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An Experimental Study of Potassium Formate as a Potential Gas Hydrate Inhibitor in a Vertical Pipe

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Abstract

Blocking of petroleum producing pipelines with clathrate hydrates of natural gases is a large issue in the industry. It causes loss of income in addition with health, safety and environmental concerns. This master thesis considers inhibition and dissociation of clathrate hydrates of natural gases with the thermodynamic inhibitor potassium formate. Potassium formate is a salt frequently used during drilling operations, but the writer has not found information about the usage of the salt as a thermodynamic inhibitor in petroleum production. Its application as a thermodynamic inhibitor is of large interest due to its properties, especially for shut-in wells as the salt is considered very heavy and has a large solubility in water.

The distribution of the salts sodium chloride (NaCl) and potassium formate (HCOOK) in a two-meter vertical pipe was investigated to simulate a shut-in well or riser. The salt solutions were added to the top of the distilled water filled pipe. Pycnometers were used to measure the brine densities at different heights in the pipe. Higher densities corresponded with more salt. The hypothesis about the heavy HCOOK salt accumulating at the bottom of the pipe was not confirmed, when it was found that both salts became almost homogeneously dispersed in the pipe after short time for all brine concentrations investigated. It means that the salt would inhibit the whole water phase and not only the lower or upper part, as the conventional hydrate inhibitors in the petroleum industry are known to do.

Potassium formate's quick distribution to a homogeneous mix could improve flow assurance in production wells. It is an advantage for producing wells to have a homogeneous salt distribution, because the whole water phase gets protected against hydrates. But it is a disadvantage for hydrate dissociation in the bottom a pipe if the inhibitor should be used to penetrate the water phase and accumulate at the bottom to dissociate hydrates.

Sammendrag

Hydratplugger som blokkerer petroleumsproduserende rørledninger er et stort problem i industrien. Plugger fører til minsket inntekt for partnerne på feltet i tillegg til helse-, miljø- og sikkerhetsutfordringer. Denne masteroppgaven omhandler hindring og oppløsning av gasshydrater ved bruk av den termodynamiske inhibitoren kaliumformat. Kaliumformat er et vanlig salt i bore- og kompletteringsfluider, men undertegnede har ikke funnet informasjon om bruk av saltet som hydratinhibitor i petroleumsproduksjon. Bruk av saltet i forbindelse med hydratinhibering er av stor interesse, spesielt i en stengt brønn på grunn av saltets høye løselighet i vann og store tetthet.

Fordelingen av saltene natriumklorid (NaCl) og kaliumformat (HCOOK) i et to meter høyt rør er undersøkt for å simulere et stengt stigerør. Saltløsningene ble tilsatt på toppen av røret som på forhånd var fylt med destillert vann. Pyknometer ble brukt for å måle tettheten av saltvannet i forskjellige høyder i røret. Høyere tetthet svarte til mer salt i vannet. Hypotesen om at HCOOK akkumulerte på bunnen av røret ble ikke bekreftet, da det viste at begge saltene fordelte seg omtrent homogent i røret etter kort tid for alle saltkonsentrasjoner undersøkt. Det betyr at saltet vil inhibere hydratformasjon i hele vannfasen og ikke bare i nedre eller øvre del, slik de tradisjonelle hydratinhibitorene i petroleumsindustrien er kjent for å gjøre.

Den raske homogene fordelingen av kaliumformat kan forbedre strømningssikkerheten i produksjonsbrønner. Den homogene fordelingen kan være en fordel i produserende brønner, da hele vannfasen vil bli beskyttet mot hydratdannelse. Men det kan være en ulempe for smelting av en hydratplugg på bunnen av et rør hvis inhibitoren skulle bli brukt til å penetrere vannfasen og akkumulere på bunnen av røret for å smelte hydratet.

Acknowledgement

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Chapter 1

Introduction

Knowledge of gas hydrates and hydrate inhibitors is important in the petroleum industry for mainly two reasons. First due to its health, safety and environmental (HSE) concerns. It is well known that hydrate plugs are related with explosion risks, and should always be handled with care if discovered. Second due to economic concerns. An impermeable hydrate plug in a pipeline will stop the oil and gas flow towards the production plant, which corresponds with no income for the partners of the petroleum producing field. Plugs are rather attended with extra risks and expenses for prevention and dissociation. The knowledge of gas hydrates and inhibitors are therefore of large interest (Larsen, 2016). The hydrate inhibitors are divided into two groups; thermodynamic inhibitors (TIs) and low dosage hydrate inhibitors (LDHIs). The TIs can both prevent and dissociate the hydrate plugs, while the LDHIs only prevent plug formation (Sloan and Koh, 2008).

This master thesis investigates the salt potassium formate (HCOOK) as a potential thermodynamic inhibitor in a shut-in well or riser. The salt sodium chloride (NaCl) is also investigated to compare the results. NaCl is rarely used as a TI in the industry; two essential reasons are corrosion of the steel pipes and equipment, in addition to relatively low solubility in water. HCOOK is not a common inhibitor in the industry either, even if corrosion is low and the solubility in water is high (Fadnes et al., 1998).

1.1 Background

The background for the subject of the thesis is hydrate dissociation problems in the bottom of a riser or a shut-in petroleum well. A shut-in well does not have circulations in the riser due to no flow. The fluids in the well will separate with respect to hydrostatic pressure (i.e. density of the fluids); water will accumulate at the bottom, with a lighter condensate and oil phase above, and a less dense gas phase at the top. Valves are rarely completely tight and some gas passes through. In producing wells, water often accumulates at the bottom of a riser. Lighter hydrocarbons can pass through the water phase. Hydrates can be formed at the interface between the water and hydrocarbon droplets if the correct pressure and temperature conditions are present. The bottom of a riser is therefore a typical location with high risks of hydrate formation during hydrocarbon production and in a shut-in well (Larsen, 2016).

Dissociation of a hydrate plug depends on several factors; e.g. temperature, pressure and type and amount of inhibitor. One other essential factor is the mixing abilities of the hydrate inhibitor in the fluids that are already present in the pipe. If the inhibitor accumulates in the top of the pipe, no hydrate dissociation mechanism will occur at the bottom of the pipe under the same pressure and temperature conditions. In other words; the inhibitor needs to reach the hydrate plug to dissociate it. Methanol, which is a largely used hydrate inhibitor, has a lower density than water and brine. The low density affects the mixing abilities when methanol is added at the top of the pipe. According to Li et al. (2000) methanol will have mixing problems with water in a vertical pipe when a lighter condensate phase is present (the condensate phase is also denser than methanol) due to the lower density of methanol. Hydrate plug dissociation with methanol in the bottom of a riser is therefore problematic. Glycols, which also are used as hydrate inhibitors, are denser than water, and will therefore have the possibility to accumulate at the bottom of the riser and dissociate a hydrate plug.

This master thesis investigates the mixing abilities of potassium formate brines and sodium chloride brines with different concentrations in a vertical pipe. If the salt accumulates at the bottom of the pipe after mixing, there are large chances that the salt can be used in shut-in wells for hydrate prevention and dissociation. Inspiration is found from similar experiments done with methanol and glycols by Li et al. (2000). Inspiration about HCOOK as a TI is mainly found from Fadnes et al. (1998), Downs (1993), Howard (1995) and Larsen (2016). Downs (1993) reported that potassium formate can lower the freezing temperature of water with over 60°C.

The antifreeze mechanism of water can be explained through colligative properties for low solute concentrations; the freezing point of a solvent (e.g. water) only depends on number of dissolved molecules in the solvent and no other properties of the dissolved molecules (Pedersen, 2014). The antifreeze mechanism is anticipated somewhat the same for hydrate inhibition (Larsen, 2016). Potassium formate, which has a high solubility in water, can therefore be used as a thermodynamic inhibitor. According to Weatherford (2010) the solubility in water is 25 wt% at 0°C, and 77 wt% at 18°C.

The reasons for investigating potassium formate as thermodynamic inhibitor are many. Examples are its availability on drilling rigs, low corrosivity towards metals, high molecular weight and high density (Fadnes et al., 1998). The high molecular weight can be an advantage in shut-in wells, since the salt may sink to the bottom and dissociate a hydrate plug. In addition to the high solubility in water, HCOOK has a favourable low solubility in hydrocarbons. The traditional TIs methanol and glycols has higher solubility in hydrocarbons (Fadnes et al., 1998).

Chapter 2

General Theory

Some of the general theory given in this chapter is copied and modified from TPG4560 Specialization Project which was written during the autumn 2016. The Specialization Project was done as a preview to the study of potassium formate as a potential hydrate inhibitor. The information given here is the basic understanding of clathrate hydrates and the building blocks for the rest of the thesis. More detailed general theory about clathrate hydrates is given in the TPG4560 Specialization Project Report. Information about potassium formate is not given in this chapter as it is not a conventional hydrate inhibitor.

2.1 What is a Clathrate Hydrate?

In the everyday use, a clathrate hydrate is a structure similar to ice that also contains gas molecules. The word clathrate means that a compound, e.g. a gas molecule, is physically enclosed inside the crystal structure of another. A hydrate is a chemical compound that contains water molecules. In other words; a clathrate hydrate is a structure of water molecules that is enclosing gas molecules. *Hydrates* and *gas hydrates* are frequently used for *clathrate hydrates*, and it has the same meaning.

2.1.1 Different Hydrate Structures

In clathrate hydrates, the water molecules are hydrogen bonded in pentagons or hexagons, which together make different cavities (enclosing gas molecules). Several cavities form unit structures, which again form hydrate clusters and a hydrate crystal. An overview is given in Figure 2.1.

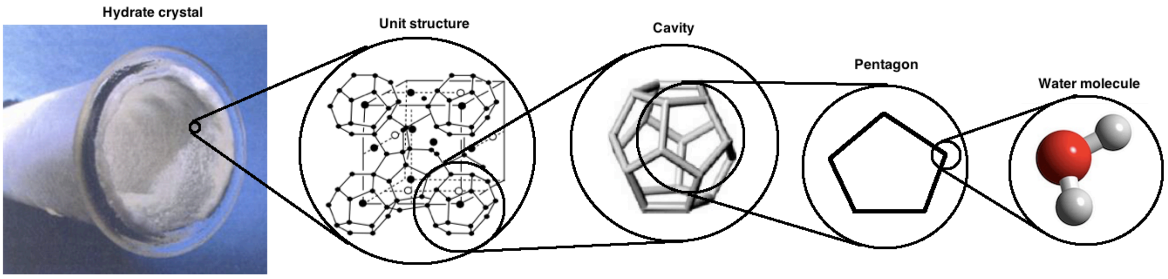


Figure 2.1 *Clathrate hydrate structure overview (parts are copied from Larsen (2015) and Sloan and Koh (2008)).*

The cavity structure can consist of only pentagons or a combination of pentagons and hexagons. 12 pentagons will make a stable cavity structure. The nomenclature is 5^{12}, since the 12 pentagons have 5 edges. Other stable cavities are e.g. 12 pentagons combined with two or four hexagons, with nomenclature $5^{12}6^{2}$ and $5^{12}6^{4}$ respectively.

Different cavities combined together form a unit structure. An example of a unit structure, called structure I, is two (small) 5^{12} cavities and six (large) $5^{12}6^{2}$ cavities combined. Unit structure II consists of sixteen (small) 5^{12} cavities and eight (large) $5^{12}6^{4}$ cavities. The unit structure is the smallest repeating unit in the hydrate crystal. Many unit structures together form a hydrate crystal.

2.1.2 The Guest Molecule’s Influence on the Structure

The cavity structures are enclosing gas molecules, or guest molecules as they are frequently named. The guest molecules make van der Waals bonds with the water molecules in the cavities. Van der Waals bonds are approximately an order of magnitude weaker than the hydrogen bonds between the water molecules.

The type of guest molecule decides which unit structure that is formed. The chemical nature and the geometry of the guest molecules are of especial importance. Firstly, the guest should not make strong hydrogen bonds to other molecules. It should e.g. not have a hydroxyl (i.e. -OH) group, or several intermediate strong hydrogen bonds. These hydrogen bonds can prevent formation of hydrates by hydrogen bonding to water molecules and then prevent cavities to form. Secondly, the ratio between the diameter of the guest molecule to cavity diameter is also of importance. If the ratio is larger than 1, the guest molecule is too large to fit in the cavity. A ratio between 0.76 and 1.0 will give a stable hydrate structure according to Sloan and Koh (2008). Natural gases have neither a hydroxyl group or several intermediate strong hydrogen bonds, but have molecular sizes to stabilize hydrate structures.

Since the different unit structures consist of small (5^{12}) and large ($5^{12}6^{2}$ or $5^{12}6^{4}$) cavities, the guest molecules may have different stabilities in the different cavities in the same structure. The guest diameter to cavity diameter for methane in structure I is about 0.86 for the small cavity, and 0.74 for the large cavity. This means that methane is stable in the small cavities, but less stable in the large cavities, and thus mainly occupies the small cavities in structure I. But all guest molecules that occupy the small cavities in one structure also occupy some of the large cavities in the same structure. Propane has a ratio larger than 1 for both the small and large cavity in structure I (i.e. it is too large to fit in either cavities in structure I**),** but is stable in the large cavity in structure II. This means that most natural gases form hydrate structure II, as a consequence of propane present in the reservoir gas. Another notice is that only one guest molecule fits into each cavity at normal pressure conditions. (Sloan and Koh, 2008).

2.2 Formation of Clathrate Hydrates

The hydrate formation process is divided in two parts; nucleation and growth. The nucleation process is stochastic, while the growth period is controlled by kinetics, heat and mass transfer. These processes are time dependent.

2.2.1 What is Needed for a Hydrate to Form?

Since hydrates consist of water and gas molecules, both these compounds are essential for hydrate formation. Thermodynamic correct temperature and pressure are also required. Low temperatures and high pressures are most common hydrate forming thermodynamic conditions. When these four conditions are present, hydrates can be formed (Sloan and Koh, 2008, pg. 644).

2.2.2 Hydrate Nucleation

According to Sloan and Koh (2008) hydrate nucleation is the first stage of forming a hydrate crystal. The process is considered uncertain and stochastic, where gas and water molecules grow unit structures and disperse random again.

The process has a metastable period, which means that even if the hydrate is in the thermodynamic hydrate stable region, hydrates are not formed. It is analogous with crystallizing of salt, where the brine can get supersaturated. A supersaturated brine does not precipitate salt even if the concentration of the salt is higher than “theoretical possible”. The metastable period of hydrates may be explained due to entropy in the liquid water versus the hydrate. Entropy favours disorder over order, and liquid water has a higher degree of disorder than the solid hydrate.

There are given several nucleation theories during the years of which hydrates are known. The theory described in this section has been modified several times and is shown in Figure 2.2. Figure 2.2 A shows pure water with no dissolved gas. Some structures of pentagons and hexagons are present in the water phase. When gases are dissolved, seen in Figure 2.2 B, water molecules immediately group around the guest molecules, make cavities, unit structures, then start to form labile clusters. The clusters can agglomerate in the metastable liquid, as illustrated in Figure 2.2 C. They can also detach. If the agglomeration becomes large enough (i.e. above a critical cluster radius), the nucleation period is over and the growth period begins, seen in Figure 2.2 D (Sloan and Koh, 2008).

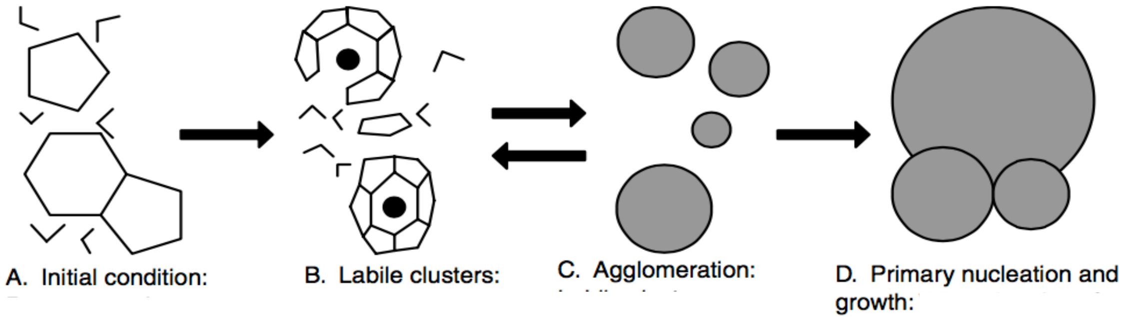


Figure 2.2 *Schematic of a labile cluster nucleation and growth (Sloan and Koh 2008, pg. 133).*

2.2.3 Hydrate Growth

2.2.3.1 Microscopic Scale: Hydrate Growth on a Crystal Surface

The hydrate growth process is exothermic; heat is released. Heat released from hydrate growth or gas availability are in most cases limiting factors for the growth process. The process consists of three stages; mass is transported to the crystal surface, hydrate grows at the crystal surface and heat is released.

The process of hydrate growth on a crystal surface is illustrated in Figure 2.3. When a gas guest molecule is dissolved in water, water molecules form a temporary cluster around the gas molecule. The gas molecule is transported to the surface of the crystal hydrate due to lower Gibbs' free energy at the surface (i). The crystal exerts a force field to the fluid that attracts the gas molecule, and the gas molecule adheres to the surface. Some water molecules are in excess and diffuse away (ii). The gas molecule can move in two dimensions along the crystal surface because of the force field perpendicular to the crystal (iii). It will eventually come across a crystal step (iv). The step is an attractive place for the gas molecule because two sides of the crystal exert the force field. Excess water is released. The gas molecule can only move along the step at this point in the process (v). It will eventually reach a kink or defect point in the step. Three (or more) surfaces exert a stronger force field, which immobilize the gas molecule (vi). The clusters will rearrange during the process to fit the cavity for the guest molecule (Sloan and Koh, 2008).

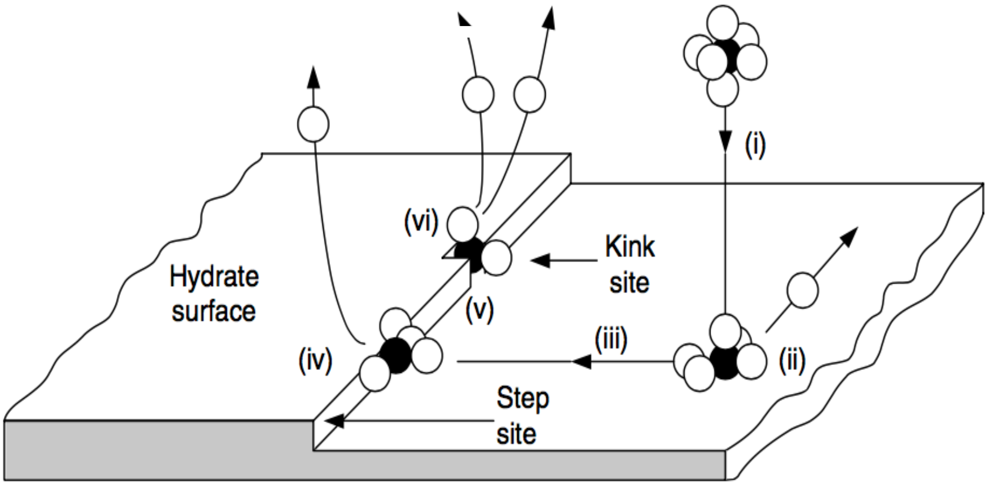


Figure 2.3 *Schematic of hydrate growth (Sloan and Koh 2008, pg. 151).*

2.2.3.2 Macroscopic Scale: Hydrate Film Growth at the Water-Hydrocarbon Interface

Sloan and Koh (2008) suggest that the hydrate growth occurs at the water-hydrocarbon interface, as illustrated in Figure 2.4. It is seen that a thin porous hydrate film is made at the interface between the hydrocarbon and the water. The film grows thicker, and will eventually become non-porous with time. The time to develop a nonporous hydrate film can take from minutes to days, depending on the system.

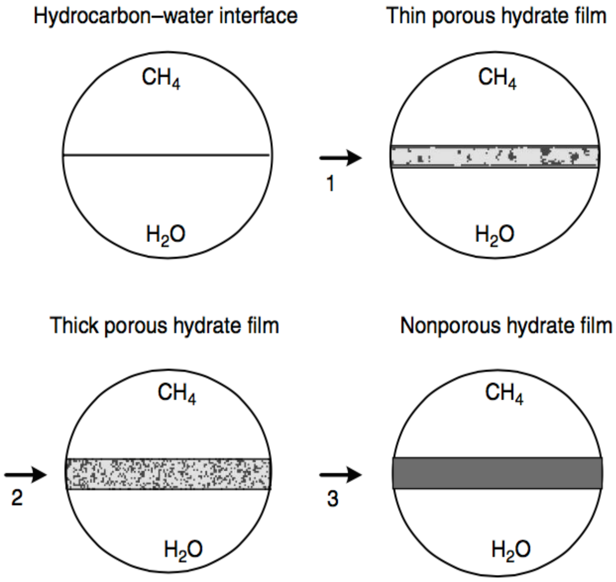


Figure 2.4 *Schematic of hydrate film growth at a water-hydrocarbon interface (Sloan an Koh 2008, pg 163).*

2.3 Prevention of Clathrate Hydrates

Pursuant to Sloan and Koh (2008), the factors needed to form a hydrate plug are high pressure, low temperature in addition to guest and water molecules. In petroleum production, high pressure is necessary for the fluids to flow towards the producing unit, as the fluids flow from high to low pressure. The pressure through the pipe can be adjusted by choking the wells on the x-mas tree. A choked well will decrease the production. A decreased pressure is therefore unfavourable for the hydrocarbon production, as it is analogous with decreased production. The guest molecules, i.e. the hydrocarbons, are the economical reason for the production. The water, in contrast, does not have an economical benefit, and can be removed. A subsea separator for the Statoil Petroleum AS's oil producing field Tordis was e.g. installed in 2007 to separate the water from the production flow (FMC-Technologies, 2017, Norwegian-Petroleum-Directorate, 2017d). One problem with the separator is that not all the water is separated from the flow, and may accumulate with time (Larsen, 2016). Heat can also be retained as an advantage. Insulation or burial is frequently used to reduce heat transfer from the reservoir fluid to the surroundings. Bundling of different pipes can also be used. Both heat preserving and water removing are expensive investments.

If these methods are considered, but hydrate formation still is a concern, inhibitors may be used to prevent hydrate formation. There are two types of inhibitors; thermodynamic inhibitors (TIs) and low dosage hydrate inhibitors (LDHIs). As the name indicates, LDHIs only need a low dosage to inhibit hydrate formation. The TIs described in Section 2.4.3 are used for both prevention and dissociation of hydrate plugs. LDHIs are only used to prevent hydrate formation. The inhibitors are injected in the water phase, as the hydrates are formed in the interphase between water and hydrocarbons. The LDHIs consist of kinetic inhibitors (KIs) and antiagglomerants (AAs). The KIs are polymers that consist of a backbone and pendants. The pendant has the same function as the guest molecule, while the backbone lies on the outside of the cavity and keeps it open and makes it hard to grow new cavities. The AAs make stable emulsions between water/hydrates and oil, so that agglomeration is hindered by separating the water/hydrate particles. Since a liquid hydrocarbon phase is needed for AAs to make the emulsion, the method is only used when a liquid hydrocarbon phase is present (Sloan and Koh, 2008).

2.4 Dissociation of Clathrate Hydrates

When a hydrate is formed in a pipeline system, it is essential to know how to remove it to maintain the production (i.e. economics) and safety. The conditions needed to preserve hydrates are high pressure and low temperature, in addition to water and gas molecules. The opposite is needed to dissociate or avoid hydrates. According to Sloan and Koh (2008), the process of dissociating a hydrate particle is endothermic; energy needs to be added to the system. When energy is added to the plug, some hydrogen bonds (between water molecules) and van der Waals bonds (between guest and water molecules) break. The hydrate particle is decomposed into water and gas molecules.

The four methods of hydrate dissociation are:

1. Hydraulic, such as depressurization
2. Thermal, such as increasing the temperature
3. Chemical, such as usage of inhibitor
4. Mechanical

The methods are often used in a combination to quicken the dissociation process. Common for the three first dissociation methods is that heat is transferred to the plug from the surroundings. Examples of these methods are given in the next sections.

To understand the different dissociation methods, the hydrate equilibrium curves must be understood. The curves state the stable temperatures and pressures for the hydrates. Hydrates are stable to the left of the equilibrium line, and are not stable to the right of the equilibrium line.

2.4.1 Depressurization, a Hydraulic Method

If a hydrate plug is created, the flow stops and the temperature of the plug decreases to the surrounding temperature (seen as the "operational point" in Figure 2.5). The pressure can be reduced to dissociate the plug. In industrial equipment, it can be in form of decreasing the pressure at one or two ends of the pipeline or flowline. The pressure rarely decreases isothermally, which also leads to a temperature decrease in the plug. It is illustrated in Figure 2.5, where the figure is reproduced from Larsen (2015).

The pressure decrease gives almost a Joule-Thomson effect, which denotes that there is no enthalpy change in the system. Enthalpy is the sum of work and heat transferred. I.e. when no work is done on the system, no heat is transferred either and the temperature decreases. With a decreased temperature in the system (i.e. the plug), a temperature difference is created between system and the surroundings, and heat is transferred from the surroundings to the plug. The plug is dissociated if the surrounding temperature is in the "no hydrate area" for the corresponding pressure (Larsen 2015).

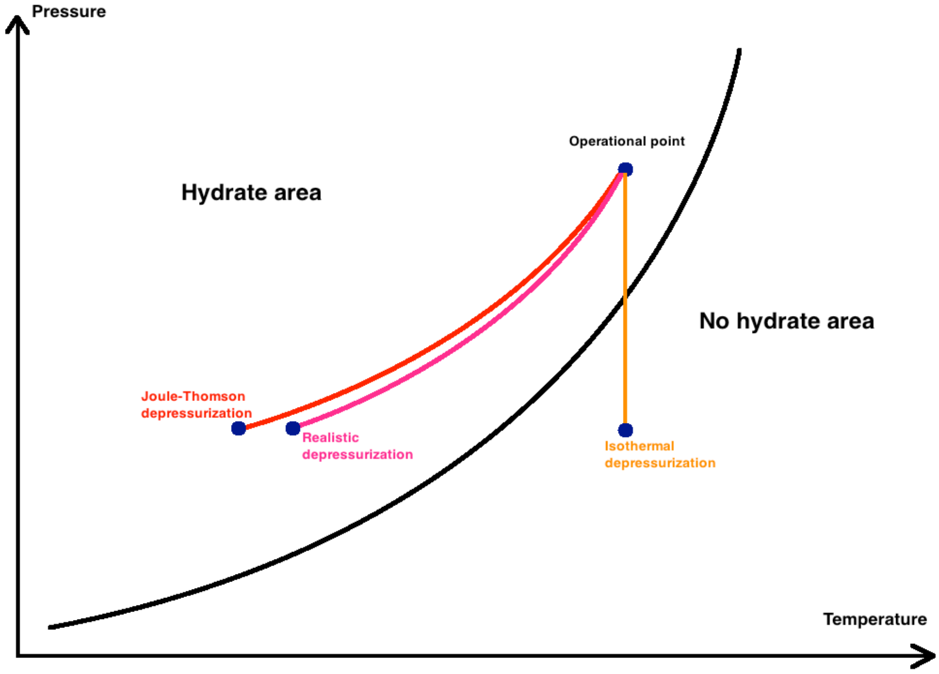


Figure 2.5 *Depressurization to dissociate a hydrate plug (reproduction from Larsen (2015)).*

2.4.2 Increasing the Temperature, a Thermal Method

The second method to dissociate a hydrate plug is to increase the temperature of the plug. Heat is transferred to the hydrate plug if the surrounding temperature is higher than the plug temperature. If the temperature is increased outside the stable hydrate area, the plug dissociates due to the temperature difference between the plug and the surroundings, as shown in Figure 2.6.

Direct electrical heating (DEH), heating topside with steam or warm water can be used in pipelines to create the temperature difference necessary. DEH is a method where an electrical circuit is used to increase the temperature of the steel in the pipe, which transfers heat to the fluids inside the pipe. (Larsen 2015).

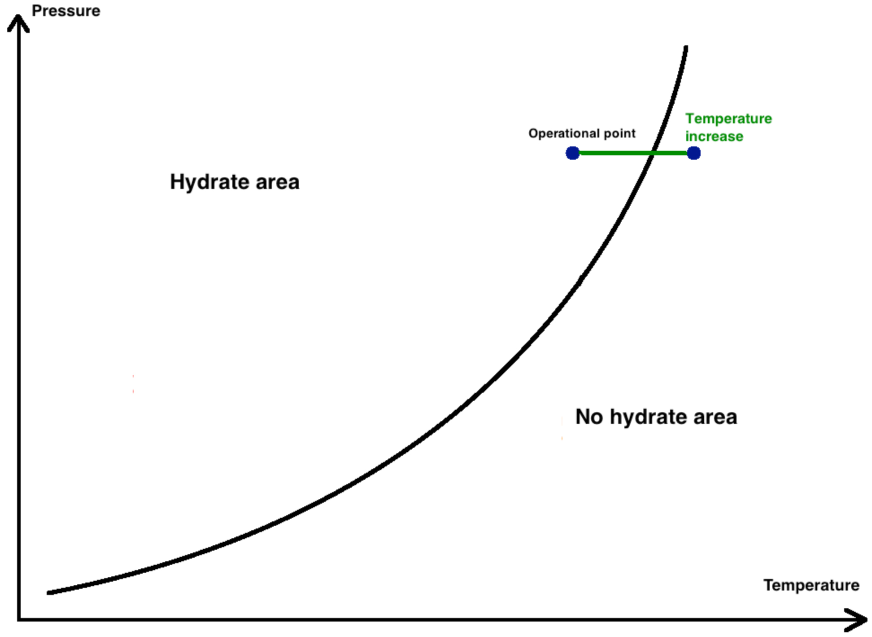


Figure 2.6 *Increase the temperature to dissociate a hydrate plug. (Reproduced from Larsen (2015)).*

2.4.3 Using Inhibitor, a Chemical Method

The third method to remove a hydrate plug is to use chemicals. The most widespread method is to use thermodynamic inhibitors. The thermodynamic inhibitors shift the hydrate equilibrium line to the left, as illustrated with methanol in Figure 2.7. When the equilibrium line changes, the operational temperature of the plug also changes. The hydrate plug gets the same temperature as the equilibrium line at the corresponding pressure. The surroundings have unchanged temperature (i.e. the operational temperature). The temperature difference melts the plug.

