80	13,17	43,90
90	14,03	46,76
100	15,03	50,10
110	16,32	54,39
120	17,03	56,78
130	17,75	59,16

Without a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 40 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,00	0,00
10	4,31	14,37
20	7,08	23,60
30	9,85	32,84
40	10,93	36,43
50	13,39	44,64
60	15,39	51,31
70	19,70	65,68
80	21,55	71,84
90	22,17	73,89

Without a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 50 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0	0
10	6	22
20	9	31
30	11	38
40	14	46
50	16	54
60	19	62

Without a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 60 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,00	0,00
10	9,73	32,44
20	12,88	42,94
30	16,03	53,44

Without a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 70 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,00	0,00
10	11,74	39,12
20	14,89	49,62

With a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 10 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0	0
30	3	9
60	4	14
90	5	18
120	7	22
150	7	22
180	7	24
210	8	28
240	9	30
270	10	32
300	11	35
330	11	36
1350	19	63

With a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 30 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,00	0,00
10	4,15	13,84
20	5,44	18,13
30	6,58	21,95
40	7,44	24,81
50	8,59	28,63
60	9,73	32,44
70	10,59	35,31
80	11,45	38,17
90	11,74	39,12
100	12,31	41,03
110	13,17	43,90
120	14,03	46,76
130	14,60	48,67

With a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 50 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,00	0,00
10	4,72	15,75
20	6,73	22,43
30	8,02	26,72
40	9,88	32,92
50	11,45	38,17
60	14,31	40,08
70	14,60	48,67

With a water-column  
 $V_{\text{hydrate}} = 30 \text{ ml}$   
 $V_{\text{HCOOK}} = 15 \text{ ml}$   
 Concentration of HCOOK = 70 wt%

Time (min)	melted hydrate (ml)	melted hydrate (%)
0	0,00	0,00
10	6,73	22,43
20	9,73	32,44
30	12,31	41,03
40	14,46	48,19
50	20,76	69,18
60	23,19	77,29