Figure 2.7 illustrates that the operational point is in the stable hydrate area if no methanol is added to the system, but outside the stable hydrate area if 20 wt% methanol is present in the water phase. The methanol will prevent hydrate formation. The salt NaCl is the most effective thermodynamic inhibitor on a weight basis, i.e. it shifts the equilibrium line most to the left with the same weight inhibitor added, but NaCl also has an upper solubility limit in water (Sloan and Koh, 2008).

Alcohols, glycols and salts are used as thermodynamic inhibitors. Mono-ethylene glycol (MEG) is often considered an alcohol with two hydroxyl (-OH) groups. The inhibition mechanism is therefore the same for alcohols and glycols. Alcohols and glycols as inhibitors have two main functions. Firstly, the hydroxyl group hydrogen bonds with water molecules. Secondly, water molecules group around the non-hydroxyls in the alcohol/glycol molecule (that contains many hydrogen atoms). The water molecules are therefore prevented in forming new hydrogen bonds with each other to create the cavity structure needed in hydrates.

The salts' main mechanism as thermodynamic hydrate inhibitor is not to hydrogen bond with water molecules, as the salts used as inhibitors do not contain any hydroxyl group or create strong hydrogen bonds. When salts are dissolved in water, ions in the solution are formed. The ions have either a positive or a negative charge. The different charges attract water molecules and form dipole bonds with the water molecules. The dipole bonds prevent hydrate formation in the same manner as hydrogen bonds. Salts also reduce the solubility of non-polar molecules, such as hydrocarbons, in the water. Less guest molecules in the water phase decreases the chances of hydrate formation (Larsen, 2015).

Another chemical method is usage of chemicals that generate heat in the system (Sloan and Koh, 2008).

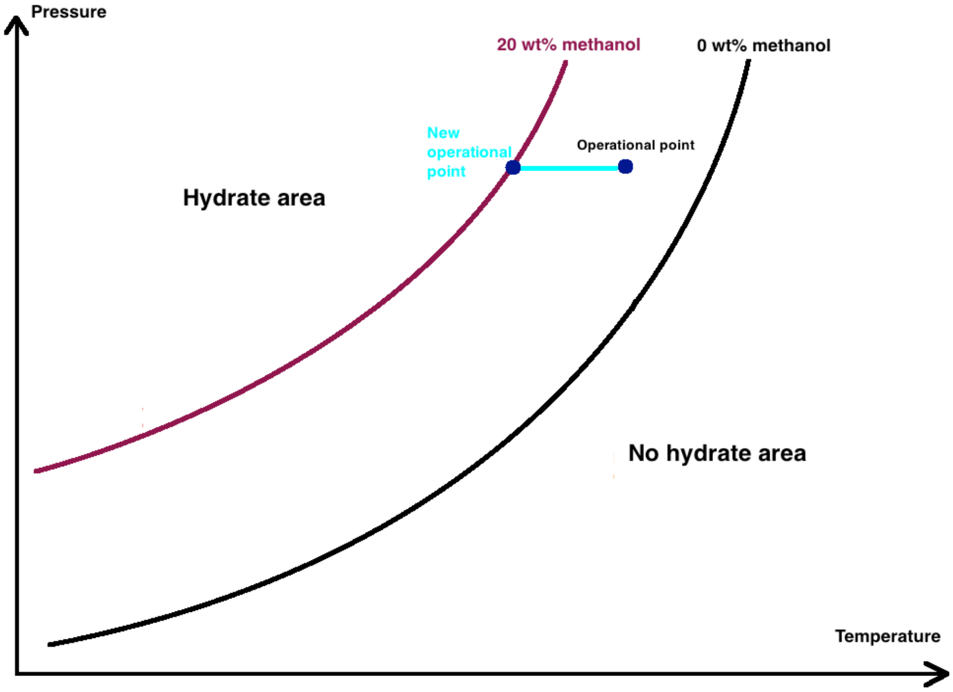


Figure 2.7 *Methanol inhibitor usage to dissociate a hydrate plug. (Reproduced from Larsen (2015)).*

2.4.4 Mechanical Methods

The mechanical methods to remove a hydrate plug are not as widespread as the other methods described above. One mechanical method is coiled tubing. This is a method where a tubing is coiled shore, transported to the platform (or other processing equipment), and “uncoiled” into the hydrate area in the pipe. The coiled tubing can contain e.g. thermodynamic inhibitor or steam to heat the plug. The method is therefore also using a combination of methods to dissociate the plug. Another mechanical method is to drill through the plug (Sloan and Koh, 2008).

2.5 Where Does Hydrate Plugs Form in Industrial Equipment?

In industrial equipment, typical hydrate formation locations are where irregularities occur, such as low points, high points, bends, valves etc. Some of these points are described briefly in this paragraph.

Water accumulates at low points in flowlines, because water is denser than oil (not always true) and gas. There is a higher risk of hydrate plug formation when the water is present at larger scales, as illustrated in Figure 2.8. The water may be stuck at the low points for a longer period due to its high density. It will then have time to build up hydrates particles over time which at the end may become a hydrate plug that blocks the pipeline. The bottom of a riser is another example of the same low point where water and hydrates can accumulate.

High points in pipelines are mostly occupied by gas. A thin layer of water will be present at the bottom. Water has higher heat capacity compared to the gas in the pipeline, which means that more energy is need to increase or decrease the temperature of the water compared to the gas. Points in the pipeline with less water content are therefore more vulnerable for heat transfers from the surroundings. Since parts of pipelines with less water content are more exposed to temperature changes, these parts are also more exposed for hydrate formation. The surroundings in e.g. subsea pipelines have lower temperature than the gas flow, which means that heat is transferred from the gas to the surroundings. The temperature of the gas is lowered. High points in subsea pipelines are also often more exposed to currents in the sea, which may decrease the temperature more. Hydrate formation will therefore often occur at high points in pipelines.

During a shut-in of a production well, valves are closed and a hydrostatic situation occurs. The temperature of the system is decreased to the surrounding temperature. The fluids separate according to densities. The water, which is assumed to have the highest density, accumulates at the top of the valve. The gas is less dense and will rise until it reaches a restriction, such as a new valve. This is illustrated in Figure 2.9. The valves often leak, and some gas will pass through. The gas will then penetrate the water phase due to its lower density. During the penetration, hydrates are formed in the water phase if the pressure and temperature conditions are correct. The water phase of a shut-in well therefore is a favourable hydrate formation location.

Other points in the system that rapidly undergo changes are also potential hydrate formation spots, such as bends or other irregularities. The principle for all these locations is the same; all are exposed for heat exchange with the surroundings, and some with accumulation of water. It is also worth mentioning that the temperature will decrease nearer the platform in the production line. It means that more water is condensed through the pipeline, and there are higher chances of forming hydrates (Larsen, 2016).

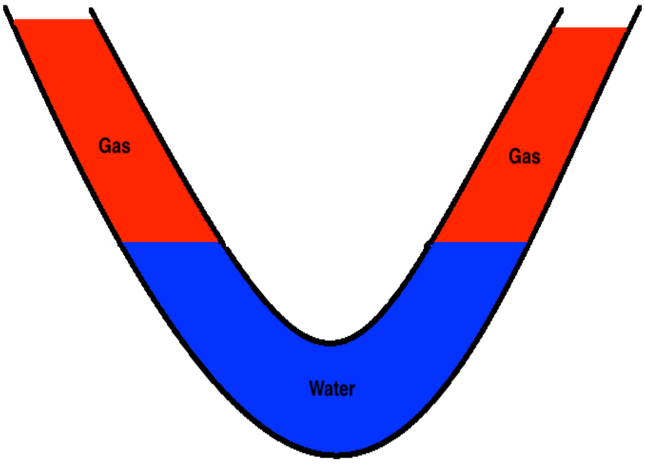


Figure 2.8 *Low point in a flowline. Only gas and water phases are shown (reproduced from Larsen (2016)).*

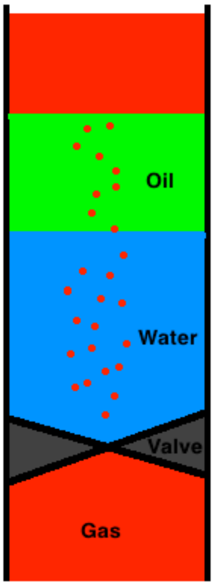


Figure 2.9 *Illustration of hydrostatic conditions in a production well with a closed, leaking valve (reproduced from Larsen (2016)).*

2.6 Recycling Thermodynamic Inhibitors

The amount inhibitor used in the water phase to prevent hydrate formation can be up to 50 wt% for the conventional TIs. It is therefore of high interest to recycle the inhibitors if possible. Methanol and salts are not common to recycle in the industry. The reason may be that it is cheaper to buy new methanol and salts. According to Yagasaki et al. (2015) methanol is “the most common TI because of its low cost”. Methanol is also very volatile. In other words, methanol easily evaporates to the gas phase.

Glycols, on the other hand, are commonly recycled. Examples are from the Ormen Lange field and the Snøhvit field at the Norwegian Continental Shelf. MEG is added at both fields continuously to prevent formation of hydrates. Both fields have long distances from the wellhead to the processing facilities, 143 km and 135 km for Snøhvit and Ormen Lange respectively. Large resources are used to recycle the huge amounts of glycol used (Johnsen, 2016).

2.7 Importance of Clathrate Hydrates

Hydrates are important in the petroleum industry due to safety concerns, and also due to economic concerns. If a hydrate plug blocks the pipeline or flowline, the production stops, and there are no economic benefits for the company. It can take months to dissociate a plug if it is created. It is therefore desirable to avoid plugging rather than removing it. If a hydrate plug is discovered, it is important to try to detect where it is located to dissociate it.

It is well known that 1m^3 hydrate equals 0.8m^3 water and 180Sm^3 gas when dissociated. The large amount of gas needs to be able to “escape”. If the gas cannot escape, an explosion can occur. This reason also makes it important to detect all the plugs if several plugs are present. Another safety issue with hydrates is if heat is added to the system, and the system is at the same time depressurized at one side (i.e. there is a large pressure difference over the plug). If the plug loosens from the wall, it may act like a projectile through the pipe.

There are at least two known deaths due to hydrate plugs, both in Canada, and several accidents related to hydrates. The first death was due to a warm, dry wind which melted the middle of a hydrate plug. The pipe exploded due to trapped gas. The second death was due to a hydrate plug that had loosen from the wall and acted like a projectile through a 90-degree bend due to pressure difference over the plug.

Clathrate hydrates can be important in many other areas than flow assurance as described above with blocking of pipes. Due to the high gas content per unit hydrate plug, hydrates can also be used for energy storage and transportation. Other purposes are e.g. removing of salts from water (i.e. demineralising). Hydrates are also found in large amounts in ocean floors and permafrost areas. These hydrates contain natural gas and may be a future energy resource (Larsen, 2016).

Chapter 3

Literature Study; Thermodynamic Inhibitors

Some of the “Literature study” is copied and modified from TPG4560 Specialization Project which was written during the autumn 2016. This chapter gives an overview of the antifreeze mechanism of water, mixing abilities of conventional thermodynamic inhibitors in water and hydrate dissociation with different conventional inhibitors. In addition, properties of potassium formate are given and linked to hydrate inhibition.

3.1 Antifreeze Activity of Water

It is well known that additives are used to prevent water from freezing. Every day examples are salting of roads in the winter and adding antifreeze to car engines. The freezing temperature of the water decreases below 0°C. Antifreeze of water is also a well-known phenomenon in the nature. Examples are antifreeze proteins found in artic fish, insects and grass. The mechanism is essential for survival of the species in cold areas. The proteins bind to ice crystals and prevent growth in supercooled water. The water has a liquid form despite the low temperature. (Knight, 2000). Antifreeze proteins can also be used in food as an advantage, e.g. in ice-creams and frozen food. Feeney and Yeh (1998) showed that small amounts antifreeze proteins added to ice creams before freezing it decreased the crystal growth in the ice cream.

The mechanism of antifreeze can be explained through its colligative properties for solutes with low concentrations. Colligative properties are properties of solutions that only depend on number of molecules dissolved in the solvent, and no other properties of the solutes. Decreasing the freezing point of a solvent is an example of a colligative property (Pedersen, 2014). The result is that all substances that can be dissolved in water affect the freezing point. More substances dissolved correspond with lower freezing temperature due to increased substance concentration. According to Senese (2015) the freezing temperature of water decreased between 1.7°C and 1.9°C per mole solute added per kilogram water, independent of solute type.

When the temperature in pure water is decreased, the water molecules move slower. The attractive forces between molecules can bind them together to a solid ice formation. When a solute is added to the water, the solute molecules block some of the attractive forces between water molecules and prevent them from hydrogen bonding. The temperature must then be decreased more to make a solid ice structure. More solutes added to the system decrease the freezing point more (Tse, 2015).

The antifreeze mechanism can also be explained through water melting and freezing on a molecular scale. This is done by both Ansell (2010) and Senese (2015). Both explain that there are always water molecules at the interface between liquid water and ice that melt, and some molecules that freeze. If more molecules freeze than melt, the solid water phase (i.e. ice) increases, but if more water molecules melt, the liquid water phase increases. If equal amounts of water molecules melt and freeze, the ice and water phase are stable. When a solute is added to the water phase (e.g. salt, alcohol, glycol, sugar), the concentration of the water is reduced. Freezing of water reduces, while melting is unchanged. An overall result is ice melting. The freezing temperature is changed.

When water with added solutes freezes, the concentration of solutes in the water phase increases. An increased solute concentration lowers the freezing temperature. If more water freezes, the concentration of solutes increases more and the freezing temperature decreases more. This can continue until the water phase is saturated with the additive (e.g. salts) or the additive freezes (e.g. alcohols).

Back to the everyday example; the antifreeze in car engines needs other properties than only decreasing the freezing point. It must be inert, which means that it must not react with e.g. the metal in the engine. Salts are, on a general basis, highly corrosive, and are therefore not recommended to use in car engines. The antifreeze must also have a high boiling point, as evaporation of the solvent increases the pressure in the closed system and can lead to explosion risks. This property is not as important in the petroleum industry when the equipment is designed to handle high pressures. But it must be considered when calculating the amount of solvent needed to inhibit hydrate formation. Since the antifreeze is used in large amounts, both in the car and petroleum industry, must it be easy and safe to produce. Mono-ethylene glycol is an antifreeze that fulfil the criteria described above, and is frequently used in cars engines and petroleum pipelines. A 50 wt% mono-ethylene glycol solution freezes at -37°C (Tse, 2015). Potassium formate also fulfil the criteria above, with its low corrosivity towards metals and low volatility (Fadnes et al., 1998). A 50 wt% potassium formate brine crystallizes the water at approximately -45°C according to Howard (1995). It could therefore be an interesting water freezing inhibitor in both car engines and petroleum pipelines.

3.2 Alcohol and Glycol Distribution in the Water Phase

According to Li et al. (2000) hydrate plugs are frequently removed by thermodynamic inhibitors in the North Sea. The usage of the different types of inhibitors depends on plug properties, such as porosity and oil content. If the adequate inhibitor is used, the hydrate dissociation time decreases dramatically compared to other inhibitors.

To understand the effectiveness of TIs, the inhibitor distribution in the water phase must be understood. The TIs are miscible with water, but if they are homogeneously mixed has been more uncertain, e.g. if the same concentration is present through the whole pipe. Li et al. (2000) conducted experiments on the inhibitor distribution in the water phase in presence of a condensate phase. The experimental setup is shown in Figure 3.1. The rig was two-meter-high with a diameter of 0.23 m. Small beakers along the pipe were present to take samples of the mixture to measure the inhibitor concentration at different levels. The beakers are shown in Figure 3.1 as small metal circles distributed vertically on the glass cylinder. The inhibitor could be injected at the bottom or the top. These options should illustrate different methods to inject the inhibitors to the well. To mix the fluids in the container, air was bubbled through from the bottom, illustrating flow through the pipe (Li et al., 2000).

Figure 3.1 shows the experimental setup with methanol as the TI. Methanol (MeOH) was dyed with a darker colour to separate the inhibitor from the water and condensate phase. The density of the condensate was less than water and higher than the MeOH. This lead to MeOH lying on the top of the condensate when injected from the top. The condensate prohibited mixing of MeOH and water. Air was bubbled through, which gave a higher amount of MeOH in the water phase.

Another experiment with a condensate containing a lower density than the MeOH was executed. MeOH was injected at the top. The MeOH easily penetrated the condensate and accumulated above the water phase. The methanol did not mix considerably with the water phase. After three days, the methanol concentration at the top of the water phase was 90%, and 0% at the bottom of the container.

To simulate the dissociation of a hydrate plug, another experiment was executed. MeOH was filled in the container. Water was injected at the bottom and gas was bubbled through to simulate released gas from the dissociation process. Some turbulence was created, but very little MeOH was mixed with the water phase. The MeOH concentration due to

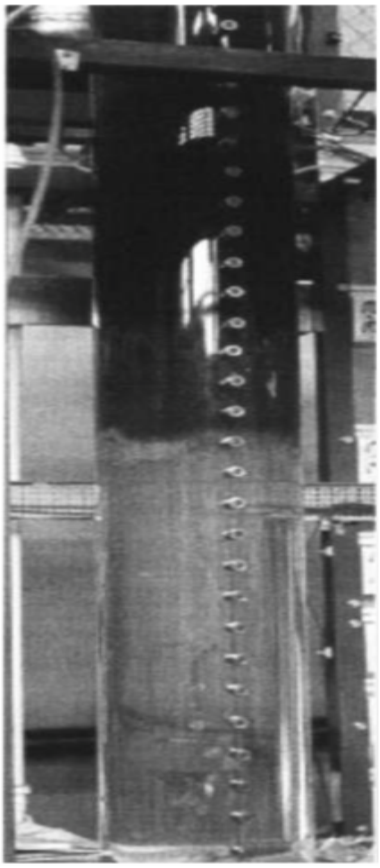


Figure 3.1 *Experimental setup for thermodynamic inhibitor mixing with water (Li et al., 2000).*

completely mixing was theoretically 44 wt%, but only 5 wt% MeOH was detected at the bottom of the cylinder.

Almost complete and fast mixing occurred when MeOH was injected to the bottom of the container, due to the higher gravity of the water.

Glycols are denser than water. Mono-ethylene glycol and tri-ethylene glycol (TEG) were investigated. When MEG was injected at the top of the container, it easily penetrated the condensate and the water phase. The degree of mixing was dependent on the amount MEG and water phase. Experiments with MEG carefully added to the top of the high water column, showed a low concentration at the upper part of the water phase. TEG has a higher density than MEG and water. When TEG was added to the system from the top, it therefore penetrated the water phase and accumulated at the bottom. For most of the experiments regarding glycols, mechanical methods were needed to mix the fluids.

Pursuant to Li et al. (2000) there is expected an immediate mixing between the inhibitor and the water phase in the oil and gas industry. The results from their experiments showed that this is not always true. The mixing of the fluids depends on the density and viscosity of the inhibitor. If the inhibitor is less dense than the condensate phase in the pipeline or riser, the inhibitor will accumulate at the top of the condensate and not mix with the water. If the inhibitor is denser than water, which is the case for MEG and TEG, the inhibitor may accumulate at the bottom of the water phase in the well. These aspects are important notices in a shut-in oil or condensate well.

Regarding viscosity of the inhibitor, Li et al. (2000) explain that a high viscosity fluid has less mixing abilities into another fluid. The viscosity of MeOH, MEG and TEG is respectively 0.539cp, 17.647cp and 37.783cp at 25°C and 1 bar. This support the easier mixing of MeOH in the water phase compared to glycols.

3.3 Usage of Alcohols and Glycols to Melt Ice

Among scientists, there is an agreement that the dissociation theory of clathrate hydrates is analogous to melting of ice. Experiments with ice at atmospheric pressure are less expensive and easier to execute. Li et al. (2000) executed experiments on ice to investigate the performances of MeOH, MEG and TEG as inhibitors. The inhibitors were dyed to see the penetration of the inhibitors into the ice plugs. Two types of ice plugs were used; porous snow plugs and solid ice plugs.

Experiments with porous snow plugs showed that MeOH was the best inhibitor, while TEG was least effective. Temperatures in the plugs were measured. When MeOH was used, a temperature gradient was found for a long period. The temperature at the top of the snow plug was -30°C, while it increased to -10°C at the bottom of the plug. The temperature gradient was the opposite for MEG, with a temperature of -10°C at the upper part to -24°C at the lower part of the porous snow plug. According to Li et al. (2000) the temperature gradient is equivalent to the melting temperature gradient. A low melting temperature (i.e. more negative) corresponds with a high inhibitor concentration, and a high melting temperature (i.e. less negative) corresponds to less inhibitor concentration. This corresponded with previous results described above; methanol accumulated at the top of the snow plug, while MEG accumulated at the bottom of the snow plug.

The results were different for solid ice plugs. Glycols showed to melt the ice plugs more than methanol, due to their ability to penetrate the solid ice plugs. It was observed that methanol melted some ice at the outer layer, but was unable to penetrate into the plug. One suggestion for that behaviour was that the water from the melted ice hinder further contact between the methanol and the ice plug (due to its low mixing abilities). The glycols on the other hand, first melted the outer layer, then penetrated the melted water. It was seen that the glycols, especially MEG, penetrated to the bottom of the ice plug. MEG showed a more efficient plug melting compared to TEG.

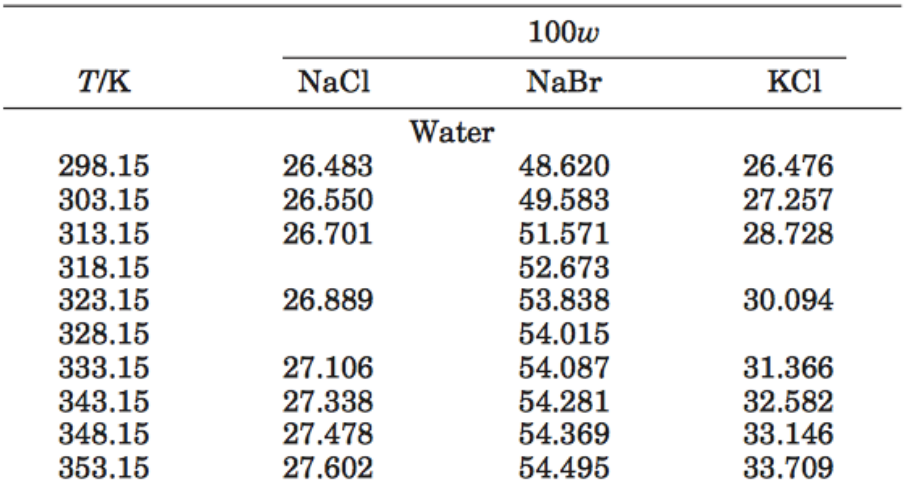
TEG was the inhibitor investigated having the highest density and viscosity. The high viscosity made a slow penetration of the plug. The temperature at the melted regions of the plug can be very low when high concentrations of TEG are used. The temperature can get lower than the freezing point for TEG, and TEG will freeze out. The solid inhibitor may block pores of the hydrate plug. Further penetration may be prohibited and melting may stop. MEG has lower freezing point and viscosity compared to TEG, which makes it a more favourable inhibitor. Li et al. (2000) also showed that TEG is a poor inhibitor at low concentrations, which means that it gets poorer when ice plug melts and more water is present. MEG is a better inhibitor at lower concentrations, i.e. when the plug melts. TEG is therefore not a recommended inhibitor for hydrate plug dissociation.

Hydrates are usually more porous and permeable than ice plugs. The results therefore showed that methanol is a better inhibitor than glycols for hydrate dissociation. But, the molecular weight of methanol is lower than water, and it is therefore a large possibility that the methanol does not reach the plug. It can be blocked by e.g. a lighter condensate phase or accumulate at the upper part of the water phase under static conditions. It can also accumulate in the upper part of the water phase when water is released during hydrate melting. MEG can therefore be a better option at static hydrate plug conditions. Potassium format may also be a better option, as investigated in this master thesis.

3.4 Solubility of Salts in Water

It is well known that salts have high solubility in water at ambient temperatures. It is assumed that salts are homogeneous distributed in water. To investigate salts as thermodynamic inhibitors, the solubility of salts in water at different temperatures is first considered.

Pinho and Macedo (2005) investigated the solubility of the salts sodium chloride (NaCl), sodium bromide (NaBr) and potassium chloride (KCl) in water at different temperatures. The results can be seen in Figure 3.2, which show that the three salts have high solubility in water. From the figure, one can see that that the solubility of NaCl, NaBr and KCl is 26.483 wt%, 48.620 wt% and 26.476 wt%, respectively at temperature 298.15 K (25°C). NaCl is the salt investigated with the smallest increase in solubility with increased temperature. As a result, NaCl is not as dependent of temperature as the other salts investigated. There may therefore only be a small decrease in solubility as the temperature decreases through a petroleum producing pipeline. This is favourable due to avoidance of precipitation of salts in pipelines when used as hydrate inhibitor. If some salt precipitate; less salt is present in the water phase to inhibit hydrate formation, which again means that the equilibrium line for hydrate formation (as seen in Figure 2.8) is shifted to the right. Hydrates are more easily formed.



	100w		
T/K	NaCl	NaBr	KCl
		Water	
298.15	26.483	48.620	26.476
303.15	26.550	49.583	27.257
313.15	26.701	51.571	28.728
318.15		52.673	
323.15	26.889	53.838	30.094
328.15		54.015	
333.15	27.106	54.087	31.366
343.15	27.338	54.281	32.582
348.15	27.478	54.369	33.146
353.15	27.602	54.495	33.709

Figure 3.2 *Solubility of the salts NaCl, NaBr and KCl in water at different temperatures. (Pinho and Macedo, 2005)*

Even if NaCl is a well-known TI in the industry, the best known thermodynamic inhibitor on weight basis and also is cheap, it is not a recommended inhibitor. It can be explained for two characteristics. Firstly, most salts are corrosive and will corrode the metal in the well. Secondly, salts can cause scale in the well if other salts are present from the formation water. This may especially be illustrated by NaBr and KCl in the study of Pinho and Macedo (2005) if bromide or potassium ions are present from the formation water. The study shows that the solubility of these salts highly depend on the temperature. The salts will crystallize as the temperature decreases in the pipeline.

A less corrosive salt towards metals according to Fadnes et al. (1998) is potassium formate (HCOOK). Potassium formate has low viscosity (i.e. it is mixable with water according to Li et al. (2000)). The aqueous solubility of the salt is 32.8 g/100mL water at 0°C and 331 g/100mL water at 18°C (Weatherford, 2010). These values correspond to an aqueous solubility of about 25 wt% at 0°C, and 77% at 18°C. The variation shows that the salt is highly dependent on temperature. Despite the large solubility difference is the solubility at 0°C still large.

3.5 Calculation Example: Shifting Equilibrium Curve with Inhibitors

To investigate the amount inhibitor needed to prevent hydrate formation, some hydrate equilibrium calculations are done, i.e. shifting the equilibrium line of hydrates. Before doing the calculations, the equilibrium line in pure water is calculated. The correlation found by Safamirzaei (2016) is used, due to its small average relative deviation and few parameters needed. The correlation only includes three parameters; temperature, pressure and specific gravity of the gas. The average relative deviation is 0.46. The well-known Hammerschmidt correlation for hydrate formation includes the two parameters pressure and temperature and has an average relative deviation of 1.4. Other correlations use more parameters and does not necessarily decrease the average relative deviation (Safamirzaei, 2016). The correlation by Safamirzaei (2016) is therefore used, and found in Appendix A. The specific gravity for pure methane is used, due to its large content in natural gases. The approximate value for the specific gravity is 0.5537.

The correlations used to shift the equilibrium curves to the left are described by Kamath and Patil (1994). Their quadratic equations for NaCl, methanol and MEG are shown in Appendix A. The equations shift the temperature of the equilibrium based on weight percentage (wt%) inhibitor in the aqueous solution. It is important to notice that some inhibitor enters the oil and gas phases as well, and it should therefore be considered when calculating the amount inhibitor needed to prevent or dissociate hydrates. This is especially the case for methanol, which is highly volatile and easily enters the gas phase. Two results are that methanol is mostly used in oil systems (with little gas) and extra methanol needs to be added to the water phase to ensure protection against hydrates. Glycols and salts can be used in both oil and gas systems (Larsen, 2016).

The main results from the calculations are shown in Figure 3.3. To compare the results from one inhibitor alone at different weight percentages, or all three inhibitors at one weight percentage, see Appendix A. The results show that NaCl is the best inhibitor on weight basis. The correlation by Kamath and Patil (1994) state that a 25 wt% inhibitor in the water phase gives temperature changes of approximately 23°C, 13.7°C and 7.1°C for NaCl, MeOH and MEG respectively. The figure is shown in Appendix A.

NaCl has the most particles dissolved in water per weight basis of the three inhibitors investigated. The calculations are showed in Appendix A. NaCl therefore has the lowest freezing point due to the colligative properties. It is also seen from Figure 3.3 that the equilibrium curves of NaCl are shifted more compared to MeOH and MEG at the same weight percentage inhibitor in the water phase. Larger alcohols and glycols have larger molecular chains and molecular weight, which corresponds with lower amounts of moles per mass. Larger alcohols and glycols will therefore have a poorer performance on weight basis as inhibitors. It is also important to notice that the inhibition mechanism for salts is different from alcohols and glycols, which may influence the amount inhibitor needed for the equilibrium line shift. In addition to dipole bonding with water, salts also reduce the solubility of the essential hydrocarbons in water (Sloan and Koh, 2008). It is therefore believed that salts have a more effective inhibition mechanism per molecule compared to alcohols and glycols.

Even if NaCl is the best inhibitor on weight basis, NaCl has a limited solubility in water of approximately 26 wt% before the salt crystallizes. Alcohols and glycols have larger

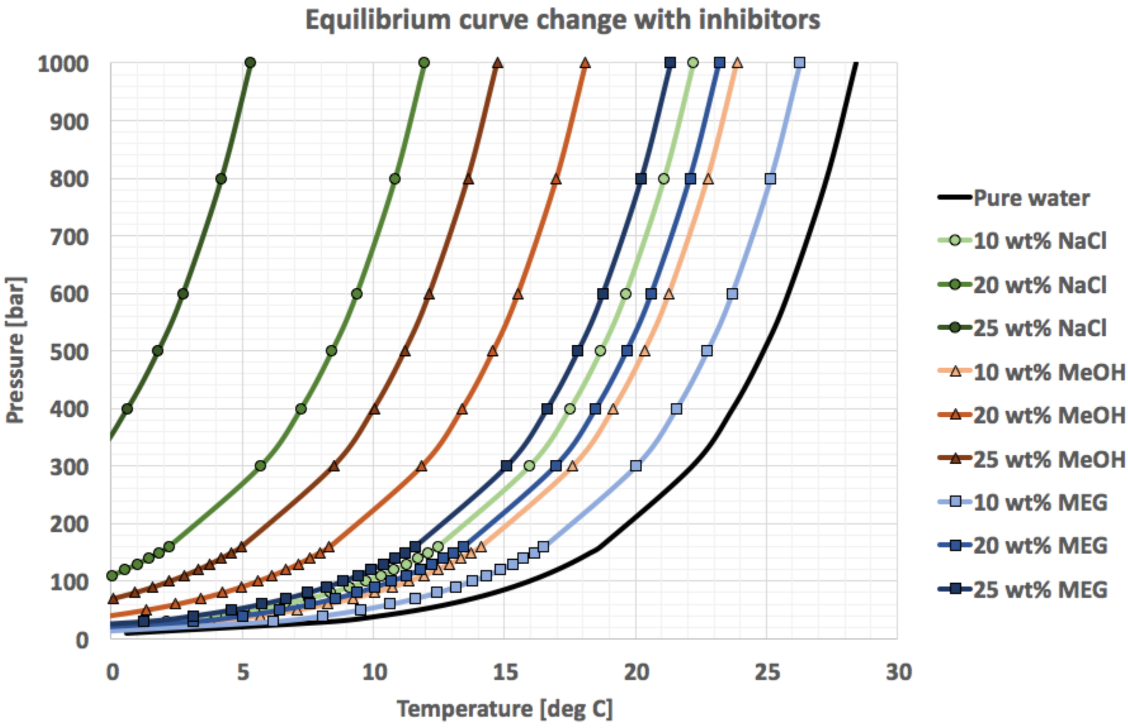


Figure 3.3 *Equilibrium curve change when inhibitors are used at different concentrations.*

solubility in the water phase. Larger amounts of MeOH and MEG can therefore be used to inhibit hydrate formation. Calculations showed e.g. that a 40 wt% MeOH solution will change the temperature by 25.6°C, which is larger than the maximum inhibition by NaCl. The writer has not succeeded in finding correlations in the literature about how much the equilibrium curve of potassium formate shifts when the salt is added to water. Some calculations are done to investigate the inhibition efficiency of potassium formate in Section 3.6.3.

During the discussion, it is important to keep in mind that alcohols and glycols may not always mix homogeneously with water, as first expected. The alcohols and glycols can therefore be useless in some cases. An example is when methanol is used to dissociate a deep hydrate plug in a condensate well, as previously discussed. These results from Li et al. (2000) correspond with the correlation from Kamath and Patil (1994); methanol shifts the equilibrium line more towards lower temperatures than MEG on weight basis.

3.6 Characteristics of Potassium Formate

Potassium formate has many favourable properties for hydrate inhibition in the oil and gas industry. Some of the properties are mentioned earlier in the thesis and will be explained more during this paragraph.

3.6.1 Fluid Parameters: Solubility, Viscosity and Density

Potassium formate is well known to have a high solubility in water at different temperatures. According to Weatherford (2010), the solubility is 33 g /100 mL at 0°C, and 331 g / 100 mL at 18°C. These values are used to estimate the solubility of HCOOK at different temperatures. The figure is shown in Appendix A. An average temperature at the bottom of a shut-in riser is 4°C, which corresponds with a solubility of 120 g / 100 mL, or 55 wt%, from the figure. Despite the large temperature change with temperature, the solubility at 4°C is large. One other notice is that a 55 wt% potassium formate brine has water crystallization temperature around -60°C. It is seen from Figure 3.4 and 3.6 combined.

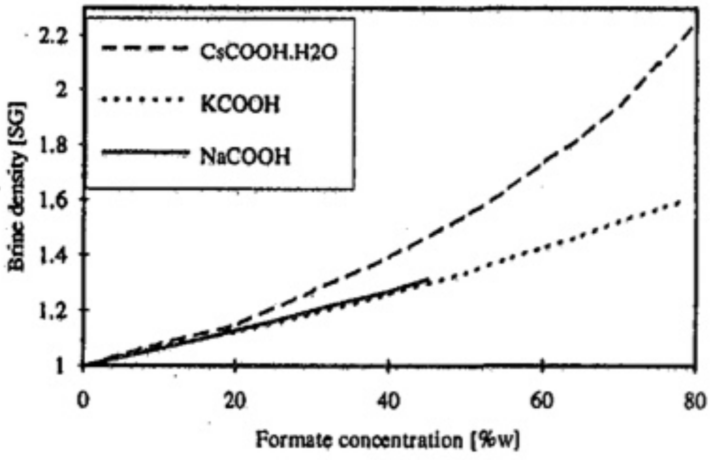


Figure 3.4 *Density vs. concentration (wt%) of sodium, potassium, and caesium formate brines at 20°C (Howard, 1995).*

According to Howard (1995) potassium formate has a high solubility in water, which can give a maximum brine density of about 1.59 SG. Laboratory experiments performed by the writer with pycnometers show that a 3 % NaCl solution (i.e. brine) has a density of about 1.019 SG at 22°C. The density can therefore be increased considerable in comparison with a 3 % NaCl brine. The correlation between three formate concentrations (wt%) and brine density (SG) is shown in Figure 3.4. The figure is made by Howard (1995).

The publication by Howard (1995) also described the relationship between viscosity and density for the same formate brines, as shown in Figure 3.5. The figure shows that the viscosity of potassium formate with a density below approximately 1.4 SG is relatively low for both 25°C and 60°C. The viscosities are below 3 cP for both temperatures. According to Li et al. (2000), the viscosity at 25°C is 0.539 cP and 17.647 cP for the conventional hydrate inhibitors methanol and MEG respectively. Lower viscosity liquids easier mix than higher viscosity liquids. The low viscosity of potassium formate and water is therefore favourable for mixing of the liquids.

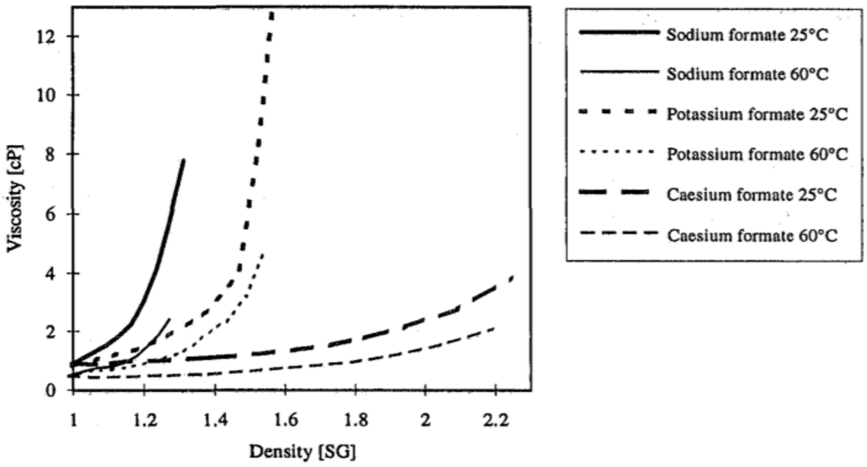


Figure 3.5 *Viscosity of different formate brines as function of brine density (Howard, 1995).*

3.6.2 Water Crystallization Temperatures with Different Salts

Figure 3.6 shows crystallisation temperatures of water when different salts are present. The figure is made by Howard (1995). Atmospheric pressure is assumed, as no pressure is given. A lower freezing temperature (i.e. water crystallization temperature) is shown for all the salts and can be explained through the colligative properties of the freezing point of water for low brine concentrations (Pedersen, 2014). It is e.g. seen that sodium chloride has a lower freezing temperature compared to potassium formate for the same brine density, as potassium formate has a higher molecular weight than sodium chloride.

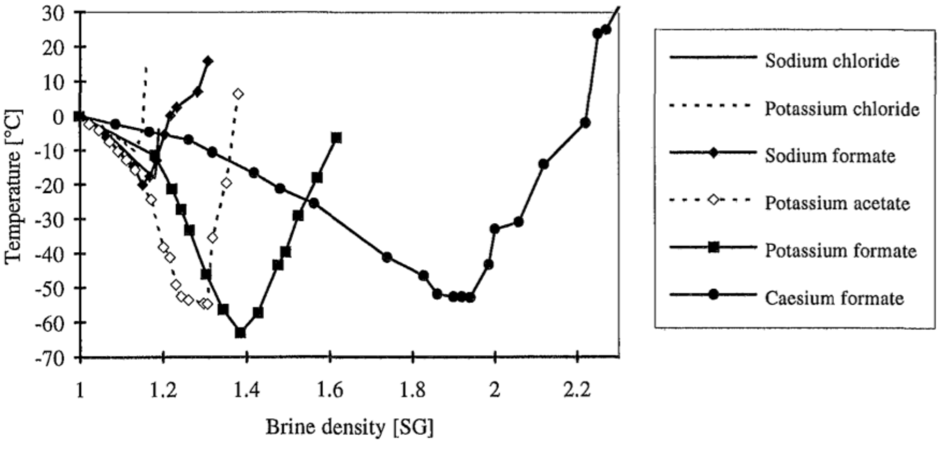


Figure 3.6 *Water crystallisation temperatures of different brines as function of density (Howard, 1995).*

Potassium formate will therefore have a lower number of particles in the solution at the same density, and then a higher crystallization temperature.

A 55 wt% HCOOK has a density of 1.4 SG (from Figure 3.4), which corresponds with a freezing temperature of water decreased to about -60°C (Figure 3.6). This decreased freezing temperature compares well with methanol and glycols in accordance to Fadnes et al. (1998). The freezing temperature of potassium formate decreases considerably with increased density until a density of 1.4 sg or a concentration of 55 wt% is reached. This concentration gives the lowest water crystallization temperature. More salt in the solution will increase the water crystallization temperature (Atkinson, 1998, Downs, 1993, Howard, 1995). It is not explained why the crystallization temperature increases with higher brine concentration. This trend is seen for all the salts in Figure 3.6. The writer has not found any explanation for this result, but has two notices. The first notice is that the viscosity of the potassium formate brine increases suddenly from about 1.4 sg. This is the same point where the water crystallisation temperature trend changes. The same trends are found for the sodium formate brine at approximately 1.2 sg in Figure 3.5 and Figure 3.6. The second notice is that a large amount of salt is present in the water phase when crystallization temperatures increase.

3.6.3 Gas Hydrate Inhibition with Potassium Formate

The writer has not succeeded in finding correlations in the literature about how much the equilibrium curve of potassium formate hydrates shifts when the salt is added to water. But Fadnes et al. (1998) reported that there is a correlation between freezing point depression and level of hydrate inhibition by the conventional TIs. The salt sodium chloride has a known equation for lowering the gas hydrate formation temperature in addition with known water crystallisation temperatures at different concentrations of the salt. A study of the salt sodium chloride is therefore done to investigate the correlation between water crystallization temperature decrease and hydrate formation temperature decrease when the salt is present.

From Figure 3.7 one can see that a sodium chloride brine density of 1.15 kg/L corresponds with 15°C decrease in water crystallization temperature. The corresponding concentration between 0°C and 20°C is approximately 20 wt% (Simion et al., 2015). The

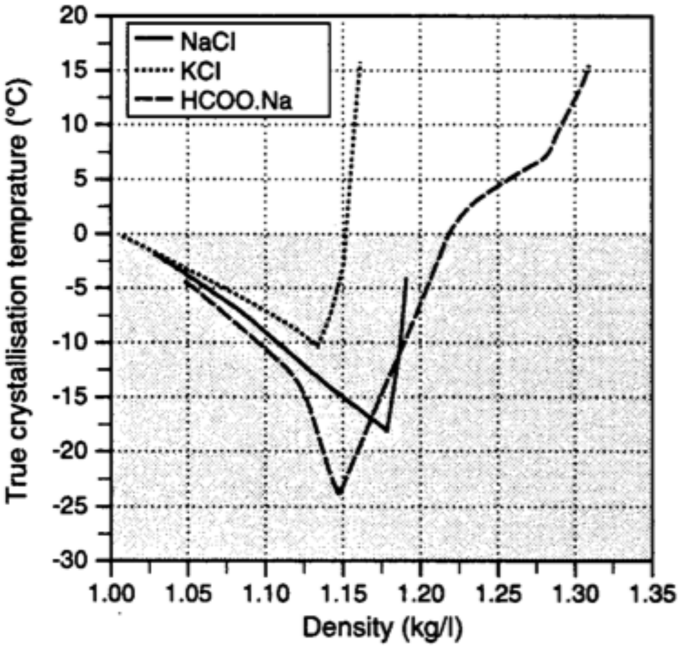


***Figure 3.7** Water crystallisation temperature as function of density for sodium chloride, potassium chloride and sodium formate (Downs, 1993).*

temperature between 0°C and 20°C is chosen because hydrates are often created within this temperature range. For hydrate inhibition with NaCl, the equation for shifting the hydrate equilibrium curve is given in Appendix A. It states that a 20 wt% NaCl solution will decrease the hydrate formation temperature with 16.48°C. The percentage difference between these two temperatures is 9.9 %. One other calculation example;1.10 kg/L sodium chloride brine corresponds with 9.2°C decrease in water crystallization temperature (from Figure 3.7). The corresponding concentration between 0°C and 20°C is approximately 13.5 wt% (Simion et al., 2015). The equation for shifting the hydrate equilibrium curve, given in Appendix A, gives a temperature decrease of 9.49°C with 13.5 wt% NaCl in the brine (Kamath and Patil, 1994). The percentage difference between these two temperatures is 3.1 %.

Readings from the graph in Figure 3.7 or estimating concentrations values from the paper by Simion et al. (2015) may be sources of errors. The equation for shifting the equilibrium curve may also have some errors. The two results have a small difference, and it is reasonable to assume that a decreased water crystallisation temperature by a salt will decrease the hydrate formation temperature with the same temperature including an error. Figure 3.6 can therefore be used as a first approximation to estimate the amount potassium formate needed to inhibit gas hydrates.

The result is compared with the equilibrium curve shifts in section 3.5, shown in Figure 3.8. It is assumed that a 30 wt% potassium formate solution shifts the equilibrium curve with 16.5°C, as it is the decrease in water crystallization temperature with the brine. It is found from Figure 3.4 and 3.6 that a 1.2 sg potassium formate brine corresponds with 30 wt% salt and a water crystallization temperature decrease of approximately 16.5°C. NaCl is not included in the result since the weight percentage investigated is larger than the maximum solubility of NaCl in water. The result shows that methanol shifts the equilibrium curve 1°C more than HCOOK with 30 wt% inhibitor in the water phase. HCOOK may therefore be comparable with methanol as an inhibitor on a weight basis. As methanol is highly volatile, a larger amount of methanol may be needed for hydrate inhibition compared with HCOOK.

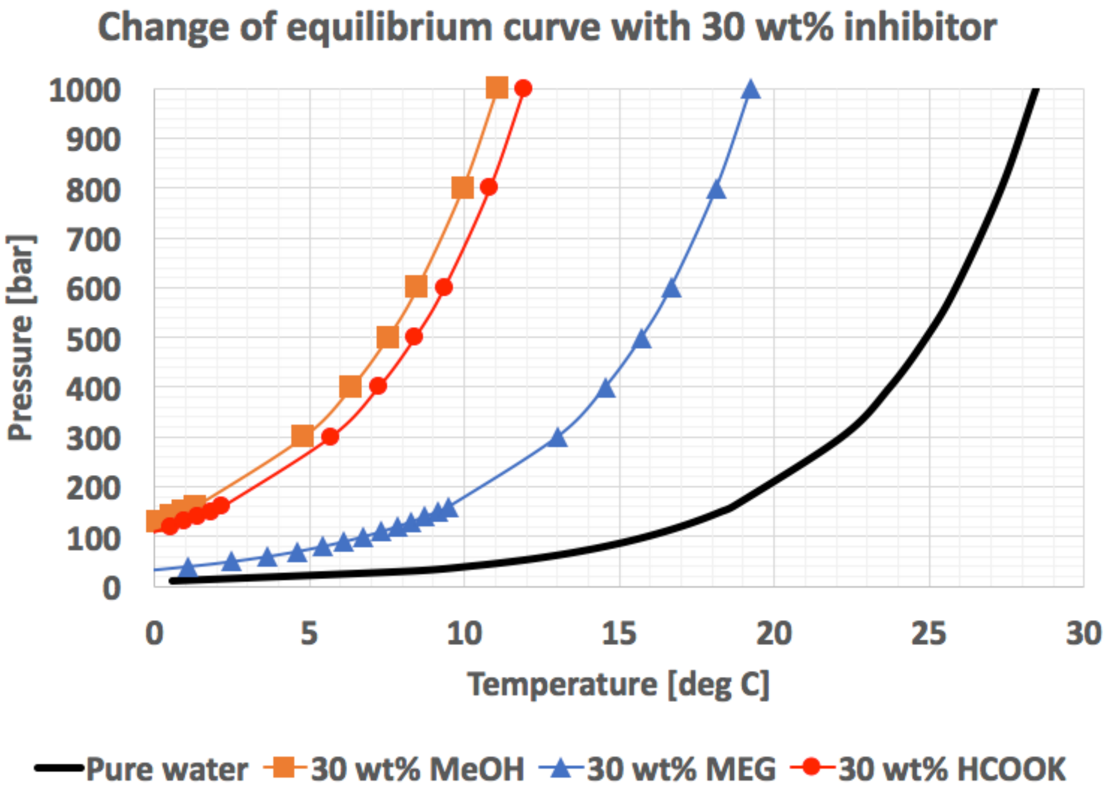


Figure 3.8 *Change of equilibrium curve with methanol, MEG and potassium formate (30 wt% inhibitor in the water phase).*

3.6.4 Volatility

Regarding mixing of HCOOK with hydrocarbons; the solubility of HCOOK in hydrocarbons is very low and the salt solution is considered non-volatile. The opposite is found for methanol and glycols, especially methanol, which will get significant losses to the gaseous and/or liquid hydrocarbon phases when used as hydrate inhibitor. Larger amount inhibitor is needed to get the required inhibitor mass in the water phase for hydrate prevention. Contamination of the hydrocarbon phases is therefore less with potassium formate as inhibitor. The income of the sales product may be affected (Fadnes et al., 1998).

The solubility of hydrocarbons and hazardous organics also is very low in aqueous HCOOK solutions (Fadnes et al., 1998).

3.6.5 Corrosivity and Scale Problems

According to Fadnes et al. (1998) potassium formate exhibits low corrosivity towards metals at alkaline pH (preferably above pH of 10). The solution can be buffered with potassium carbonate if acid gases are present, as potassium carbonate is known to create a strongly alkaline solution. The carbonate ion (CO_3^{2-}) has two protolysis stages and may react with two acid ions to neutralize the solution. The results are in accordance with Howard (1995); the formats' pH is easily adjusted, which again probably cause fewer corrosion problems.

Scaling is normally not an issue with potassium formate in brines or drilling fluids. The opposite effect can occur; potassium formate is seen as a sulphate scale dissolver at high concentrations. But the scale dissolving activities can contaminate the fluid with ions, insoluble solids and radioactive isotopes from the scale. If the contaminated particles accumulate, corrosion problems may occur (Fadnes et al., 1998).

3.6.6 pH

When HCOOK dissolves in water, K^+ and $HCOO^-$ ions are created. Some of the $HCOO^-$ ions react with water molecules, H_2O, and crate HCOOH and OH^- ions until an equilibrium has occurred. An alkaline solution is created due to the OH^- ions. The equilibriums and equations are shown in Appendix A. Calculations from Appendix A state that a 35 wt% potassium formate brine has a pH of 9.56, while a 55 wt% potassium formate has a pH of 9.66. Higher pH corresponds with higher concentration of salt in water. The high pH is preferable to avoid corrosion and may be preferable for scale dissolving.

3.6.7 HSE Aspects

The HSE aspects for potassium formate are favourable compared with the traditional hydrate inhibitors methanol and glycols. Large amounts of environmental testing are performed on formate brines due to their applicability as drilling fluids. The results show that potassium formate is non-toxic. This is related to mammalian toxicity, eco-toxicity (aquatic toxicity) and biodegradability. Mammalian toxicity test results show that potassium formate has a comparable oral toxicity with sodium chloride (Howard, 1995). It can be compared through LD_{50} values. LD_{50} is the lowest dosage where half the population tested are killed. The oral toxicity LD_{50} values when tested on mice are 4000 mg/kg for sodium chloride, 5500 mg/kg for potassium formate, and 7300 mg/kg for methanol. This means that potassium formate has a higher oral “poisoning potential” compared to methanol, and less compared to sodium chloride (Syndel-Laboratories-Ltd., 2008, Sciencelab.com, 2005b, National-Oilwell-Varco, 2010).

Downs (1993) reported a test of the aerobic biodegradability of potassium. Figure 3.9 shows the result. The test showed that potassium formate is readily biodegradable since over 70% of the potassium formate was biodegraded within 28 days. Howard (1995) also concluded that potassium formate is readily biodegradable in dilute solutions. The high biodegradation of HCOOK is favourable if a leakage in a production system is present, since the brine solution will be diluted when it gets in contact with either sea water or ground water.

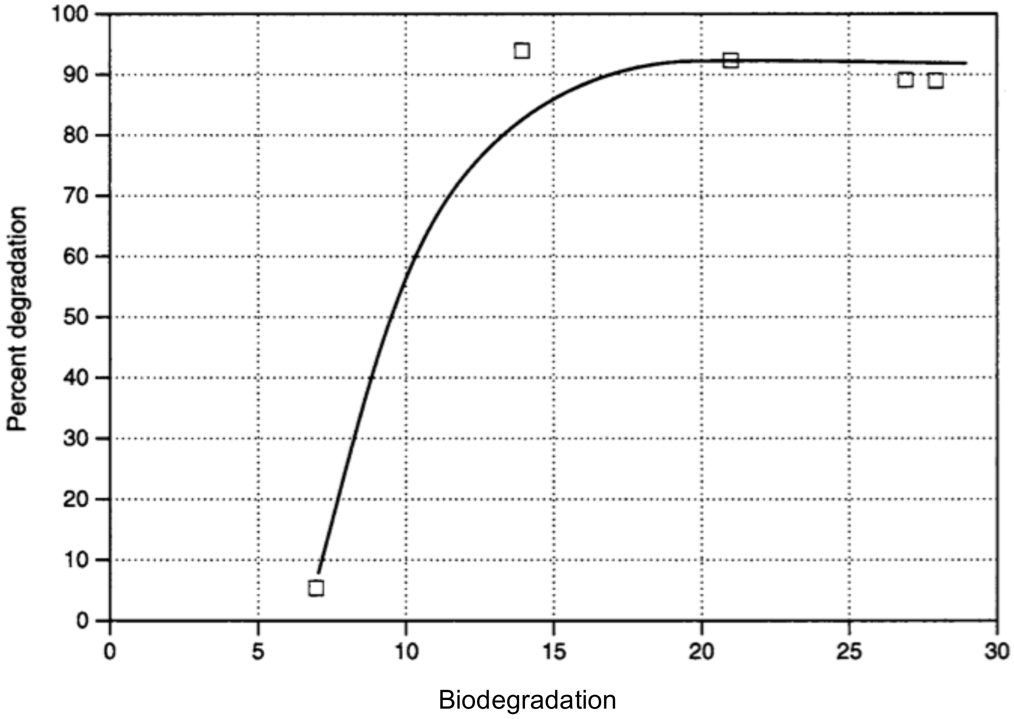


Figure 3.9 *Percent degradation of HCOOK vs. number of days. The initial HCOOK concentration was 30.4 mg/L (Downs, 1993).*

Material Safety Data Sheets (MSDSs) for methanol, MEG and HCOOK have been compared. The MSDSs show that methanol and glycols are associated with larger hazards than HCOOK. Some of the results are summarized in Table 3.1. It can be seen from the table that both skin and eye irritation are worse for the conventional hydrate inhibitor compared to HCOOK. Inhalation of methanol, which is volatile, may have a major hazardous effect. It can cause e.g. headaches, loss of consciousness, permanent visual disturbances and death. The inhalation effect may therefore be of large interest. Fatal consequences can be present if MEG is swallowed. It can cause e.g. nausea, vomiting and diarrhoea.

The flash point (i.e. the lowest temperature where the vapour of a volatile material will ignite if an ignition source is present) is lower for methanol and MEG compared to 75 wt% potassium formate brine, according to the MSDSs. Lower flash point is considered as more hazardous.

Table 3.1 *Some HSE properties for methanol, MEG and HCOOK.*

Property\Inhibitor	Methanol	MEG	HCOOK
Oral LD_{50} (mouse)	7300 mg/kg	5500 mg/kg	5500 mg/kg
Eye irritation	Mild to moderate	Irritating	Slight irritation
Skin irritation	Moderate	Slight irritation	Mild
Flash point	11°C	111°C	Solid: > 100°C 75 wt% brine: > 190°C
Other notices	Should not be inhaled.	Should not be swallowed.	

Potassium formate is also classified as non-flammable, in addition with non-hazardous for transport and handling purposes. According to Fadnes et al. (1998) methanol and glycols are classified as more hazardous. Methanol is considered with high fire hazard, and therefore has strict handling and storage regulations. If a methanol fire is present, water can be used to cool the methanol container, but should not be used to put out the fire. Water has a higher density compared with methanol, and may disperse the fire and cause more damage.

Regarding storage of the inhibitors, HCOOK can be interpreted to have lower handling and storage considerations from the MSDSs. Methanol storage tanks e.g. need vapour emission control and have to be designed to avoid ignition. Corrosion of the metal in a storage tank must also be considered. For MEG, the storage tanks should be kept tightly closed, cool, well-ventilated and away from sparks and open flames. Avoidance of dust and aerosol breathing from the salt must be considered when handling potassium formate as solid, but is not an issue if handled as a brine. Potassium formate containers do not need vapour control system and systems to avoid ignition. The solid salt can be stored in a closed, dry and ventilated container (OXEA-Corporation, 2015, Sciencelab.com, 2005a, Methanex-Corporation, 2005, National-Oilwell-Varco, 2010, Perstorp-AB, 2015, Petrochem-Carless-Limited, 2008, Sciencelab.com, 2005b, Syndel-Laboratories-Ltd., 2008, Chiron-AS, 2003).

It can be concluded that potassium formate is a relatively benign chemical with better HSE properties than the conventional thermodynamic gas hydrate inhibitors methanol and glycols. The handling and storage aspects are favourable for potassium formate, the salt has a lower skin and eye irritation compared with methanol and MEG, higher flash point compared to methanol, in addition to high biodegradability. These aspects are not easily measured in the economics when a hydrate inhibitor for a petroleum field should be determined, but are regardless important factors.

3.6.8 Re-use and Efficiency of Inhibitor Recovery

The efficiency of inhibitor recovery depends on mainly two processes. First, the inhibitor losses to the liquid and gaseous hydrocarbon phases are of large matter. Potassium formate has low solubility in both hydrocarbon phases. The losses to those phases are therefore minimal. The conventional hydrate inhibitors have substantial losses to the hydrocarbon phases. Second, the efficiency of the inhibitor recovery process influences the recovery rate and economics. The process is in theory simple; the separated aqueous phase is dehydrated with a vacuum evaporation unit. The recovery factor can be up to 95%. The recovery processes for methanol and MEG are more sophisticated, with e.g. distillation column and condenser units. Calculations also show that a HCOOK recovery unit has half the weight of a methanol recovery unit with the same capacity. In other words, there will be more spare space on a platform with potassium formate as inhibitor compared to methanol and MEG (Fadnes et al., 1998).

A disadvantage with the proposed HCOOK recovery process is contamination of the salt. Accumulation of contaminating salts may occur when evaporation is used to remove the water. The fluid corrosivity may increase. A solution can be to use HCOOK as a hydrate inhibitor in pipelines with low salinity (Fadnes et al., 1998).

3.6.9 Economical Aspects

It has been illustrated that potassium formate can be effectively used as a hydrate inhibitor. Pursuant to Fadnes et al. (1998), these six factors are vital for the cost of hydrate inhibitors:

- Dosing rate of inhibitor
- Unit cost of inhibitor
- Inhibitor recovery efficiency
- Used inhibitor regeneration costs
- Environmental and engineering costs associated with use, storage and handling of the inhibitor
- Reduced value of hydrocarbon stream due to contamination with the inhibitor.

Estimations on the economics reported by Fadnes et al. (1998) show that HCOOK is a comparable hydrate inhibitor at Troll Oseberg Gas Injection system in a case study. The case study considered continuously hydrate inhibitor injection. The high recovery factor of 95% was favourable for HCOOK. Another case study from the same report; the condensate system of Oseberg Gamma Nord used inhibitor only when wells were shut-down. No hydrate re-generation process was used. The results showed that it was economically favourable to use methanol as the gas hydrate inhibitor. As described under “Re-use and efficiency of inhibitor recovery”, the recovery process of potassium formate is easily done. The results may be different with hydrate re-generation system. Another notice from the Oseberg Gamma Nord system is the mixing abilities of methanol, as reported by Li et al. (2000). They found that methanol does not mix homogeneously with a water column. Methanol has a lower density compared to water. If a condensate phase is present, as it is in this case study, there may be larger mixing problems, especially if the methanol is mixed into the well topside.

Some calculations are done to investigate the amount potassium formate needed to inhibit hydrate formation in a petroleum flow. It is assumed that the same amount potassium formate is needed for hydrate inhibition as for decreasing the water crystallization temperature, as previously described. The amount salt to inhibit the whole water phase is also considered. It was found from Figure 3.4 and 3.6 that a 1.2 sg potassium formate brine corresponds with 30 wt% salt and a water crystallization temperature decrease of approximately 16.5°C. 30 wt% potassium formate in the water phase is used as a basis for the calculations. The first calculation done considers the amount salt needed in a riser (e.g. when the well is shut-in). If the riser is 200 m high with an inner diameter of 12 inches, it will contain a volume of 14.6 m^3. The worst case scenario is if the whole riser is filled with water, as the salt is soluble in water and gives little contamination to the hydrocarbon phases. In that case, an amount of approximately 9700 kg of 75 wt% potassium formate brine is needed to reach 30 wt% potassium formate in the riser. With a density of 1570 kg/m^3 at 20°C does 9700 kg HCOOK brine correspond with a volume of 6.2 m^3 (Perstorp-AB, 2015). If only half of the riser volume is water, the mass of potassium formate is halved to approximately 4850 kg or 3.1 m^3 of 75 wt% potassium formate brine. The fact that there is no spare space for the added brine is not considered in the example.

The calculations show that the mass added potassium formate brine to original formation water is 0.67, as 670 kg of 75 wt% potassium formate brine is needed in 1000 kg formation water to reach a total potassium formate concentration of 30 wt%. The volume potassium formate brine to original formation water is 0.43, as 0.43 m^3 of 75 wt% potassium formate brine is needed in 1 m^3 formation water to reach a total potassium formate concentration of 30 wt%. It is a large amount of inhibitor. The reason for using 75 wt% potassium formate is that it is more realistic to buy and store the salt as a brine solution. The reason for choosing a 200 m riser is that this is a normal water height in the North Sea. The sea depth of Gullfaks field is e.g. between 130 and 220 m (Norwegian-Petroleum-Directorate, 2017b). The water depth of the Ekofisk field in the North Sea is between 70 and 75 meters, which would decrease the amount inhibitor needed in a shut-in riser substantially (Norwegian-Petroleum-Directorate, 2017a).

Another example is from the Gullfaks field. The field's water production was approximately 16.5 MSm^3 (≈ 16.5 M-metric-tonne) in 2016 (Norwegian-Petroleum-Directorate, 2017b). With 30 wt% potassium formate in the water phase, approximately 7 Mm^3 or 11 M-metric-tonne of 75 wt% potassium formate is needed each year to reach the required concentration if no recirculation system is present. Re-use of the thermodynamic inhibitor would decrease the amount new inhibitor needed substantially with its 95% recovery. Gullfaks is also an oil field at its tale production, which means that the water production is large. A newer case example is the Snøhvit field in the Barents Sea. It started the production in 2007, and is still producing at its plateau in 2017. It is a gas/condensate field that produced over 8 M o.e. Sm^3 in 2016. The water production started in 2015, and increased to 0.0225 M Sm^3 in 2016 (Norwegian-Petroleum-Directorate, 2017c). The low water production results in a lower inhibitor amount needed. 0.00955 M m^3 or 15 Mkg of 75 wt% potassium formate brine must be added to the system each year to get a total of 30 wt% inhibitor in the production system (if the water production remains constant).

The calculations have shown that large masses of inhibitor are needed to decrease the water crystallization temperature (and then also the hydrate crystallization temperature). HCOOK has a high density, which makes it the most efficient thermodynamic inhibitor on volumetric basis. The storage volume needed for the salt should therefore be less than for the other conventional hydrate inhibitors. Transport costs is less for HCOOK as well, but probably not vital (Fadnes et al., 1998).

A unit cost of a 75 wt% potassium formate brine is EUR 900 per metric tonne. The information is given in an email May 17th 2017 by Git Malmros, Product Manager Formates & Sulfates at Perstorp AB. A quick google search was used to find comparable methanol prices. It showed that a methanol solution has half the price as the potassium formate brine. As there is a large price difference and uncertain how much HCOOK that is inhibitor needed to shift the equilibrium curve for hydrate formation, it should be investigated more or other aspects should be vital to use potassium formate as inhibitor in a well. One aspect can be a shut-in well, where potassium formate may be a much better hydrate inhibitor.

The engineering costs associated with HCOOK is probably lower than for methanol and MEG due to the simple recovery process. HCOOK also has low contamination of the hydrocarbon phase, and will hence not reduce the value of the hydrocarbon stream substantial. Potassium formate is a more favourable inhibitor than ethylene glycol on an environmental perspective; both are readily biodegradable, but the oxygen demand for HCOOK is ten times lower, and hazardous volatile aromatic (BTX) compounds' solubility is higher in ethylene glycols than formates. Formates are also more desirable than conventional hydrate inhibitors on an overall HSE perspective. These properties are not easily measured economically, but are still important in the process of choosing the best hydrate inhibitor (Fadnes et al., 1998).

Chapter 4

Method

Laboratory experiments were done to investigate the dispersion of the salts sodium chloride and potassium formate in a plastic pipe. The purpose was to simulate a riser or a shut-in well. The pipe was originally filled with distilled water and a salt solution was poured into the pipe from the top. An orange background and a blue colouring powder in the brine were used to easier see the mixing of the salt solutions in the pipe. The vertical plastic pipe used was 2 m high with an inner diameter of 0.19 m. It is shown to the left in Figure 4.1. The dimensions give a total volume of approximately 56 L.

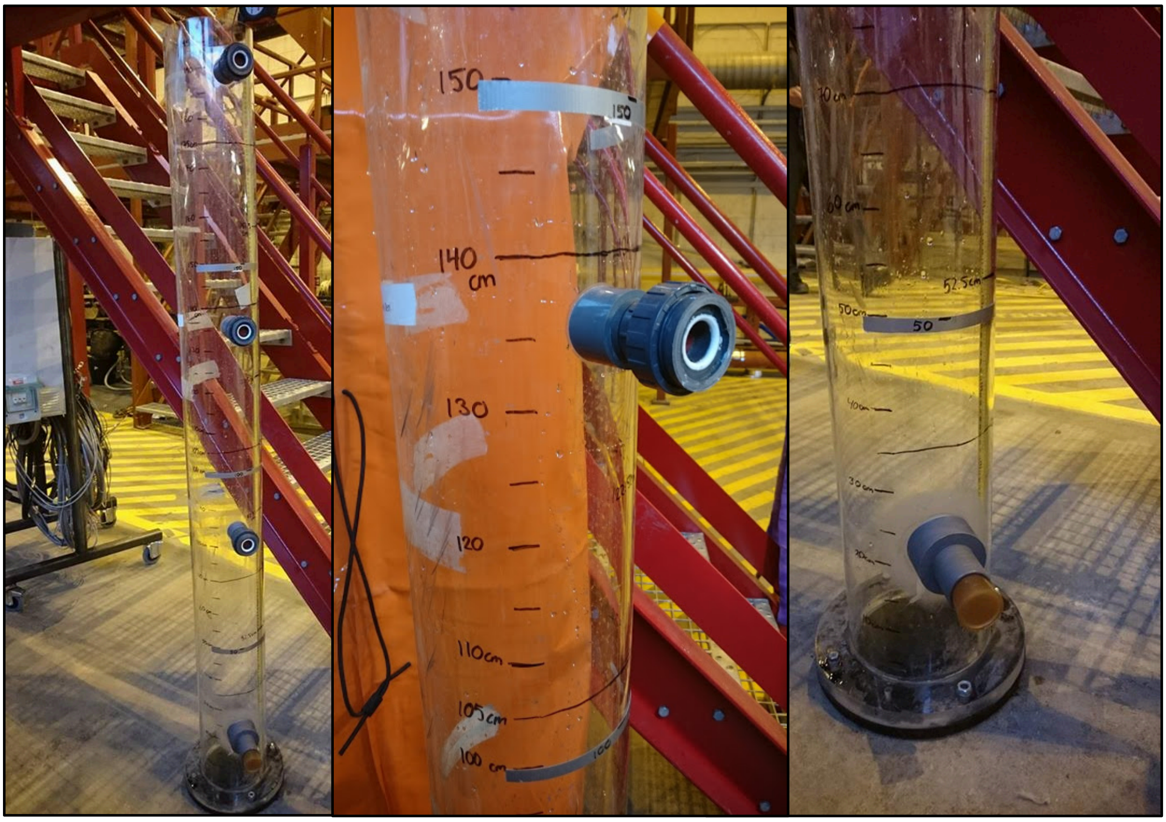


Figure 4.1 *Experimental setup of the 2 m vertical plastic pipe to the left. Detailed photos in the middle and to the right.*

The pipe was sealed at the bottom, as seen in Figure 4.1 to the right. Volume and height from the bottom was marked on the plastic. It also consisted of four rubber sealed openings, as seen at different heights to the left Figure 4.1. The heights from the bottom were 20 cm, 85 cm, 135 cm and 190 cm. A thick, long needle was punctured through the rubber to take brine samples at the different heights. It was important to use long needles to reach the inner part of the pipe. A rubber sealed opening with a pinpoint is shown in Figure 4.2.

To prepare the experiments, the pipe was filled with distilled water to a predetermined height (i.e. volume and mass). A less dense oil column could also be added above the distilled water to simulate a condensate column in the shut-in well. The condensate phase was not used in the experiments due to practical reasons. It would require more HSE considerations, as e.g. a separation unit, as the salt water was poured to a drain between the experiments. The salt solutions would most likely penetrate a condensate column due to higher density of the brines and low solubility in hydrocarbons.

A predetermined concentration of distilled water and salt were mixed in a bucket with the colouring powder “Methyl Blue”. The scale used to measure the salt and water had an accuracy of 2 g. A magnet stirrer was used to properly dissolve the salt and mix the solution. The different amounts of salt and water are found in Table 4.1 and Table 4.2. The base case used was 50 L distilled water in the pipe and 5 kg brines poured into the pipe. When the salt was completely dissolved and mixed in the water in the bucket, the

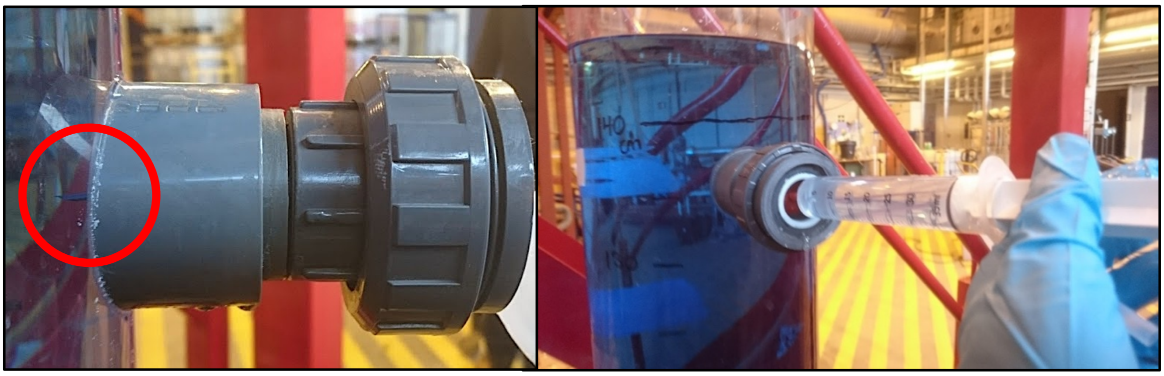


Figure 4.2 *Detailed pictures of a rubber sealed opening and sample taking. The red circle marks the pinpoint.*

brine in the bucket was poured into the pipe from the top. It could be done in two ways; with turbulence or without as much turbulence as possible (referred to as laminar). If turbulence should be present; the solution was poured directly into the pipe from the bucket. If turbulence should not be present; the solution was poured into a plastic bag before entering the pipe. The plastic bag was removed slowly to add the salt solution at the top of the pipe without influencing the mixing of the solutions.

When the brine solution was poured into the pipe, water samples were taken with the needles at the different heights at different times. The time intervals depended on brine concentrations and hence stabilization time. To be consistent, the samples were always taken first from the top and downwards in the pipe.

Pycnometers, a funnel, a thermometer and a precise scale were used to measure the densities of the samples. It is shown in Figure 4.3. The pycnometers were made of glass and had a precise volume engraved into it. The volumes were approximately 50 mL with 3 decimals after the dot. The scale used was also very precise, measuring the weight in gram, also with 3 decimals behind the dot. It had an accuracy of 0.001 g during the whole range. The measurements of the densities were therefore very precise.

The theory behind a pycnometer is simple; the mass of the pycnometer with and without liquid in addition to the volume of the pycnometer are used to calculate the density of the liquid. The density of the liquid is the mass of the liquid divided by the volume of the same liquid. The temperature was measured because density is temperature dependent. The volume and mass of the empty, dry pycnometer were read from the pycnometer and

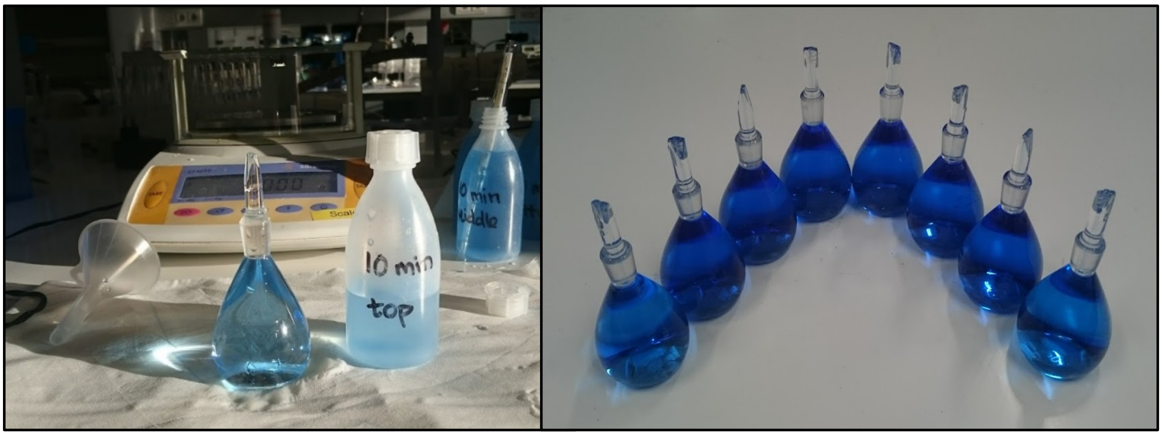


Figure 4.3 Left: funnel, brine filled pycnometer, brine sample with the scale used in the background. Right:8 brine filled pycnometers.

the scale. It was important to measure the weight of the pycnometer with the lid, as the lid ensured the correct volume in the pycnometer. A funnel was used to pour the brine water sample into the pycnometer. The lid was put on. It was important to make sure that some of the brine solution was floating out of the top of the lid to be sure that the lid was filled with liquid. Paper was used to dry excess water from the outer part of the pycnometer before the scale was used to measure the mass of the pycnometer with the liquid. The mass of the liquid is equal the mass of the liquid filled pycnometer minus the mass of the air filled pycnometer. The volume of the liquid is the volume engraved on the pycnometer. The density of the liquid is the mass of the liquid divide on the volume of the liquid. The densities of all the samples were calculated and plotted with respect to height in the pipe and time.

Table 4.1 *Experimental information with NaCl as the inhibitor. Experiment number is the order the experiments were executed.*

Experiment number	Mass H_2O originally in pipe [kg]	Mass brine in bucket [kg]	NaCl brine concentration in bucket [wt%]	Laminar (L) or turbulent (T) mixing
1	45	5	20	T
2	35	7.5	20	L
3	50	5	10	L
4	50	5	10	T
5	50	5	20	L
6	50	5	18	T
7	50	5	17	T
8	50	5	18	T
9	50	5	19	T
10	50	5	26	T
11	50	5	20	T
12	50	5	10	T
13	50	5	26	L
14	35	5	20	L
15	35	5	20	T

Table 4.2 *Experimental information with HCOOK as the inhibitor. Experiment number is the order the experiments were executed*

Experiment number	**Mass H_2O originally in pipe [kg]**	**Mass brine in bucket [kg]**	**HCOOK brine concentration in bucket [wt%]**	**Laminar (L) or turbulent (T) mixing**
1	50	5	10	L
2	50	5	10	T
3	50	5	20	L
4	50	5	20	T
5	50	5	55	T
6	50	5	75	T
7	50	5	10	T
8	50	5	25	T
9	50	5	55	L
10	50	5	75	L
11	50	2.5	55	T
12	50	7.5	55	T
13	35	5	20	L
14	35	5	20	T

Chapter 5

Results and Discussions

Figure 5.1 and 5.2 show mixing of a 55 wt% potassium formate brine in the plastic pipe for the first 20 seconds. The pipe was originally filled with 50 L distilled water. 5 kg, or 3.67 L, of 55 wt% potassium formate brine was poured turbulent into the pipe. The blue colouring agent illustrated how fast the heavy brine solution penetrated the distilled water. The bucket used for the brine is seen in the upper part in some of the photos.

There are done 29 experiments and over 600 pycnometer measurements to investigate the distribution of the salts NaCl and HCOOK in the plastic pipe. Not all the results are given

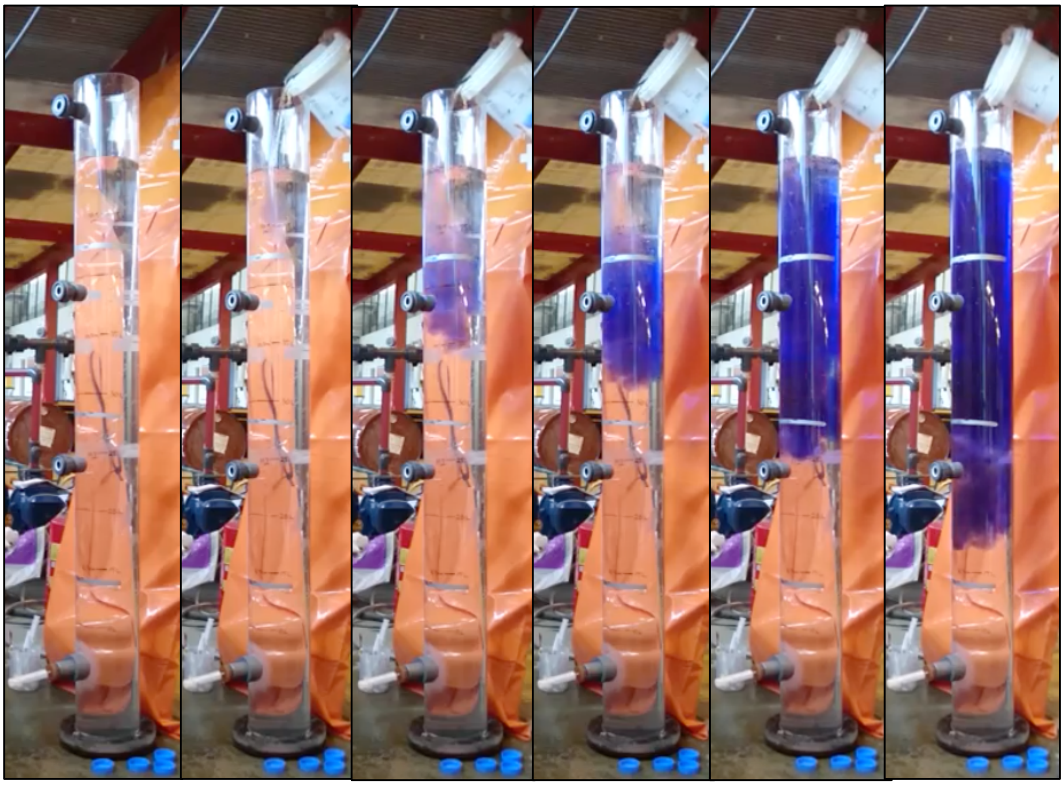


Figure 5.1 *55 wt% potassium formate brine poured turbulent into the pipe after - 0 seconds - 0 seconds - 2 seconds - 4 seconds - 6 seconds - 8 seconds (from left to right).*

Figure 5.2 55 wt% potassium formate brine poured turbulent into the pipe after - 10 seconds - 12 seconds - 14 seconds - 16 seconds - 18 seconds - 20 seconds (from left to right).

in this chapter. The rest are given in Appendix B. The results are compared and discussed as they are given. The base case with 50 L distilled water in the pipe and 5 kg brine is discussed if no other information is given.

5.1 10 wt% NaCl and HCOOK Brines (Base Case)

The results from the experiments with 10 wt% brines are given in Figure 5.3 and 5.4, for both laminar and turbulent mixing of NaCl and HCOOK. It is seen from the figures that the HCOOK brines have the same density trends as the NaCl brines. The small density differences initially in the pipe for the turbulent flows indicated an initially larger salt dispersion. A different immediate (t = 0 min) density distribution was seen for the laminar and turbulent flow, but an almost homogeneous density distribution was found for the experiments after short time. The initial density was larger at the top of the pipe for the laminar flow, but a density peak was found at the middle upper of the pipe for the turbulent flow. As the density peak was found at the middle upper part of the pipe for the turbulent mixing, the turbulence may not influence the mixing as deep down the pipe as maybe first expected. Another notice is that the mixing of the brine with the distilled water probably would be laminar with presence of a condensate phase because the brine would have to penetrate the condensate phase before reaching the water phase.

The highest density at the top of the pipe for the laminar flow illustrated the small density difference between the brine and the distilled water. As 10 wt% brines contained little salt, they used longer time to disperse down the pipe in comparison to heavier fluids. The initial value was therefore higher at the top of the pipe. The mixing of two fluids with almost the same densities can also be seen as more unpredictable compared to fluids with

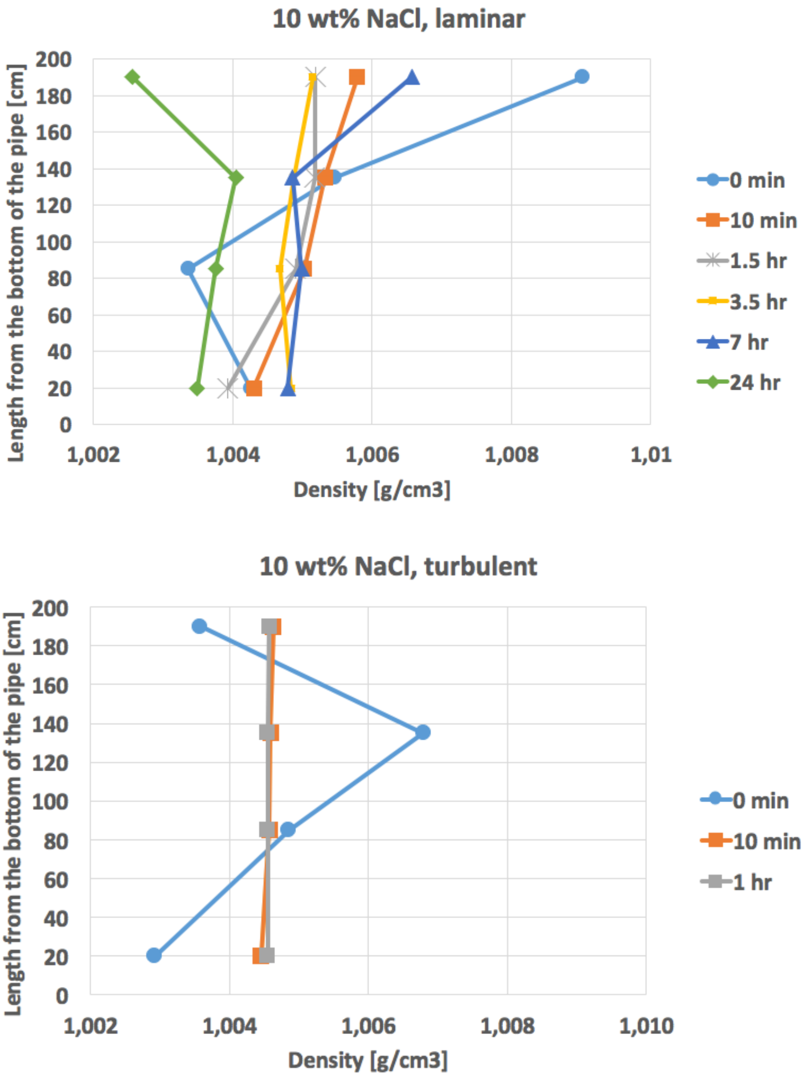


Figure 5.3 *Density distribution with respect of pipe height for 10 wt % NaCl brines. Laminar and turbulent flow. Different pycnometers are used for each point for the laminar flow. The same pycnometer is used for all the measurement for the turbulent flow.*

higher density differences. If the density difference is large (e.g. air and water), the heavier fluid tends to accumulate at the bottom. When the densities are more equal, the mixing can be more chaotic. The results can therefore diverge if the experiments are done several times.

It is seen from Figure 5.3 that the laminar flow has larger variation in values compared to the turbulent flow. The curves are not smooth. The large difference can be interpreted as noise. The reason was likely due to different pycnometers used to measure the density of each point in the graphs for the laminar flow. The same pycnometer was used for all the density points in the turbulent mixing. The pycnometers had some inaccuracies that seem to have influenced the results. The results show the trend of the values, but the values itself may diverge from each other.

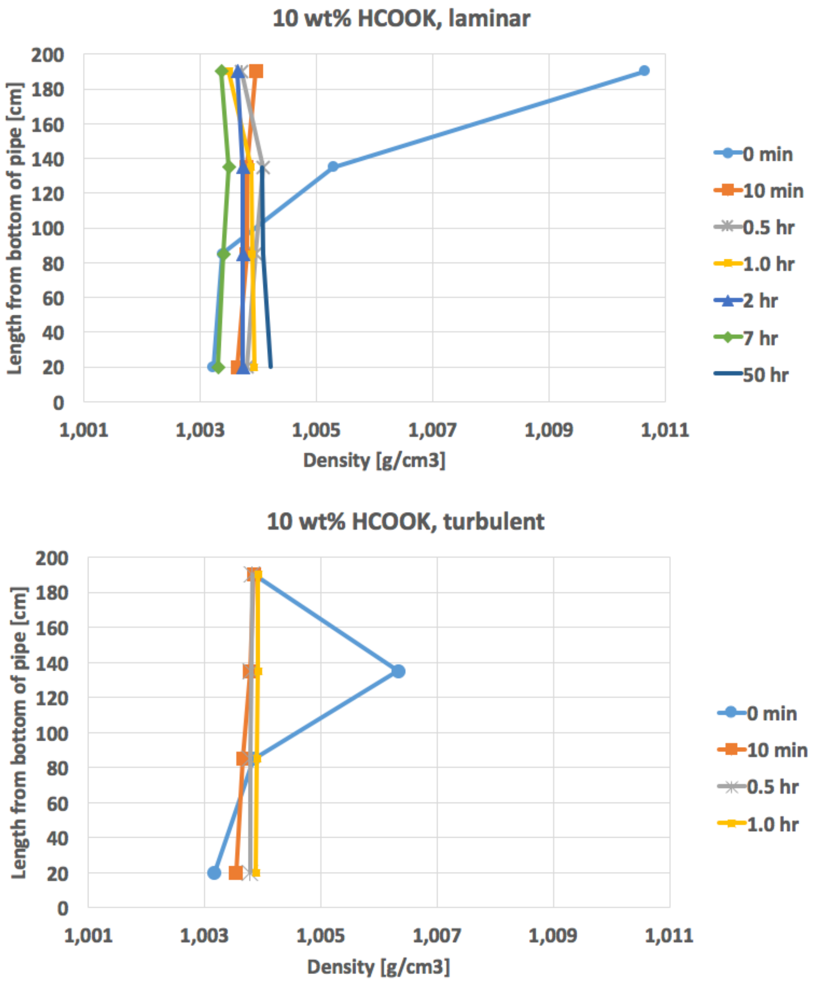


Figure 5.4 Density distribution with respect of pipe height for 10 wt % HCOOK brines. Laminar and turbulent flow.

The inaccuracy can be in e.g. pycnometer volume inaccuracy, not completely dried pycnometers (some water droplets inside it when weighing it “dry”), or e.g. dirty pycnometers. Calculations were done with both different pycnometers and the same pycnometer for some experiments, and the trends were the same. The results had less noise and were smoother and more reliable due to the inaccuracies given by the pycnometers when one pycnometer was used per measurement. Due to more accuracy and less work, it was decided to do all the measurements for one experiment with only one pycnometer.

The inaccuracy was especially the case when the concentration of the salt in the brine was low. When the brine then was mixed with distilled water, the total small amount of salt made the density calculation more vulnerable for inaccuracies in different pycnometers. E.g. the 10 wt% brines mixed with distilled water gave a total homogeneous salt concentration of 0.91 wt% in the pipe. Small errors in the measurements would influence the density calculations more compared to larger density brines. Larger brine densities in the bucket would give higher homogeneous densities in the pipe and would not be as vulnerable for inaccuracies in the pycnometers. The laminar flow in Figure 5.3 clearly shows the inaccuracy and difficulty of interpreting the results. It is also worth mentioning that the density range in Figure 5.3 is very low.

It can also be observed form both Figure 5.3 and 5.4 that the densities of the lowest points in the pipe did not change considerably with time. It may be due to a very fast penetration of the salt in the water column. All the samples were taken from the top and down to the bottom. When the sample at the top was taken, the salt continued to penetrate down the pipe. The salt had probably reached down to the bottom of the pipe when the samples further down were taken. It gave an indication of the fast mixing rate of the salt.

It can be seen that the salts were homogeneously dispersed in the pipe after 10 minutes for the turbulent flows, seen through an equal density distribution in the pipe. When the salts were homogeneously dispersed, the concentration did not seem to change further with time (i.e. accumulate in parts of the pipe). The salt was almost homogeneously dispersed in the pipe for the laminar NaCl mixing after 10 minutes. These measurements were done with different pycnometers, so they may diverge from the truth. But the trends showed an almost homogeneous distribution of the salt through the pipe for times equal to or larger than 10 minutes. The laminar HCOOK mixing also showed a homogeneous mixing after 10 minutes. It is therefore reasonable to believe that the noise from the pycnometers gave the diverged NaCl density values. The results illustrate that low concentrations of salt become homogeneously distributed in the pipe after short time, regardless of the mixing method.

5.2 20 wt% NaCl and HCOOK Brines (Base Case)

The results for the 20 wt% NaCl and HCOOK brines are shown in Figure 5.5 and 5.6. The NaCl results showed the same trend as for the 10 wt% NaCl brines; the salt was immediately uneven distributed in the pipe. The laminar flow showed an initial higher brine concentration at the top of the pipe, while the turbulent flow showed a density peak

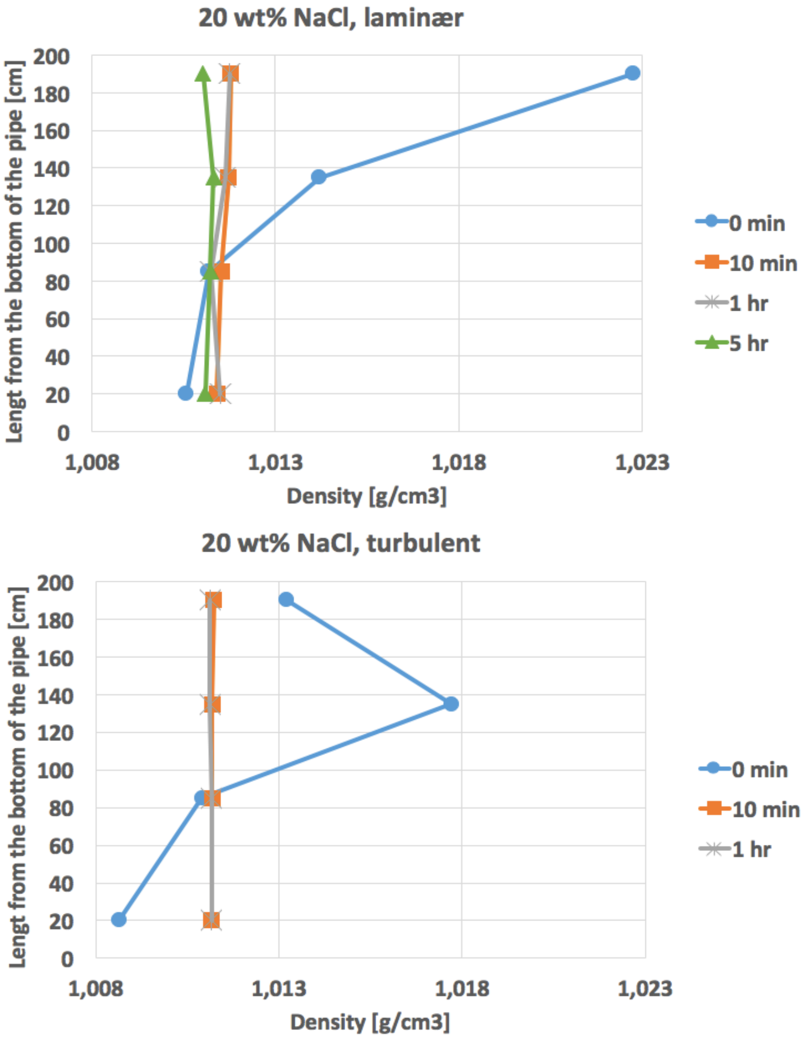


Figure 5.5 *Density distribution with respect of pipe height for 20 wt% NaCl brines. Laminar and turbulent flow.*

at the middle upper part of the pipe. After few minutes, the salt was homogeneously distributed in the pipe. It was seen with an equal density through the whole pipe. When the salt was first homogeneously distributed, the distribution did not change more with time.

The high salt density for the initial upper point for the turbulent flow in Figure 5.5 was due to a user mistake. When pouring the brine in the pipe, it was discovered that some undissolved salt was left in the bucket. (A magnet stirrer was not used to mix the brine for this experiment.) A spoon was used to get the undissolved salt in the pipe, which would increase the density at the top of the pipe.

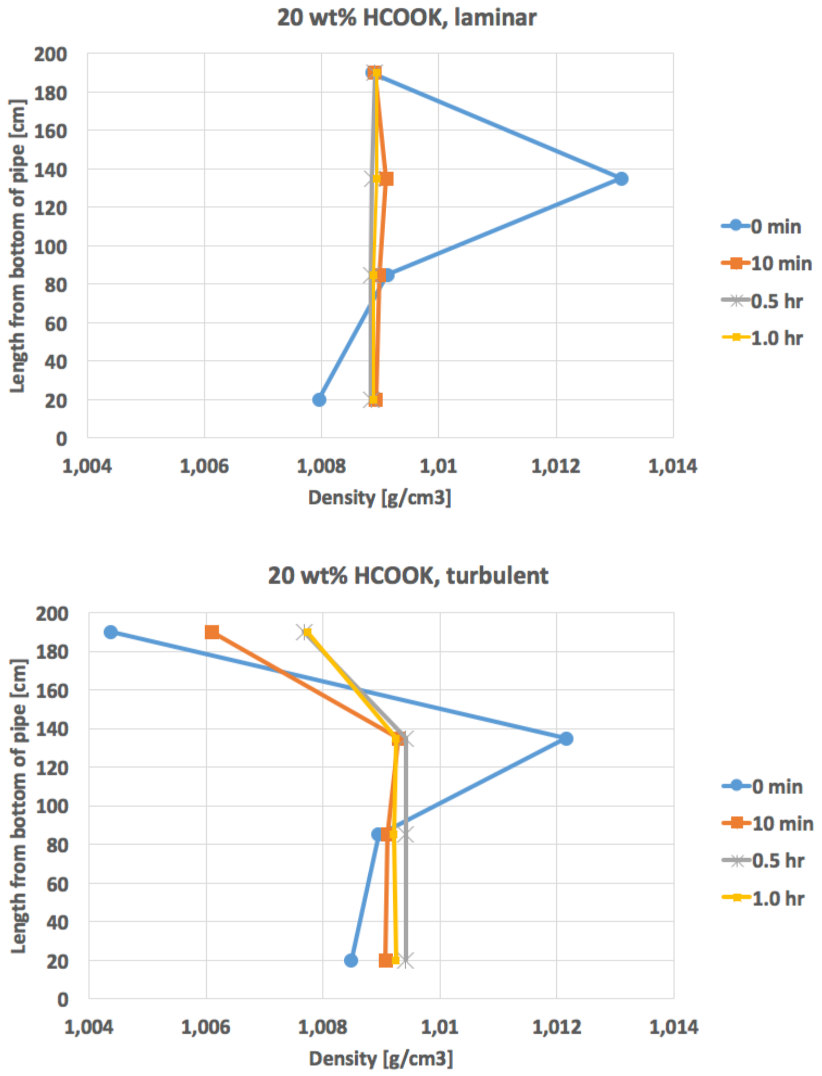


Figure 5.6 *Density distribution with respect of pipe height for 20 wt % HCOOK brines. Laminar and turbulent flow.*

The density profiles of the 20 wt% HCOOK brines, given in Figure 5.6, show a different result than the lower density brines. The turbulent flow had the same initial density profile as the lower density brines, but used longer time to reach towards a more homogeneous density distribution. The values showed an equal density for the three lowest points. The initial laminar density profile showed the same distribution as for the turbulent flows. Both the laminar and turbulent density profile with 20 wt% HCOOK showed that the brine solution immediately penetrated the distilled water in the pipe. This may be due to heavier brine poured into the pipe. Even if this is true, it can be seen that the laminar flow had a higher initial upper density (i.e. concentration) compared to the turbulent flow. This can be due to the same reason as for 10 wt% brines; the turbulence had a larger immediately mixing effect. It can also be seen from the figure that the laminar flow had a noticeable higher initial density at 135 cm from the bottom and lower initial density at the bottom compared to the turbulent flow. That indicated a higher amount of salt dispersed to the bottom for the turbulent flow. The small differences can be stochastic. The time used to take the samples may have some variation from time to time, in addition to difference in pouring time.

The laminar HCOOK flow had small noticeable higher concentration at 135 cm from the bottom after 10 minutes. The salt was homogeneously mixed in the pipe after 30 minutes. For the turbulent flow on the other hand, the mixing seemed approximately homogeneously from the bottom to 135 cm for times 10 minutes, 30 minutes and 1 hour. The upper density point increased with the time. It is important to notice the small interval on the density axis. It was also noticeable that the salt was homogeneously mixed after 10 minutes for lower density brines. It is naturally to believe that these density profiles would follow the same trend and the upper density would increase more with time until the salt became homogeneously mixed.

5.3 26 wt% NaCl Brines (Base Case)

The salt distribution in the pipe with the highest possible amount dissolved salt was of interest. The highest amount NaCl dissolved in water is approximately 26 wt% for a large temperature range. The results are given in Figure 5.7. Highest amount HCOOK dissolved in water was approximately 75 wt% at 18°C. HCOOK results are given in the next section.

The turbulent flow in Figure 5.7 showed the same trend as for the lower wt% brines. The laminar mixing on the other hand showed a new density distribution. It showed an immediately very low salt distribution at the top of the pipe, with a density peak at the middle upper part of the pipe and a slow decreasing density downward from the peak. After 10 minutes, the salt was homogeneously distributed in the three lowest points measured, with the same low density at the top. The same result was present after 1 hour.

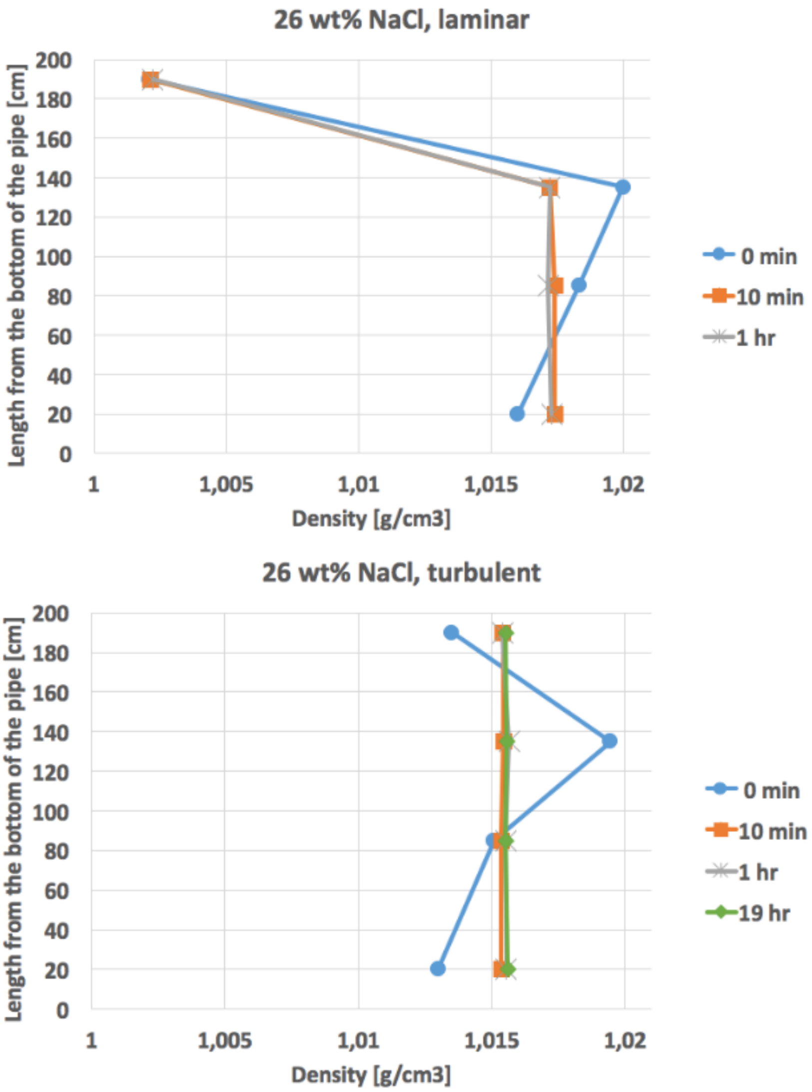


Figure 5.7 *Density distribution with respect of pipe height for 26 wt % NaCl brines. Laminar and turbulent flow.*

The results indicated that the heavy brine in the laminar flow penetrated the distilled water fast and accumulated at the lower part of the pipe compared to the less dense brines. As there were only four measurement points in the pipe, it was not known how far up the homogeneous distribution reached in the vertical pipe. It could reach further up than to 135 cm from the bottom. The homogeneous turbulent density was 1.0155 g/cc, while the homogeneous laminar density was 1.0172 g/cc. The larger laminar density indicated that the homogeneous salt distribution did not reach the top of the laminar flow. The writer has not found any reasons for this behaviour. The gravitational forces of the salt in water could most likely be neglected as the ions' molecular weight is not especially high compared to water molecules.

The turbulent flow showed an initial NaCl concentration close to the homogenous concentration. It may explain the fast homogeneous salt distribution. The turbulent pouring of the brine mixed the solutions more and the salt was then initially more dispersed down the pipe (seen through smaller density dispersion of the turbulent flow). As the more dispersed salt contained lower NaCl concentrations, the salt seems to become homogeneously dispersed after short time, as for the lower density brines. The results suggest that the turbulent flow helps the immediately mixing of the fluids, and creates a homogeneously distributed solution after a short time, in contrast with the laminar flow that may accumulate at the lower part of the pipe. These heavy brine experiments showed that the mixing method may be vital for the inhibitor distribution in the water phase.

5.4 55 and 75wt% HCOOK Brines (Base Case)

Figure 5.8 shows the density distribution for the 75 wt% HCOOK brines. The 55 wt% HCOOK brines showed the same density distribution trend, shown in Appendix B. The density graphs from Figure 5.8 showed an immediately initial penetration of the salt down the pipe for both the laminar and turbulent flow. The densities at the top of the pipe were very low at the initial state. From these experiments it was interpreted that the salt accumulated at the lower part of the pipe, but dispersed slowly upwards with time, seen through an increased density in the upper measurement point with time. A more homogeneously solution was reached with increased time. After several days, the salt was not homogeneously mixed in the pipe for neither the laminar or turbulent mixing. When the experiments were done over so many days, other factors may also influence the dispersion. One example is the effect of the sunlight. The sunlight might heat the water in the pipe which causes convections.

These experiments showed that heavier potassium formate brines had a quick penetration of the distilled water and showed a tendency of accumulating more at the lower part of the pipe. A homogeneously solution was present in the three lowest measurement points after short time. But, the results also indicated that an almost homogeneously mix would occur in the whole pipe with time. As there were only four measurement points in the pipe, it is not known how far up the pipe the homogeneous salt concentration reached. Experiments done later with one more measurement point (see Chapter 5.6) showed that a

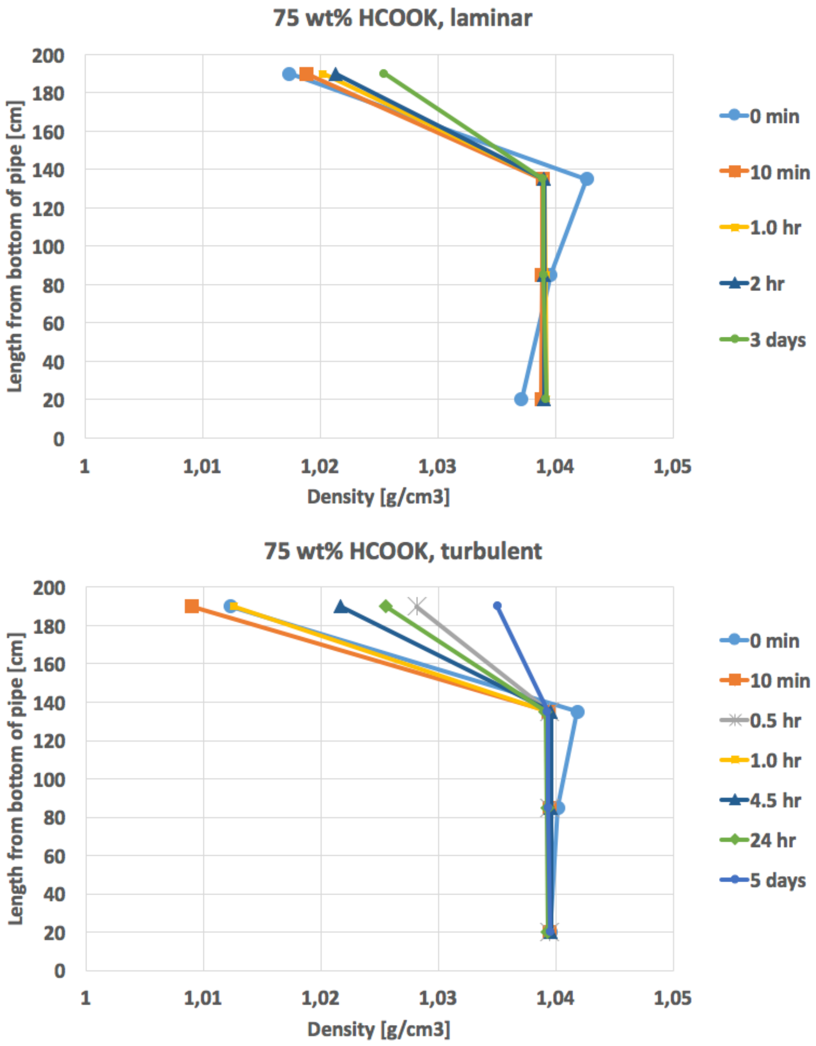


Figure 5.8 *Density distribution with respect of pipe height for 75 wt % HCOOK brines. Laminar and turbulent flow.*

homogeneous solution was present in almost the whole pipe after short time. The results also indicated an equal density distribution for the laminar and turbulent flow for high concentrations, both initially and with increased time.

5.5 HCOOK Experiment with Shorter Time Intervals (Base Case)

Figure 5.9 shows the density profile of a 25 wt% potassium formate brine for the first 10 minutes after mixing. Measurements were taken every minute, but some of the points were removed to easier see the density change with time.

A pycnometer with a volume of 5.029 mL was used in the measurement of these points due to the short time interval between the measurements. Smaller amounts of brine samples were taken to be able to take new samples every minute. The small volumes of water made the density calculations more vulnerable for errors, as e.g. excess water or scale errors. The high accuracy of the scale used made it vulnerable for a breath of wind and other factors that may influence the weighing. These errors may be more significant as the mass measured was smaller. The errors seemed to be large for the same experiment executed with a 10 wt% brine. The figure is found in Appendix B. It is seen that the graphs had a large and unsystematic variation.

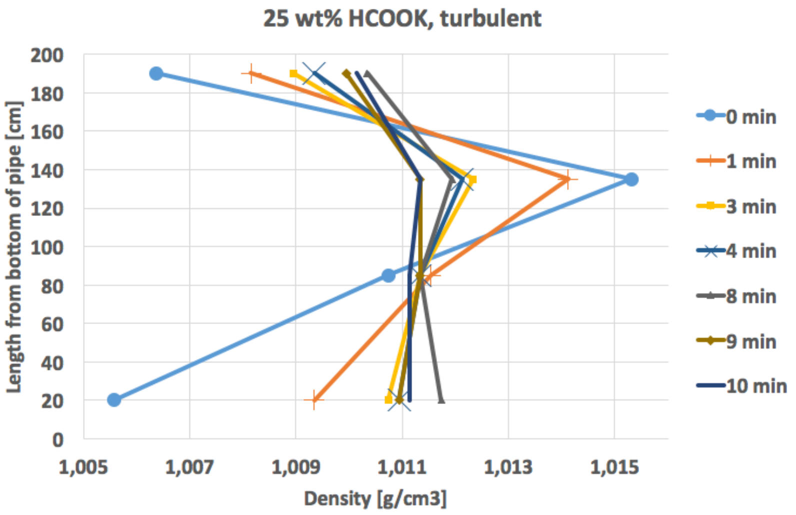


Figure 5.9 *Density distribution with respect of pipe height for a 25 wt % HCOOK brine. Turbulent flow and short time intervals.*

The graphs for the denser 25 wt% HCOOK brine seemed to have smaller errors. The heavier brine created a larger density difference through the pipe, which easier illustrated the dispersion of the salt with time. This figure shows the largest density at the initial state at a height 135 cm from the bottom. The densities at the top and bottom of the pipe were also at their lowest at the initial state. As expected, the densities at the bottom and top of the pipe increased with time, and the density at 135 cm from the bottom decreased with time until a stable density in the water column was reached. It did not take many minutes to disperse the salt in the pipe. It happened much faster than expected before the experiments started.

5.6 HCOOK Experiments with Less and More Brine

To investigate if the mass inhibitor brine to mass distilled water was of large importance, two experiments were done (experiment number 13 and 14 in Table 4.2). The original water content in the pipe was 50 L. The amount 55 wt% brine was decreased and increased with 50 % in each experiment to 2.5 kg and 7.5 kg respectively. These experiments had one more measurement point in comparison with the other experiments executed; samples were taken with a needle from the top of the pipe. The pinpoint was 10 cm under the water surface when the samples were taken. The reason for increasing the measurement points was to investigate how far up the homogeneous dispersion of the salt reached. The results from the experiments are shown in Figure 5.10.

The figure shows the same density distribution trends as for the base case; there was an initial density peak at the middle upper part of the pipe before an almost homogeneous solution was present. The extra measurements showed the same density as for the points measured further down the pipe. The homogeneous density was therefore present from the bottom of the pipe and up to 10 cm from the water surface. It illustrated that the salt also became homogeneous distributed in the pipe after short time for high brine concentrations, disregarded the density at the surface. The reason for the low brine content near the surface is uncertain. It is worth noticing that the HCOOK concentration was higher at the surface for the 55 wt% brines compared to the 10 wt% brines. But it does not explain why the density at the surface slowly increased with time.

The two experiments gave two vital results. First, the HCOOK concentration in the pipe became homogeneously dispersed in the pipe after short time disregarded the density at the surface. Second, the mass inhibitor brine to mass distilled water did not seem to affect the salt distribution in the pipe.

It is general knowledge that heavier particles tend to accumulate at the bottom in a lighter fluid. The results from the experiments were therefore different than first expected for the heavy HCOOK brines. The brines seemed to be almost homogeneously dispersed in the pipe after short time for all brine concentrations investigated. When it comes to the usage of potassium formate as a hydrate inhibitor, the results are promising. But the usage of the inhibitor in a shut-in well would require more inhibitor mass than first expected, as the

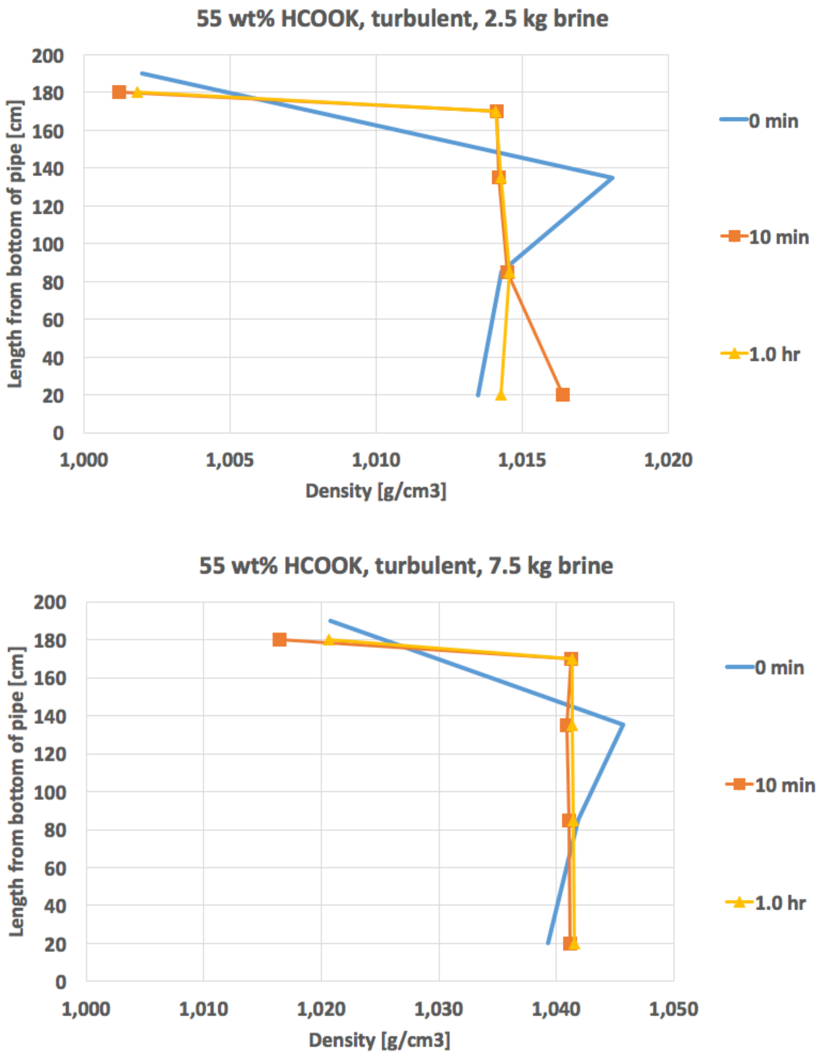


Figure 5.10 *Density distribution with respect of pipe height for 55 wt % HCOOK brines. Turbulent flow. The brine mass was decreased and increased with 50 % compared to base case.*

salt did not seem to accumulate at the bottom of the pipe. The salt would inhibit the whole water phase and not only the lower or upper part, as glycols and methanol would do. Usage of the salt in a producing well may be more interesting.

5.7 Experiments with Less Distilled Water

Figure 5.11 and 5.12 show the NaCl and HCOOK distribution in the water phase when less distilled water was filled in the pipe. 35L distilled water was used in comparison with the 50 L used in the previous experiments. The amount brine poured into the pipe was 5 kg and had a salt concentration of 20 wt%. The purpose with these experiments was also

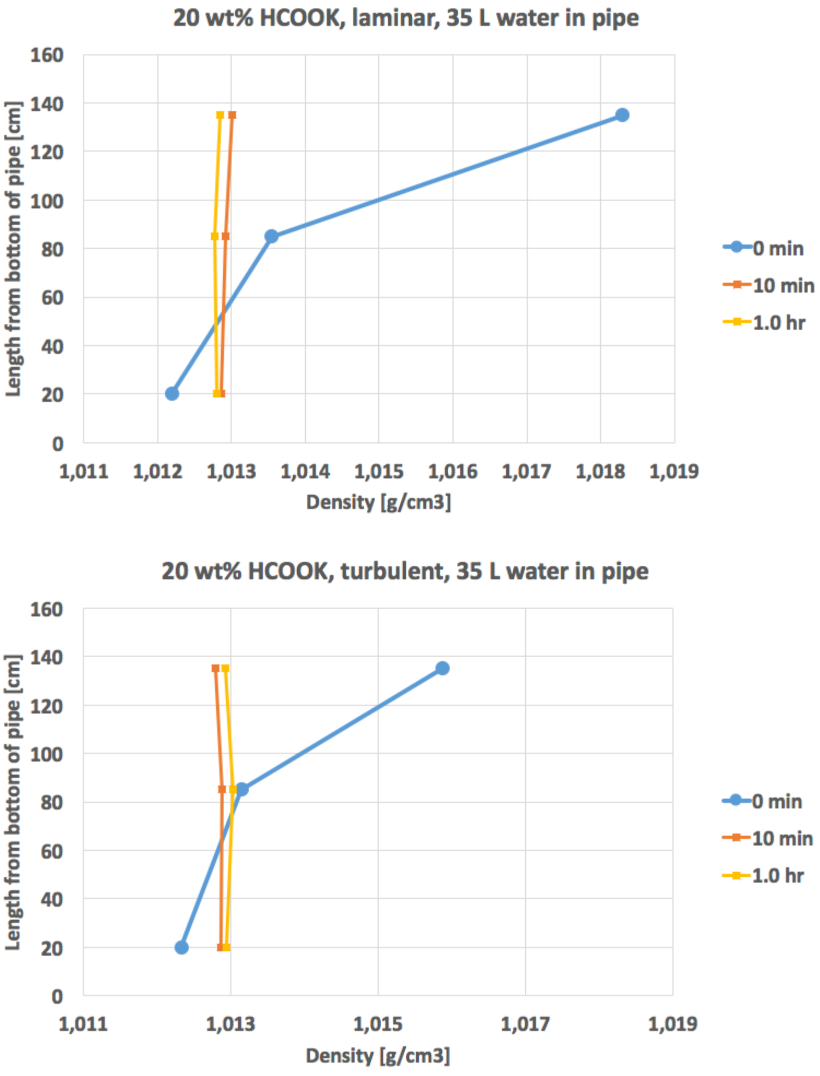


Figure 5.11 *Density distribution with respect of pipe height for 20 wt % HCOOK brines. Laminar and turbulent flow.*

to investigate if the amount brine to amount distilled water had a large effect on the salt dispersion in the pipe.

When the brines were poured turbulent into the pipe in these experiments, much of the water flowed down to the distilled water at the plastic pipe wall. The mixing was therefore not as turbulent as wished in these experiments. But it indicated that the inhibitor brine tended to flow towards the pipe wall if only a gas phase was present under static conditions.

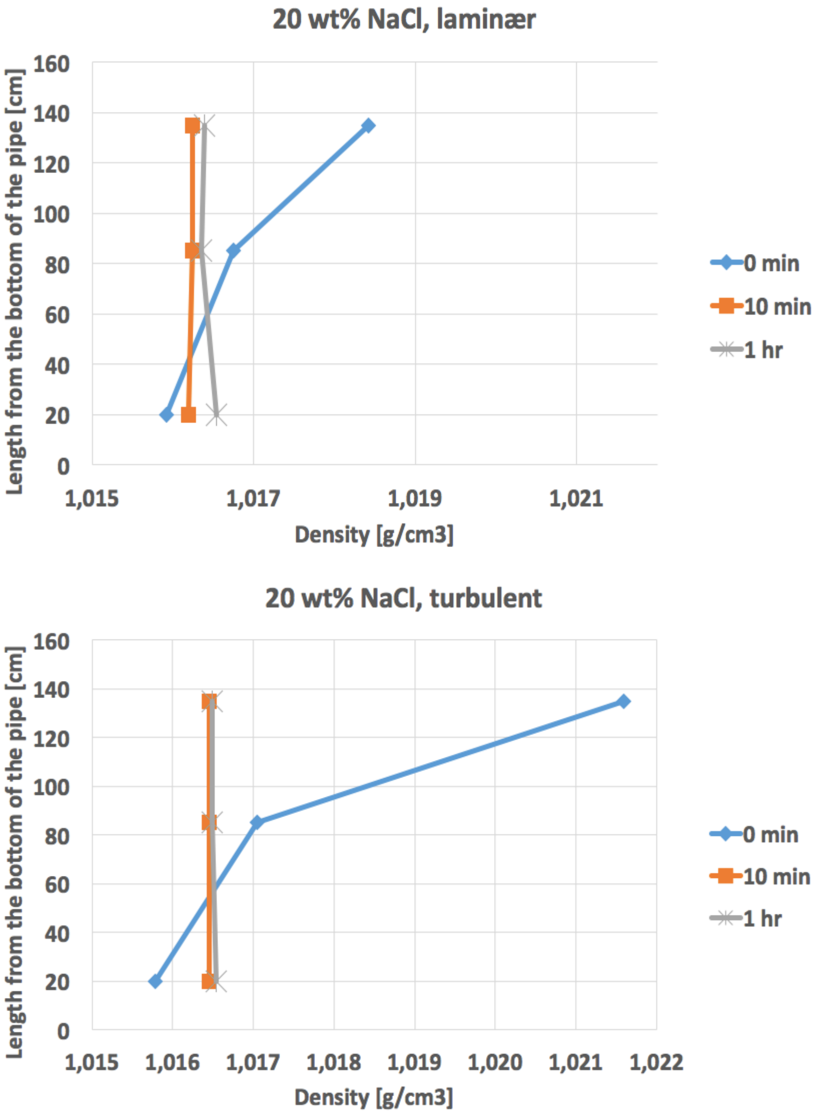


Figure 5.12 *Density distribution with respect of pipe height for 20 wt % NaCl brines. Laminar and turbulent flow.*

The results showed a homogeneous solution after short time for all mixings. The measurement at the upper point was few cm below the water surface. The trends suggested that the mass brine to mass distilled water did not influence the results.

Chapter 6

Conclusions

The experiments done showed that the initial salt distribution in the pipe was influenced by laminar and turbulent mixing for low brine concentrations. The laminar mixing had an initial higher density at the uppermost measurement point in the pipe. It illustrated the small density difference between the distilled water and low brine concentrations. The turbulent flows seemed to mix the brines more with the distilled water. A density peak at the middle upper point in the pipe was seen. The height of the density peak illustrated that the turbulence only affected the mixing in the upper part of the water column. If the salt should be used in a shut-in well, only the uppermost part of the high well would probably have advantage of the turbulent mixing when brine is poured into the pipe at the top of the well. With presence of a condensate column, it is a high probability that the brine poured into the pipe would have a laminar flow when it reaches the denser water phase, because the brine would have to penetrate the condensate phase before reaching the water phase. In practice, it is believed that the mixing method does not influence the salt distribution after short time.

For higher density HCOOK brines, only small initial density peaks at the middle upper point were found, both for laminar and turbulent mixing. The dense HCOOK brines had a quick penetration of the distilled water, explained by the high density difference between the distilled water and brine.

The density distributions in the pipe were not influenced by the mixing method after short time. For low brine concentrations it only took a few minutes (or seconds) for both salt to become homogeneously distributed. It was illustrated through an equal density distribution through the whole pipe. It did not matter if the pouring of the brine into the pipe was laminar or turbulent. For higher brine concentrations, both salts seemed to accumulate at the lower part of the pipe, as the uppermost measurement point in the pipe had considerably lower brine density than the three lower points. The three lower points showed homogeneous salt distributions. New experiments with samples 10 cm down from the water surface had the same density as for the lower points; the salt was homogeneously distributed in the pipe from the bottom and up to 10 cm from the water surface. All the results therefore showed an almost homogeneously salt distribution in the pipe after short time, independent of brine concentration and mixing method.

It is general knowledge that heavy particles tend to accumulate at the bottom in a lighter fluid. The results from the experiments were different than first expected for the heavy brines. It was believed that the heavy HCOOK molecules would accumulate to the bottom of the water phase. The brines showed to be almost homogeneously dispersed in the pipe after short time for all brine concentrations investigated. The pouring method did not seem to influence the mixing of the fluids other than in the initial state.

When it comes to the usage of potassium formate as a hydrate inhibitor, the results were promising. But the usage of the inhibitor in a shut-in well requires more inhibitor mass than first expected, as the salt did not accumulate at the bottom of the pipe. The heavy HCOOK brine should therefore not be used to penetrate the water phase and accumulate at the bottom to dissolve a hydrate plug. The salt would inhibit the whole water phase and not only the lower or upper part, as glycols and methanol would do (Li et al., 2000). This is a characteristic that could especially be an advantage in producing wells, as the whole water phase would be inhibited. The hydrocarbons' lower solubility in water in presence of salts is also a large advantage. Potassium format's quick distribution to a homogeneous mix could improve flow assurance in production wells.

As the results indicate, potassium formate should be investigated more as a potential hydrate inhibitor in the petroleum industry. The favourable HSE properties and homogeneous distribution of the salt in water should be important factors in the decision of an inhibitor for a petroleum well. But at last, it is the economy that decides the type of inhibitor. More research should be done to investigate e.g. the economic aspects, salt distribution in presence of a condensate phase and hydrate dissociation with the salt.

Chapter 7

Recommended Future Research

It has been shown that potassium formate has a potential as a thermodynamic hydrate inhibitor. The salt has favourable HSE properties compared to traditional thermodynamic inhibitors, in addition with high solubility in water. To investigate the potential in more detail, some recommended further research is given:

- One of the simplest and most important next step could be to execute new experiments with presence of a condensate column. It is vital to know if the inhibitor penetrates the condensate and reaches the potential hydrate formation areas in the well, in addition to investigate if the salt distribution in the pipe changes.
- Another suggestion is to use a pipe with more rubber sealed openings or beakers (as used by Li et al. (2000)) to get more precise values and height of the largest density peaks of the salt. These experiments could also be done with a condensate column present. More precise information about how high up the homogeneous concentration reaches with heavy HCOOK brines would also be given with more rubber sealed openings in the pipe.
- An idea can also be to use a larger pipe to investigate the dispersion of the salt. Most preferable would be to have a real riser, but a higher pipe than 2 m would be preferable to investigate the results on a larger scale.
- Another suggestion for further work is to do experiments with present of turbulence in the flow to simulate fluid flow in the pipe.

- The best way to test the salt as an inhibitor is to execute a field study on a real system with hydrates or thermodynamic properties present for hydrate formation. The study would give realistic results for the potential of the salt.
- Studies should be done to dissociate hydrates with the salt. It could be done in a pressure chamber. A less complex study could be to use the salt to dissociate ice and snow plugs. The results would give an idea of the inhibition degree of the salt.
- A study to calculate or simulate the shifting of the equilibrium curve of the salt should also be done. It is found that the decrease in freezing temperature of water in a NaCl brine is almost the same as the decrease in hydrate formation temperature for the same amount of NaCl brine. A study to investigate if this also is true for HCOOK would be of large interests.

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Appendices

Appendix A: Additional calculations

Appendix B: Additional experimental results

Appendix C: Conducting risk assessments

Appendix D: Nomenclature

Appendix A Additional Calculations

A.1 Solubility of HCOOK in Water at Different Temperatures

The solubility of HCOOK in water varies with temperature. An approximation for the solubility versus temperature is given with basis in the three temperatures given by Weatherford (2010).

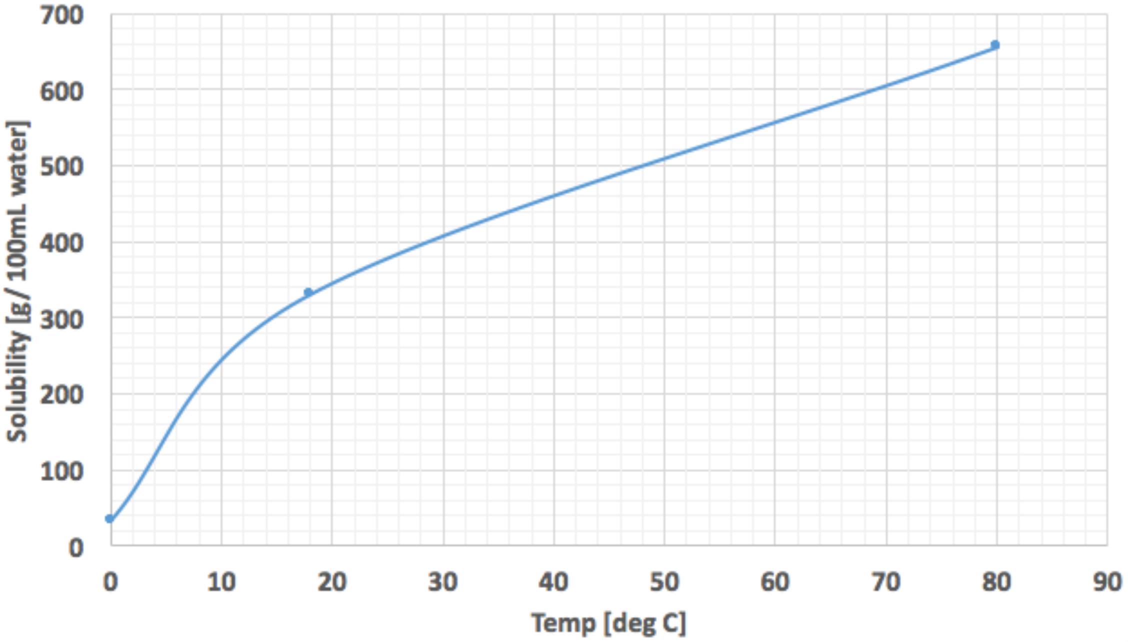

Figure A.1 *Aqueous solubility of potassium formate at different temperatures. Values form Weatherford (2010).*

A.2 Shifting the Equilibrium Curve with Inhibitors

Calculations are done to shift the equilibrium curve for hydrate formation with the conventional hydrate inhibitors sodium chloride, methanol and mono ethylene glycol. The equations used and plotted equilibrium curves are given in this section.

Correlation for clathrate hydrate formation by Mani Safamirzaei (2016):

$$T_{(K)} = A\gamma^{B}\left(lnP_{(kPa)}\right)^{C} \qquad \text{Eq. A.1}$$

Where

T: temperature in kelvin

P: pressure in kPa

γ: specific gravity of the gas

A: the number 194.681789

B: the number 0.044232

C: the number 0.189829

Correlation for equilibrium shift due to inhibitors by Kamath and Patil (1994):

$NaCl$: $$\Delta T = 0.42x + 0.0202x^{2} \qquad \text{Eq. A.2}$$

MeOH: $$\Delta T = 0.3938x + 0.006166x^{2} \qquad \text{Eq. A.3}$$

MEG: $$\Delta T = 0.1721 + 0.004466x^{2} \qquad \text{Eq. A.4}$$

Where

ΔT: temperature change

x: wt% inhibitor in the water phase

Plotted equilibrium curves are given in the next pages.

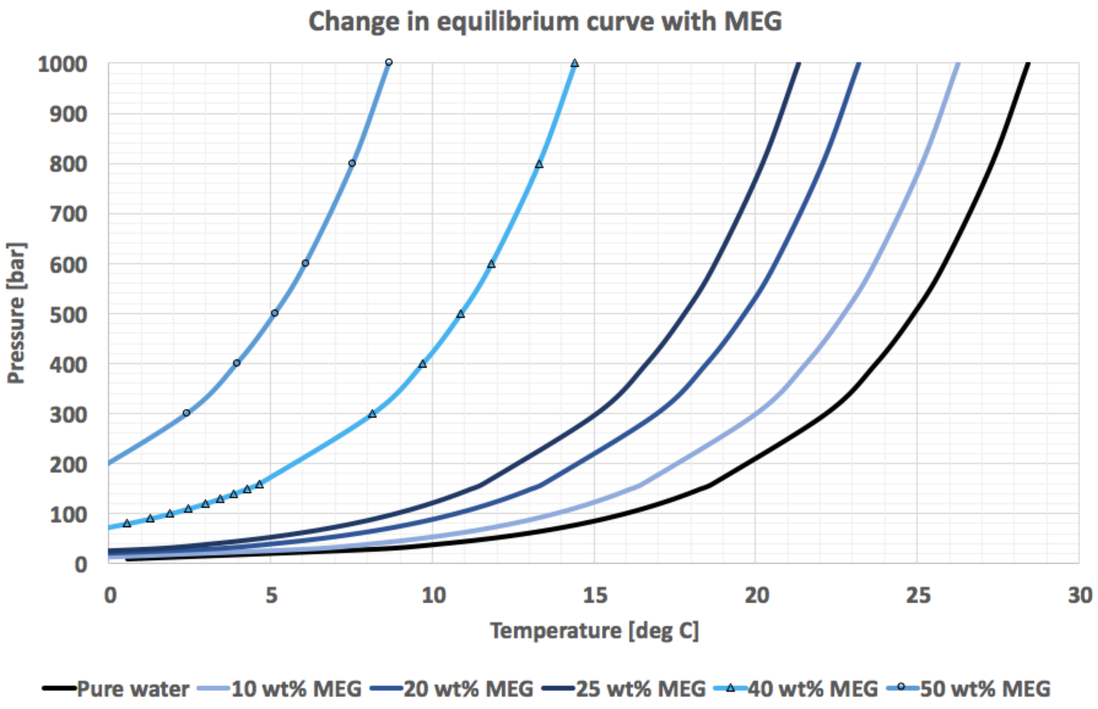

Figure A.3 *Equilibrium curves with MEG as the inhibitor.*

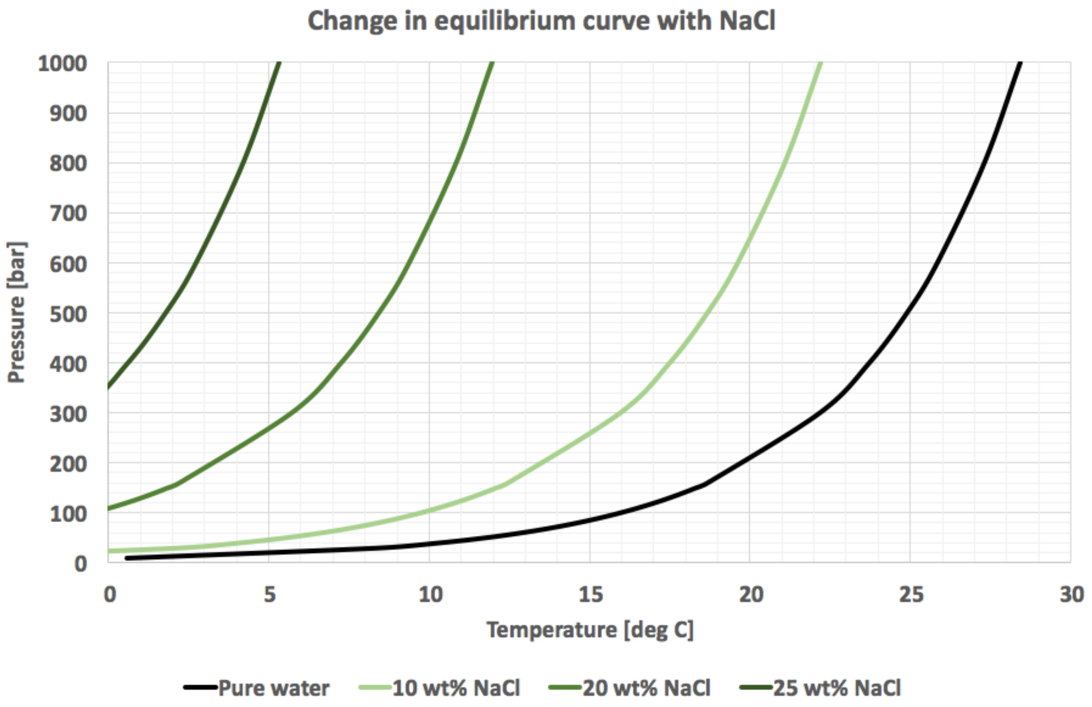

Figure A.2 *Equilibrium curves with NaCl as the inhibitor.*

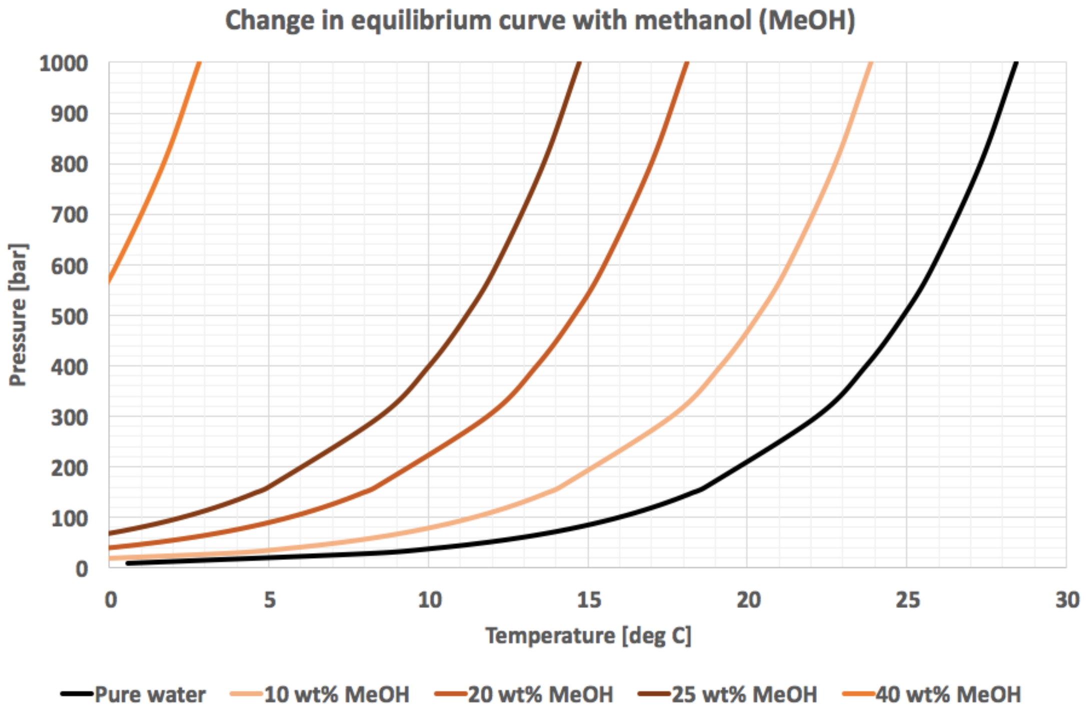

Figure A.5 *Equilibrium curves with methanol as the inhibitor.*

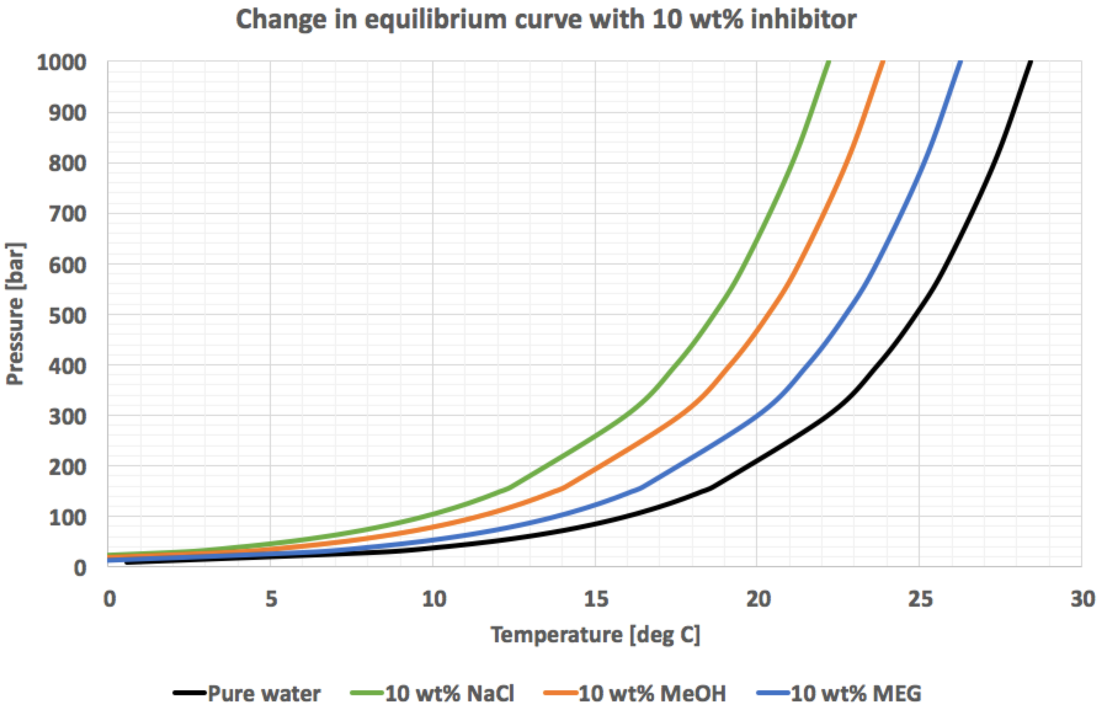

Figure A.4 *Equilibrium curves with 10 wt% inhibitor.*

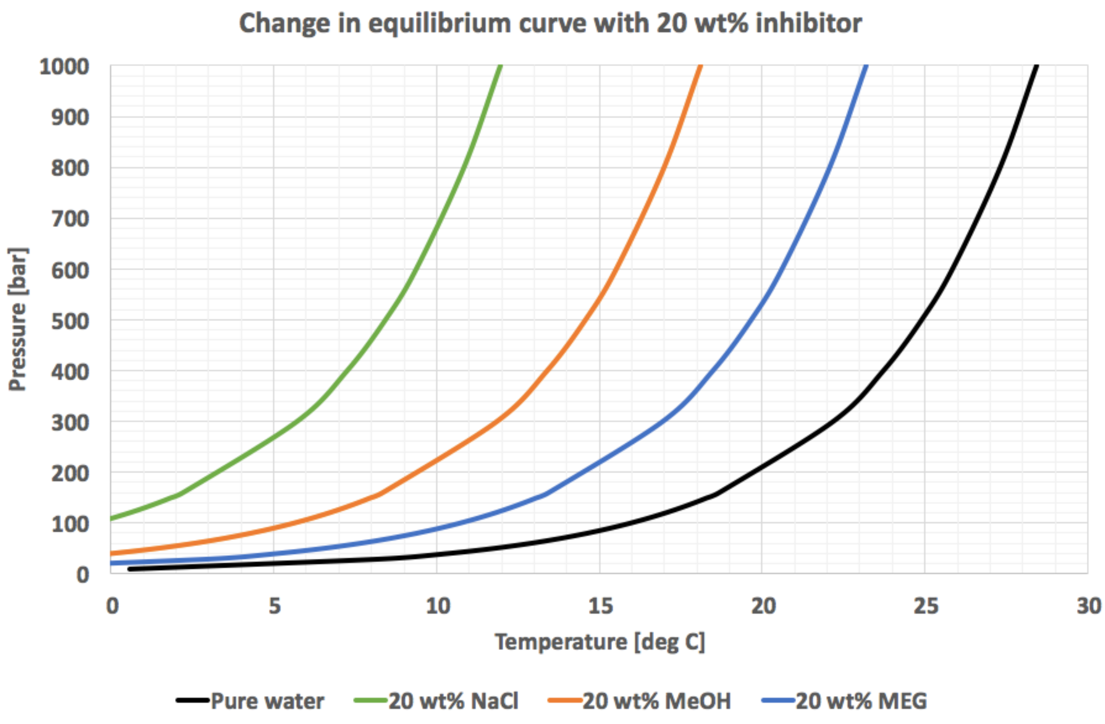

Figure A.7 Equilibrium curves with 20 wt% inhibitor.

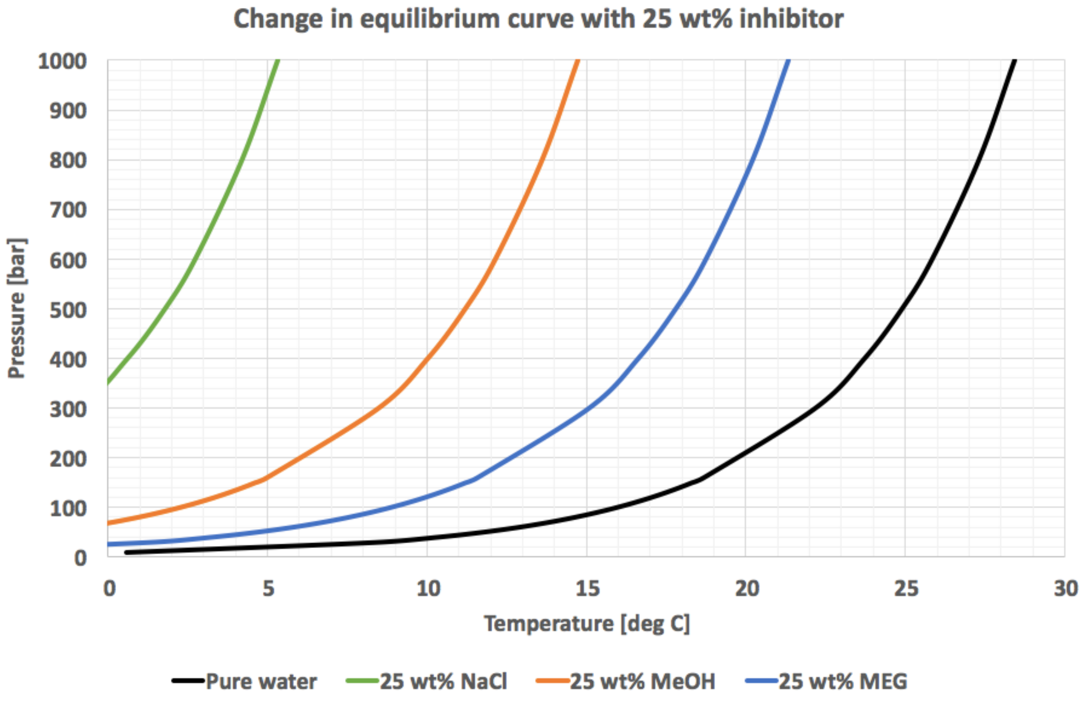

***Figure A.6** Equilibrium curves with 25 wt% inhibitor.*

Excel calculation spreadsheets:

Table A.1 *Excel calculation spreadsheet for equilibrium curve for 10 wt%, 20 wt% and 25 wt% inhibitor*

		wt% inhib. 10			wt% inhib. 20			wt% inhib. 25		
		NaCl ΔT	**MeOH** ΔT	**MEG** ΔT	**NaCl** ΔT	**MeOH** ΔT	**MEG** ΔT	**NaCl** ΔT	**MeOH** ΔT	**MEG** ΔT
Pure water		6,2	4,6	2,2	16,5	10,3	5,2	23,1	13,7	7,1
T	**p**	**T**	**T**	**T**	**T**	**T**	**T**	**T**	**T**	**T**
[deg C]	**[bar]**	**[deg C]**	**[deg C]**	**[deg C]**	**[deg C]**	**[deg C]**	**[deg C]**	**[deg C]**	**[deg C]**	**[deg C]**
0	0	0	0	0	0	0	0	0	0	0
1	10	-6	-4	-2	-16	-10	-5	-23	-13	-7
8	30	2	4	6	-8	-2	3	-15	-5	1
10	40	4	6	8	-6	0	5	-13	-3	3
12	50	5	7	10	-5	1	6	-11	-2	5
13	60	7	8	11	-4	2	8	-10	-1	6
14	70	8	9	12	-3	3	9	-9	0	7
15	80	8	10	12	-2	4	9	-9	1	7
15	90	9	11	13	-1	5	10	-8	2	8
16	100	10	11	14	-1	6	11	-7	2	9
16	110	10	12	14	0	6	11	-7	3	9
17	120	11	12	15	1	7	12	-6	3	10
17	130	11	13	15	1	7	12	-6	4	10
18	140	12	13	16	1	8	13	-5	4	11
18	150	12	14	16	2	8	13	-5	5	11
19	160	12	14	17	2	8	13	-4	5	12
22	300	16	18	20	6	12	17	-1	8	15
24	400	18	19	22	7	13	18	1	10	17
25	500	19	20	23	8	15	20	2	11	18
26	600	20	21	24	9	16	21	3	12	19
27	800	21	23	25	11	17	22	4	14	20
28	1000	22	24	26	12	18	23	5	15	21

Table A.2 *Excel calculation spreadsheet for equilibrium curve for 40 wt% inhibitor and 50 wt% inhibitor.*

		wt% inhib. 40		wt% inhib. 50	
		MeOH ΔT	**MEG** ΔT	**MeOH** ΔT	**MEG** ΔT
Pure water		25,6	14,0	35,1	19,8
T	**p**	**T**	**T**	**T**	**T**
[deg C]	**[bar]**	**[deg C]**	**[deg C]**	**[deg C]**	**[deg C]**
0	0	0	0	0	0
1	10	-25	-13	-35	-19
8	30	-17	-6	-27	-11
10	40	-15	-4	-25	-10
12	50	-14	-2	-23	-8
13	60	-13	-1	-22	-7
14	70	-12	0	-21	-6
15	80	-11	1	-21	-5
15	90	-10	1	-20	-4
16	100	-10	2	-19	-4
16	110	-9	2	-19	-3
17	120	-9	3	-18	-3
17	130	-8	3	-18	-2
18	140	-8	4	-17	-2
18	150	-7	4	-17	-1
19	160	-7	5	-16	-1
22	300	-3	8	-13	2
24	400	-2	10	-11	4
25	500	-1	11	-10	5
26	600	0	12	-9	6
27	800	2	13	-8	8
28	1000	3	14	-7	9

A.3 Number of Molecules per Kilogram Inhibitor

Number of molecules per kilogram inhibitor is calculated.

The molar mass, M, for the three substances are:

$$M_{NaCl} = 58.44\ g/mole$$

$$M_{MeOH} = 32.04\ g/mole$$

$$M_{MEG} = 62.07\ g/mole$$

$$M_{HCOOK} = 84.12\ g/mole$$

Number of moles, n, per mass, m = 1 kg, inhibitor:

$$n_{NaCl} = \frac{m_{NaCl}}{M_{NaCl}} = \frac{1000\ g}{58.44\ g/mole} = 17.112\ moles\ \rightarrow 34.224\ moles\ of\ ions$$

$$n_{MeOH} = \frac{m_{MeOH}}{M_{MeOH}} = \frac{1000\ g}{32.04\ g/mole} = 31.211\ moles$$

$$n_{MEG} = \frac{m_{MEG}}{M_{MEG}} = \frac{1000\ g}{62.07\ g/mole} = 16.111\ moles$$

$$n_{HCOOK} = \frac{m_{HCOOK}}{M_{HCOOK}} = \frac{1000\ g}{84.12\ g/mole} = 11.888\ moles\ \rightarrow 23.776\ moles\ of\ ions$$

One mole dissolved salt in water creates two moles of ions. Number of dissolved particles is therefore doubled compared to number of undissolved particles. In other words, 1 kg NaCl corresponds to 34.224 moles (2*17.112 moles) of ions and 1 kg of potassium formate corresponds with 23.776 moles (2*11.888 moles) of ions.

To find number of particles per kilogram inhibitor, Avogadro's number is used.

$$number\ of\ Na^{+} and\ Cl^{-}\ particles \approx 6.0221415 * 10^{23} \frac{particles}{mole} * 34.224\ moles \approx 20.61 * 10^{24}\ particles$$

$$number\ of\ MeOH\ particles \approx 6.0221415 * 10^{23} \frac{particles}{mole} * 31.221\ moles \approx 18.80 * 10^{24}\ particles$$

$$number\ of\ MEG\ particles \approx 6.0221415 * 10^{23} \frac{particles}{mole} * 16.111\ moles \approx 9.70 * 10^{24}\ particles$$

$$number\ of\ K^{+}\ and\ HCOO^{-}\ particles \approx 6.0221415 * 10^{23} \frac{particles}{mole} * 23.776\ moles \approx 14.32 * 10^{24}\ particles$$

A.4 pH Calculations of Potassium Formate Brines

When HCOOK (s) dissolves in water, K^{+} (aq) and $HCOO^{-}$ (aq) ions are created. Some of the $HCOO^{-}$ (aq) ions will react with water molecules, H_2O (l), and crate HCOOH (aq) and OH^{-} (aq) ions until an equilibrium has occurred. (s), (aq) and (s) indicate solid, aqueous solution and liquid respectively. Potassium formate in water will create an alkaline solution due to the OH^{-} (aq) ions. The equilibriums are shown below.

$$HCOOK\ (s) \rightleftharpoons HCOO^-\ (aq) +\ K^+(aq) \qquad \text{Eq. A.5}$$

$$HCOO^-\ (aq) + H_2O\ (l) \rightleftharpoons HCOOH\ (aq) + OH^-(aq) \qquad \text{Eq. A.6}$$

Overall:

$$\begin{aligned} &HCOOK\ (s) + H_2O\ (l) \\ &\qquad \rightleftharpoons HCOOH\ (aq) + K^+(aq) + OH^-(aq) \end{aligned} \qquad \text{Eq. A.7}$$

The basicity (pK_b) of HCOOK is 10.25 (Themark-Corporation, 2014), which indicates a weak base. Normal basicity values for weak bases are between 2 and 13, where a lower value indicates a stronger base (Zinck, 2014). The base dissociation constant (K_b) illustrates a pH above 7 for dissolved potassium formate in water. pH depends on the molar concentration of the salt; higher concentration of salt will give a higher pH. The relationship can be seen from these formulas:

$$\begin{aligned} K_b^{HCOOK} &= 10^{-pK_b^{HCOOK}} = 10^{-10.25} mol/L \\ &\approx 5.623413 * 10^{-11}\ mol/L \end{aligned} \qquad \text{Eq. A.8}$$

$$K_b^{HCOOK} = \frac{[HCOOH] * [OH^-]}{[HCOOK]} = \frac{x^2}{original\ HCOOK\ (s)\ concentration\ in\ water - x} \qquad \text{Eq. A.9}$$

Some notices:

1. The concentrations should be in mol/L.
2. The value of the equilibrium constant (Eq. A.9) is given by equation A.7. Alkali metals (K^+) and water (H_2O) are neutral.
3. When x moles of $HCOO^-$ react in equation A.6 are x moles of both HCOOH and OH^- created. Concentration of HCOOK (aq) after equilibrium, is concentration of HCOOK (s) before the reaction minus the concentration that has reacted.

The concentration of OH^- ions (or x) can be found from Eq. A.9 if the original salt concentration in the water phase is known. The H_3O^+ concentration and pH can now be found by Equation A.10 and A.11.

$$[H_3O^+] * [OH^-] = 10^{-14} \left(\frac{mol}{L}\right)^2 \qquad \text{Eq. A.10}$$

$$pH = -\log([H_3O^+]) \qquad \text{Eq. A.11}$$

A simple calculation example: 500 g HCOOK is added to a flask and filled with distilled water to a total volume of 1 L. HCOOK has a molar mass of 84.12 g/mol. The concentration of dissolved salt in the water is 5.944 mol/L from Eq. A.12.

$$c_{HCOO^{-}-original} = \frac{moles\ salt}{total\ volume} = \frac{\frac{mass\ salt}{molar\ mass\ salt}}{total\ volume} \qquad \text{Eq. A.12}$$

From Eq. A.9; the OH^{-} concentration (i.e. x) is found to be around $3.6565*10^{-5}$ mol/L, which will give a pH of 9.56 from equation A.10 and A.11. According to Figure 1 a) and b) by Howard (1995) does 5.9 mol/L HCOOK correspond to around 35 wt% HCOOK. A 55 wt% potassium formate brine has a molar concentration of approximately 9.5 mol/L (Howard, 1995). It corresponds with a OH^{-} concentration of $4.62266*\ 10^{-5}$ mol/L and a pH of 9.66.

The calculations have shown that potassium formate creates an alkaline solution in water. Higher pH corresponds with higher concentration of salt in water. The high pH is preferable to avoid corrosion and may be preferable for scale dissolving.

Appendix B Additional Experimental Results

Additional results from the experiments are given in this section. The graphs of the results will be shown, but not commented or discussed.

B.1 NaCl Results

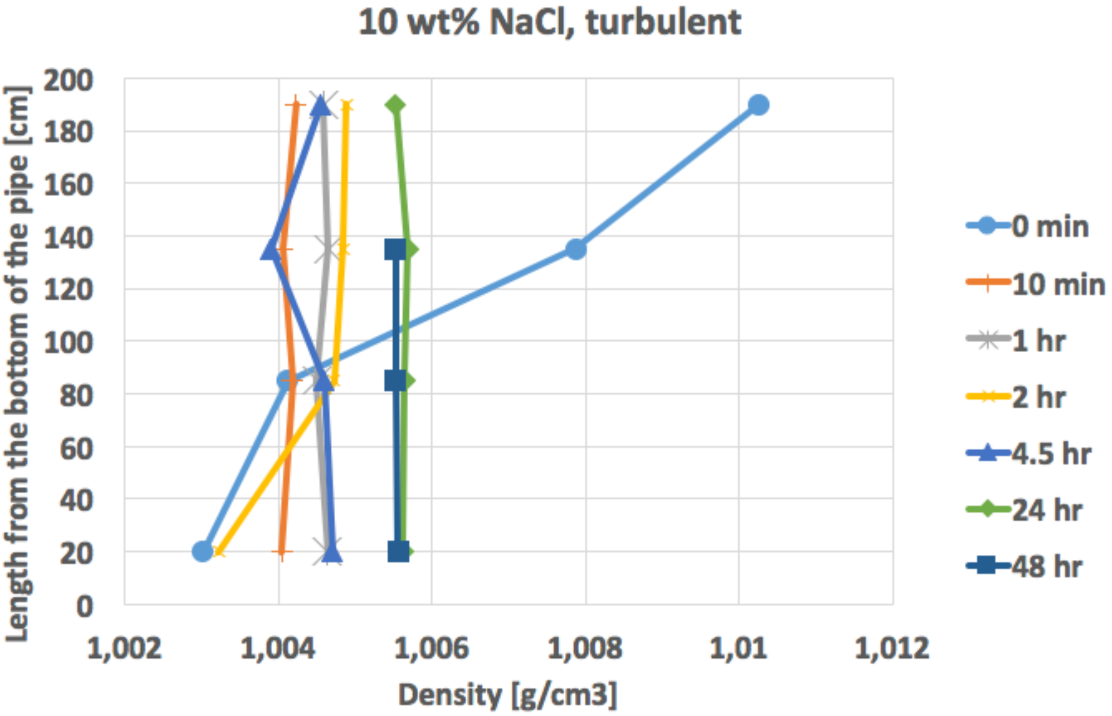

Figure B.1 Density distribution with respect to pipe height for a 10 wt % NaCl brine. Turbulent flow.

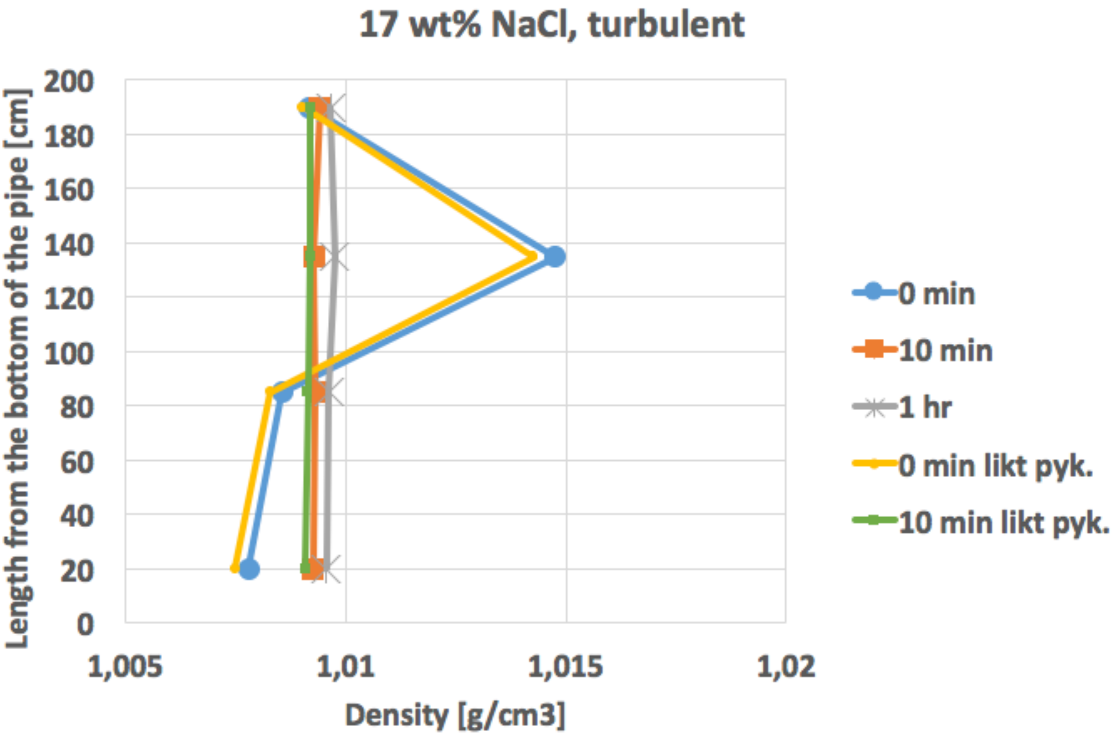

Figure B.2 *Density distribution with respect to pipe height for a 17 wt % NaCl brine. Turbulent flow.*

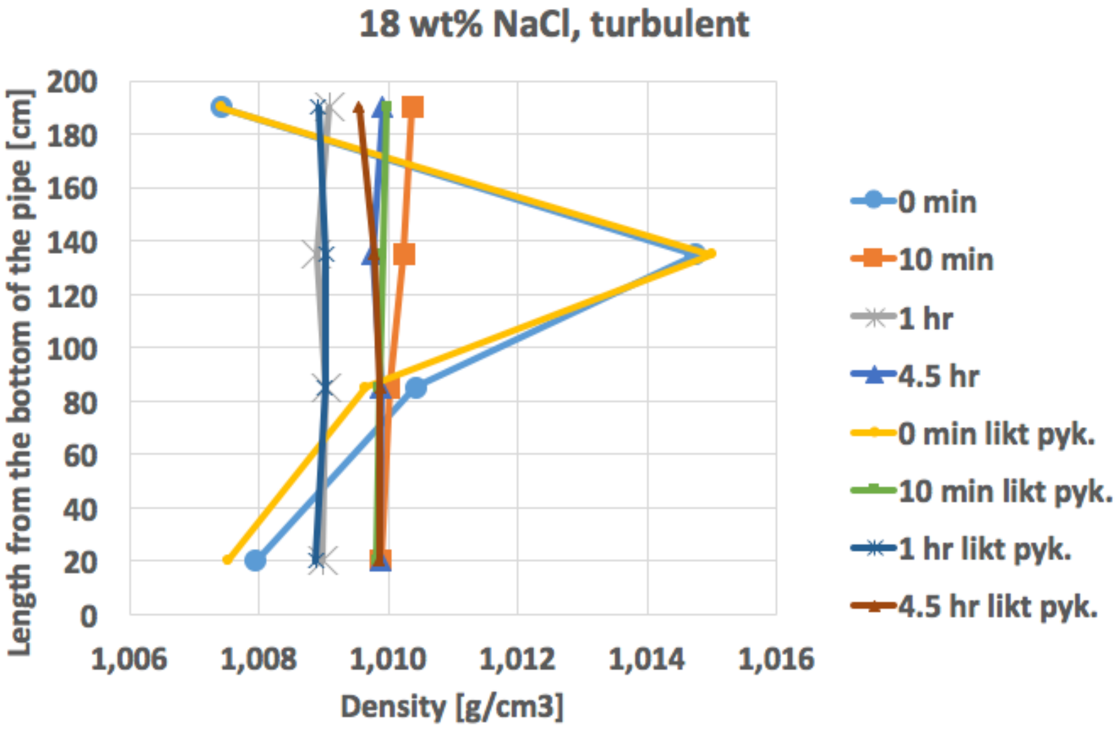

Figure B.3 *Density distribution with respect to pipe height for a 18 wt % NaCl brine. Turbulent flow.*

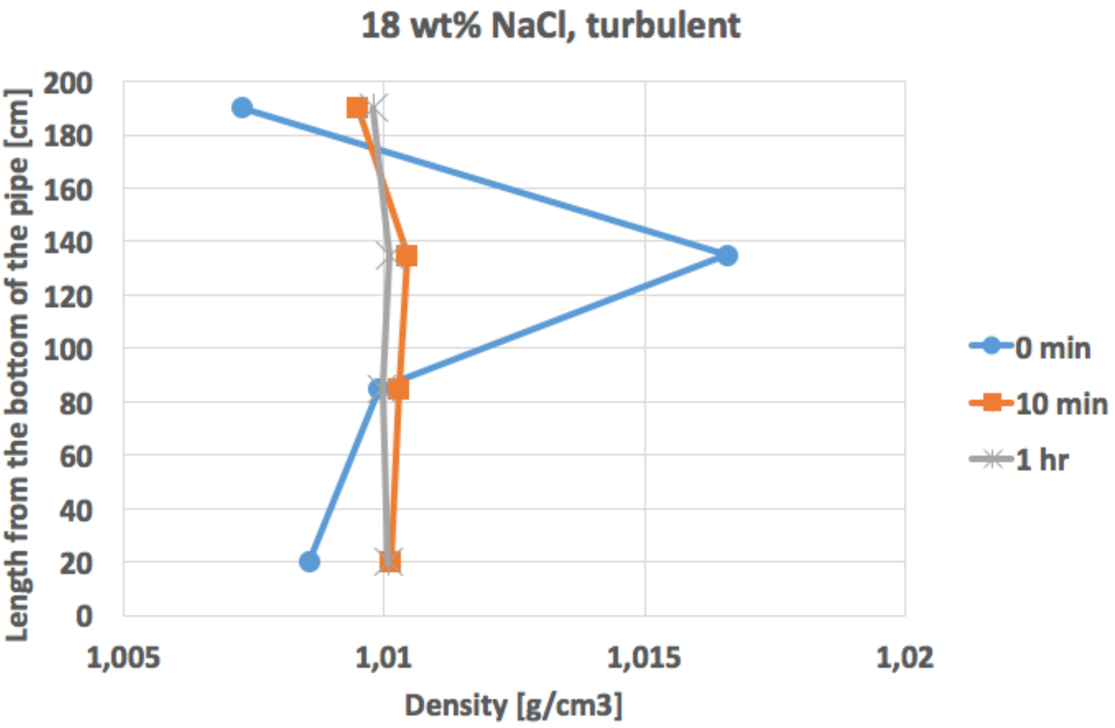

Figure B.4 *Density distribution with respect to pipe height for a 18 wt % NaCl brine. Turbulent flow.*

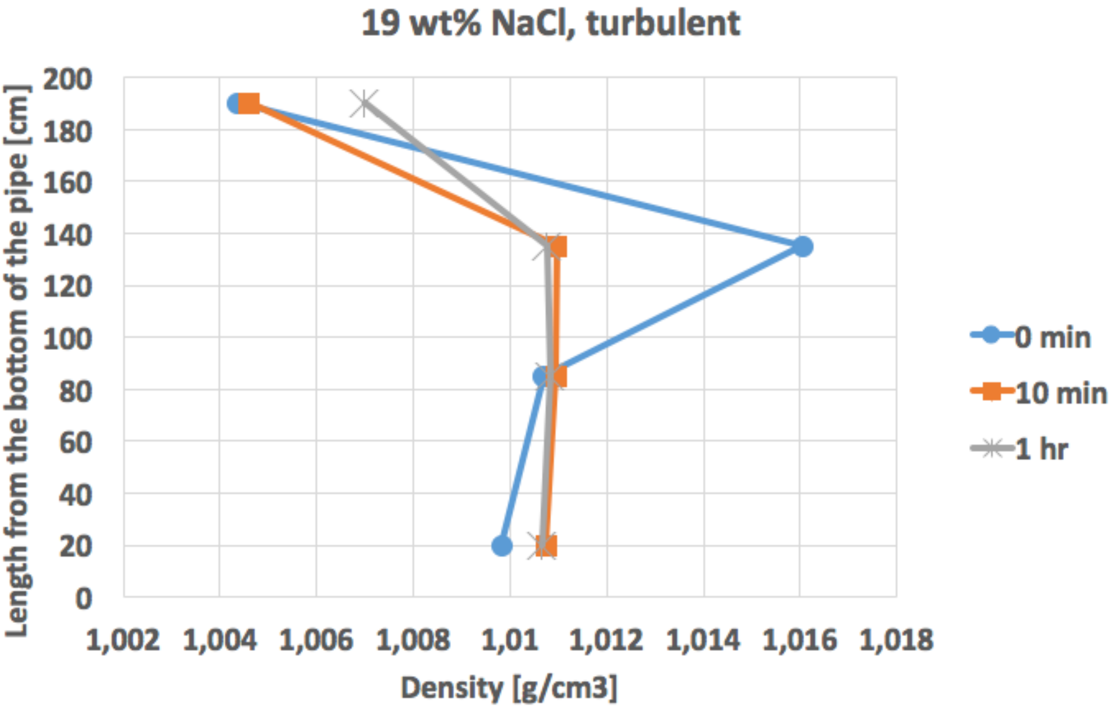

Figure B.5 *Density distribution with respect to pipe height for a 19 wt % NaCl brine. Turbulent flow.*

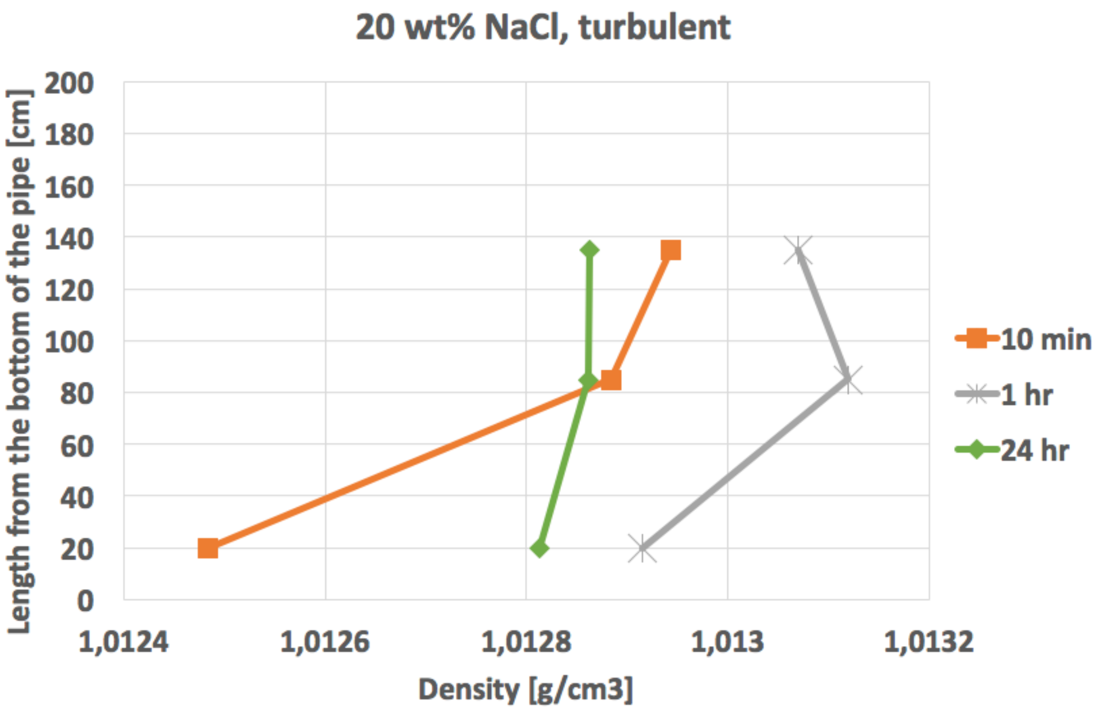

Figure B.6 *Density distribution with respect to pipe height for a 20 wt % NaCl brine. 45 L distilled water was filled in the pipe. Turbulent flow.*

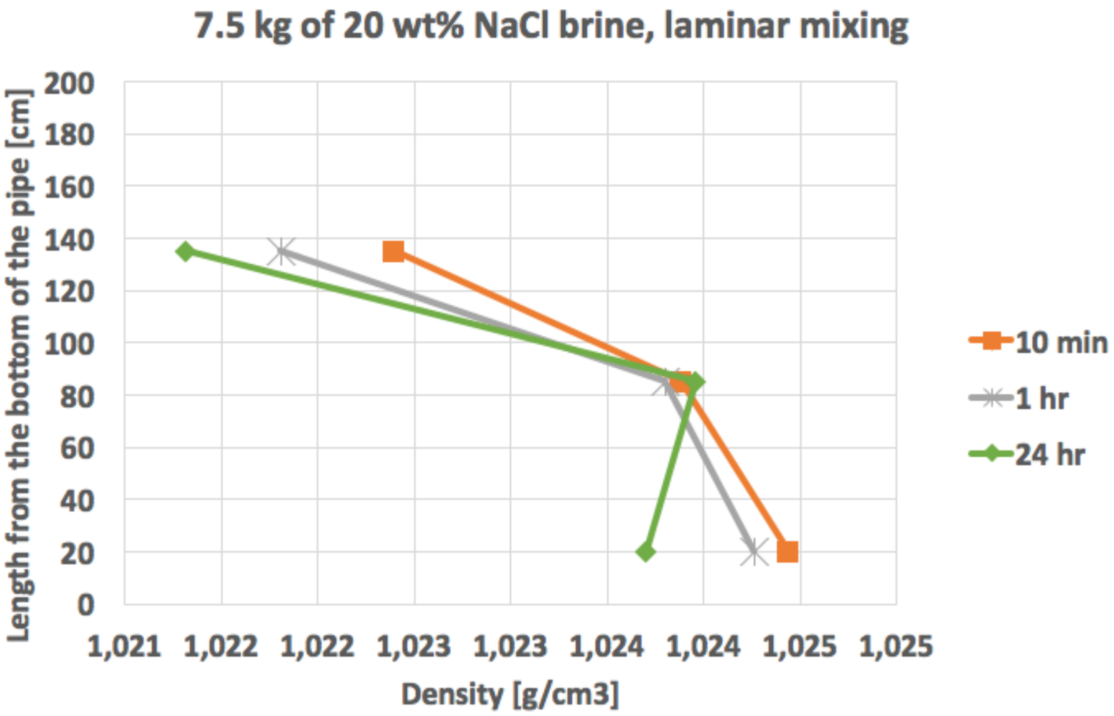

Figure B.7 *Density distribution with respect to pipe height for a 20 wt % HCOOK brine. 35 L distilled water was filled in the pipe. Laminar flow.*

B.2 HCOOK Results

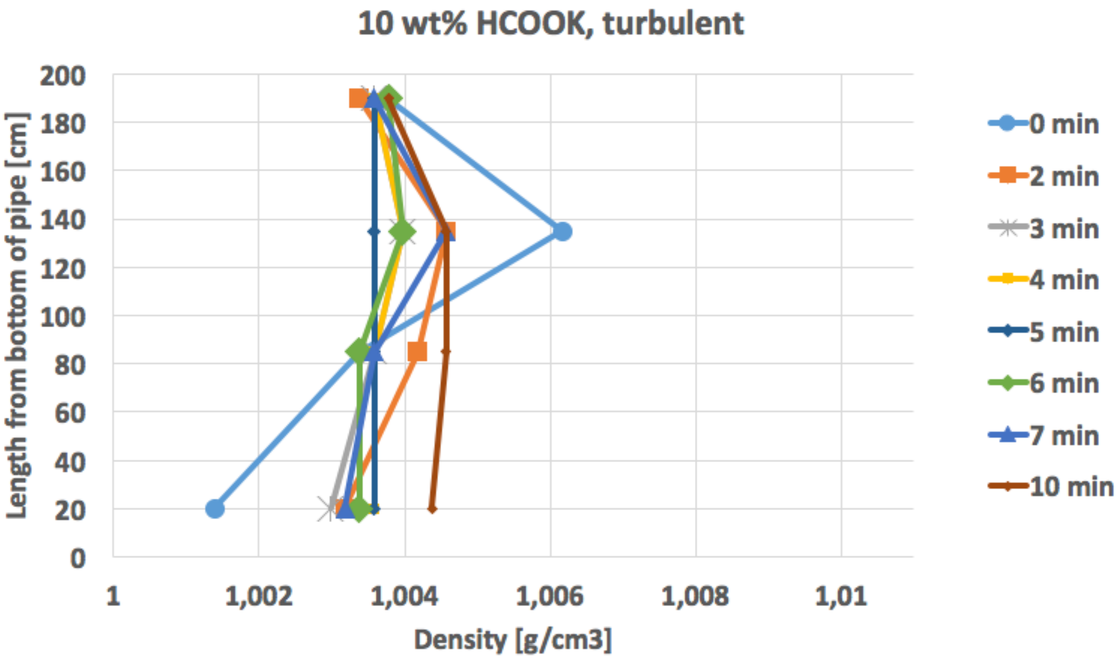

Figure B.8 *Density distribution with respect to pipe height for a 10 wt % HCOOK brine. Turbulent flow.*

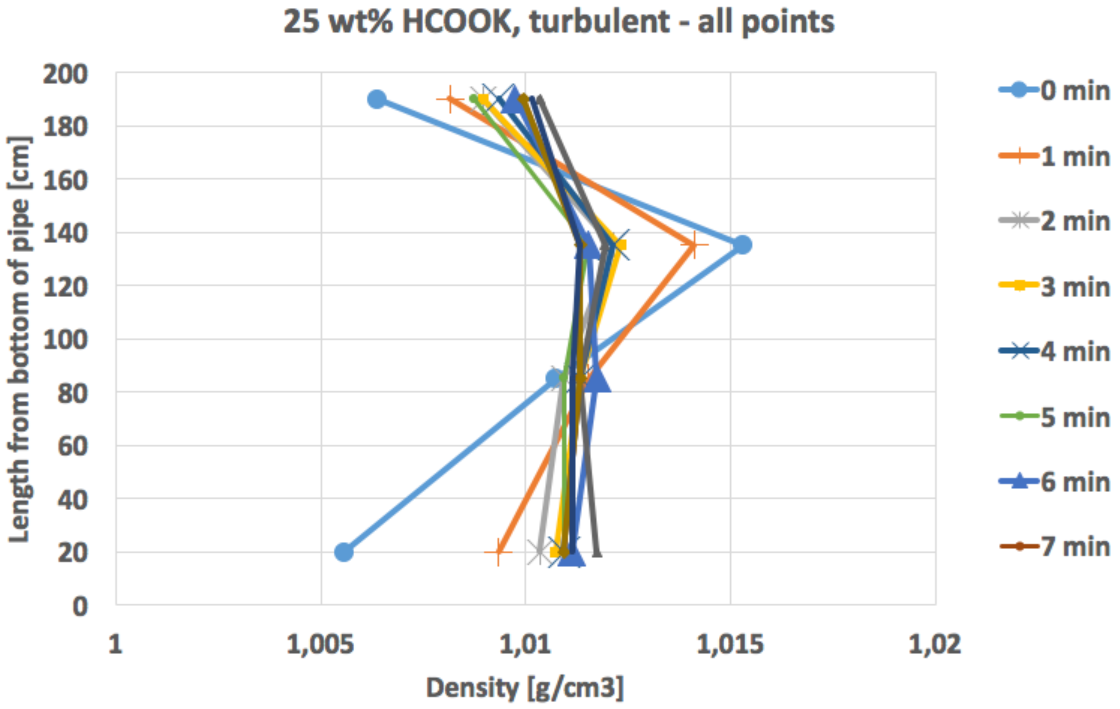

Figure B.9 *Density distribution with respect to pipe height for a 25 wt % HCOOK brine. Turbulent flow.*

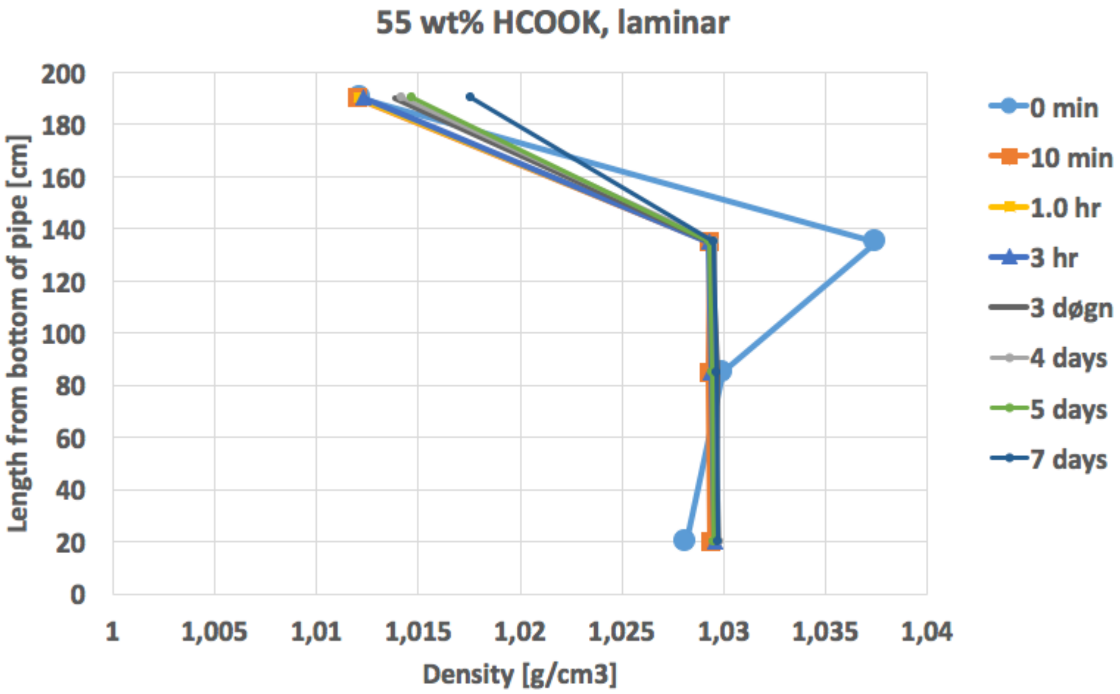

Figure B.10 *Density distribution with respect to pipe height for a 55 wt % HCOOK brine. Laminar flow.*

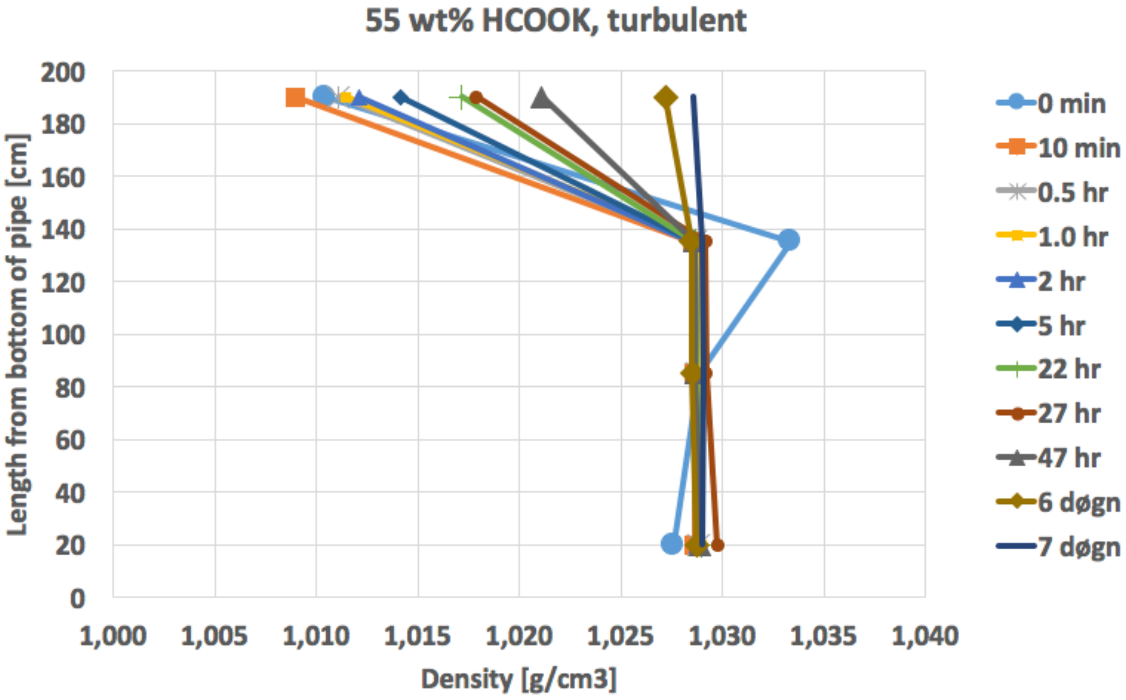

Figure B.11 *Density distribution with respect to pipe height for a 55 wt % HCOOK brine. Turbulent flow.*

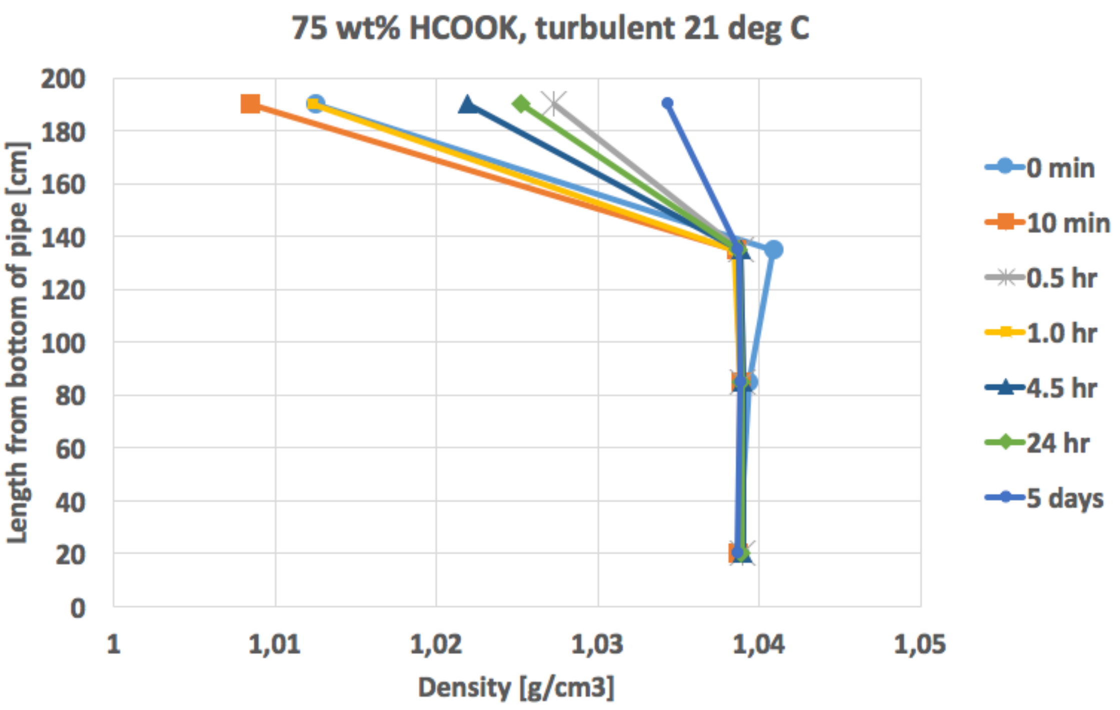

Figure B.4 *Density distribution with respect to pipe height for a 75 wt % HCOOK brine. Turbulent flow. All the pycnometer measurements are done at 21℃.*

Appendix C Conducting Risk Assessments

Detailed Risk Report

ID	20199	**Status**	**Date**
Risk Area	Risikovurdering: Helse, miljø og sikkerhet (HMS)	Created	11.05.2017
Created by	Karoline Oen	Assessment started	11.05.2017
Responsible	Karoline Oen	Actions decided	11.05.2017
		Closed	28.05.2017

Risk Assessment:

Risk assessment for the master thesis; mixing of salts with various concentrations

Valid from-to date:

1/15/2017 - 12/31/2017

Location:

Trondheim, Norway

Goal / purpose

The goal is to find mixing abilities of different salt with various concentrations in a 2 m vertical pipe. During the risk assessment I would like to be more aware of the hazards that can occur.

Background

Investigate the salt potassium formate as a potential gas hydrate inhibitor in a shut-in well. The experiments are simple, with few risks. It is standard procedure to make a risk assessment sheet.

Description and limitations

Two different laboratories are used for the experiments, both at PTS (NTNU). One laboratory for the mixing of the salts. The other laboratory is used when the density of the samples are measured with pycnometers.
Hydrocarbon oil, condensate and gas phases are not used during the experiments for practical and HSE reasons.

Prerequesites, assumptions and simplifications

No gas hydrates are made. The mixing of the salt in the pipe is investigated to investigate the mixing of the salt in water for hydrate dissociation and prevention purposes.

Attachments

[Ingen registreringer]

References

[Ingen registreringer]

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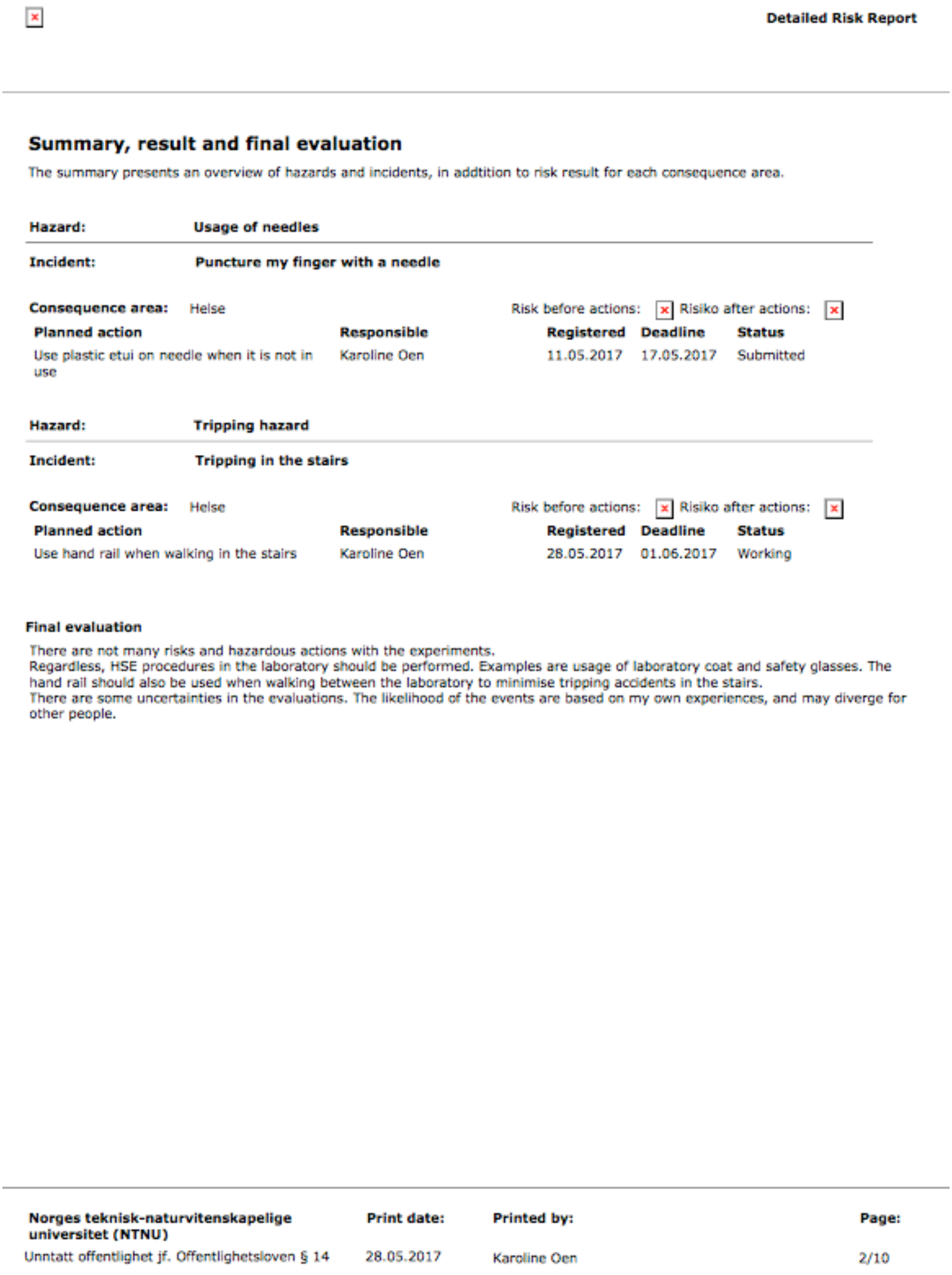

Detailed Risk Report

Summary, result and final evaluation

The summary presents an overview of hazards and incidents, in addtition to risk result for each consequence area.

Hazard: **Usage of needles**

Incident: **Puncture my finger with a needle**

Consequence area: Helse Risk before actions: ☒ Risiko after actions: ☒

Planned action	**Responsible**	**Registered**	**Deadline**	**Status**
Use plastic etui on needle when it is not in use	Karoline Oen	11.05.2017	17.05.2017	Submitted

Hazard: **Tripping hazard**

Incident: **Tripping in the stairs**

Consequence area: Helse Risk before actions: ☒ Risiko after actions: ☒

Planned action	**Responsible**	**Registered**	**Deadline**	**Status**
Use hand rail when walking in the stairs	Karoline Oen	28.05.2017	01.06.2017	Working

Final evaluation

There are not many risks and hazardous actions with the experiments.
Regardless, HSE procedures in the laboratory should be performed. Examples are usage of laboratory coat and safety glasses. The hand rail should also be used when walking between the laboratory to minimise tripping accidents in the stairs.
There are some uncertainties in the evaluations. The likelihood of the events are based on my own experiences, and may diverge for other people.

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Detailed Risk Report

Organizational units and people involved

A risk assessment may apply to one or more organizational units, and involve several people. These are lsited below.

Organizational units which this risk assessment applies to

- Institutt for geovitenskap og petroleum

Participants

Georg J. B. Voss
Roar Larsen

Readers

[Ingen registreringer]

Others involved/stakeholders

The employees at the laboratory who helps me with practical problems.

The following accept criteria have been decided for the risk area Risikovurdering: Helse, miljø og sikkerhet (HMS):

Helse	Materielle verdier	Omdømme	Ytre miljø

Detailed Risk Report

Overview of existing relevant measures which have been taken into account

The table below presents existing measures which have been take into account when assessing the likelihood and consequence of relevant incidents.

Hazard	Incident	Measures taken into account
Usage of needles	Puncture my finger with a needle	
Tripping hazard	Tripping in the stairs	

Existing relevant measures with descriptions:

Protective goggles
[Ingen registreringer]

Lab coat
[Ingen registreringer]

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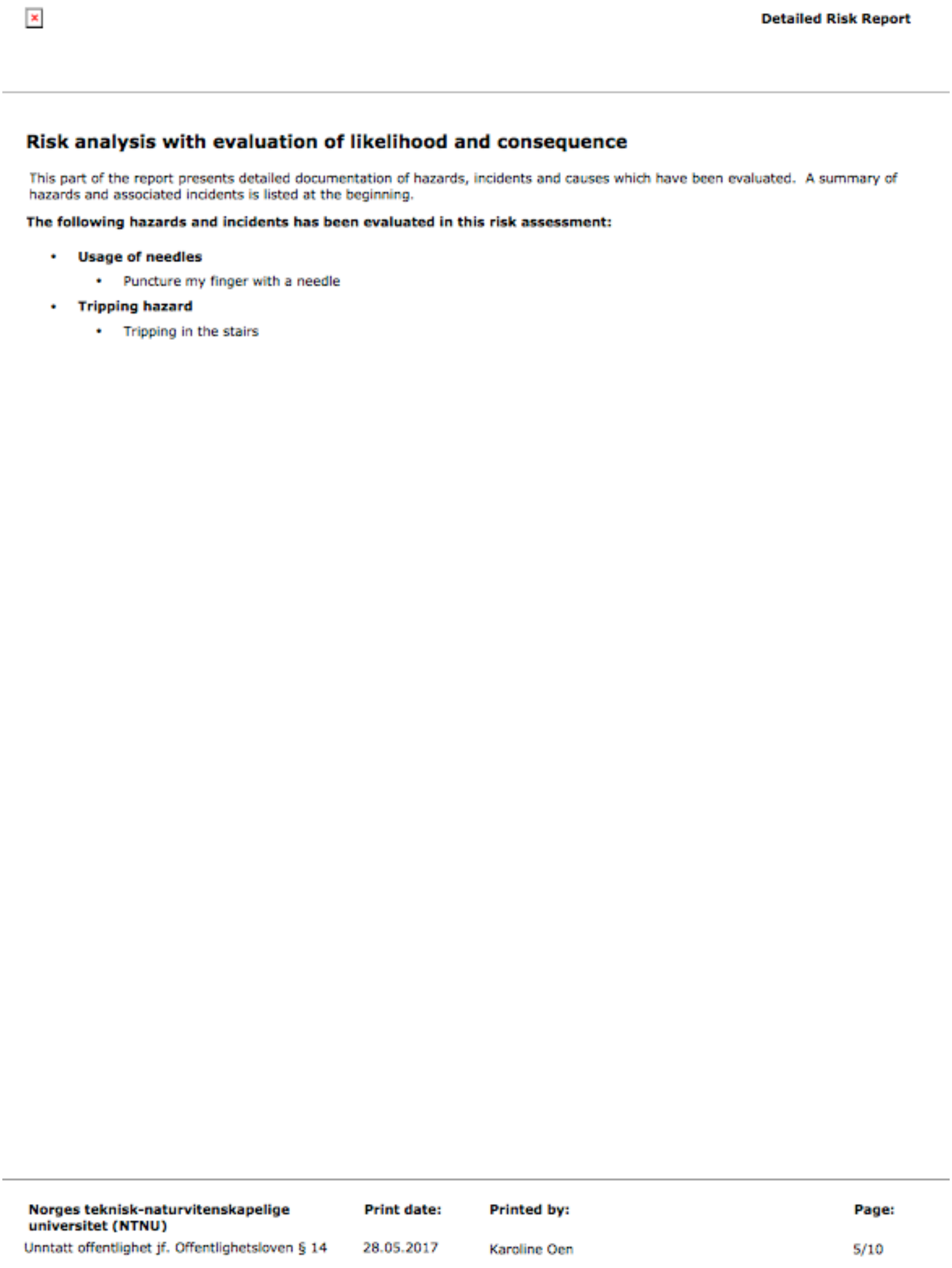

Detailed Risk Report

Risk analysis with evaluation of likelihood and consequence

This part of the report presents detailed documentation of hazards, incidents and causes which have been evaluated. A summary of hazards and associated incidents is listed at the beginning.

The following hazards and incidents has been evaluated in this risk assessment:

- **Usage of needles**
  - Puncture my finger with a needle
- **Tripping hazard**
  - Tripping in the stairs

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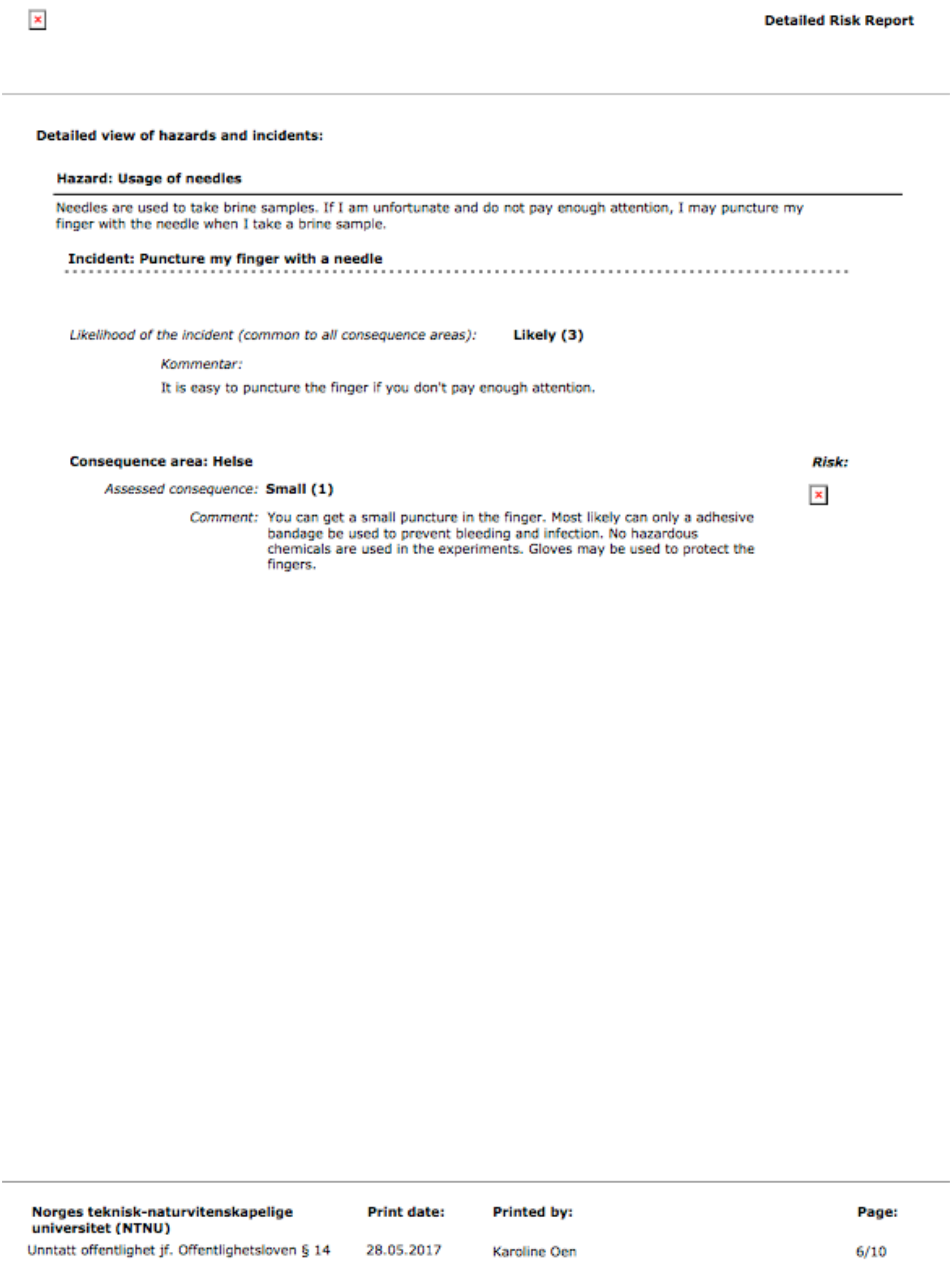

Detailed Risk Report

Detailed view of hazards and incidents:

Hazard: Usage of needles

Needles are used to take brine samples. If I am unfortunate and do not pay enough attention, I may puncture my finger with the needle when I take a brine sample.

Incident: Puncture my finger with a needle

Likelihood of the incident (common to all consequence areas): **Likely (3)**

Kommentar:

It is easy to puncture the finger if you don't pay enough attention.

Consequence area: Helse

Risk:

Assessed consequence: **Small (1)**

Comment: You can get a small puncture in the finger. Most likely can only a adhesive bandage be used to prevent bleeding and infection. No hazardous chemicals are used in the experiments. Gloves may be used to protect the fingers.

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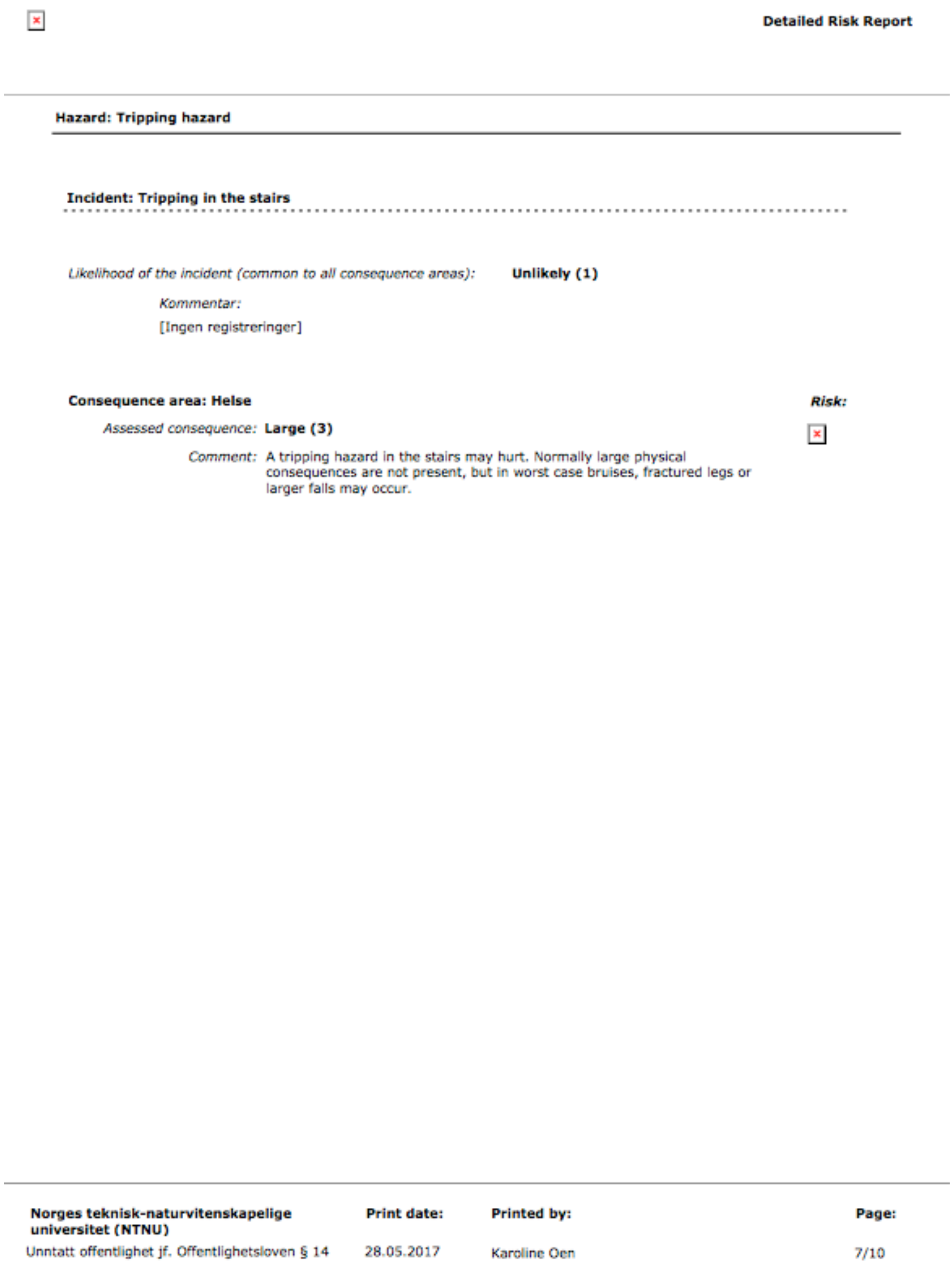

Detailed Risk Report

Hazard: Tripping hazard

Incident: Tripping in the stairs

Likelihood of the incident (common to all consequence areas): **Unlikely (1)**

Kommentar:

[Ingen registreringer]

Consequence area: Helse

Risk:

Assessed consequence: **Large (3)**

Comment: A tripping hazard in the stairs may hurt. Normally large physical consequences are not present, but in worst case bruises, fractured legs or larger falls may occur.

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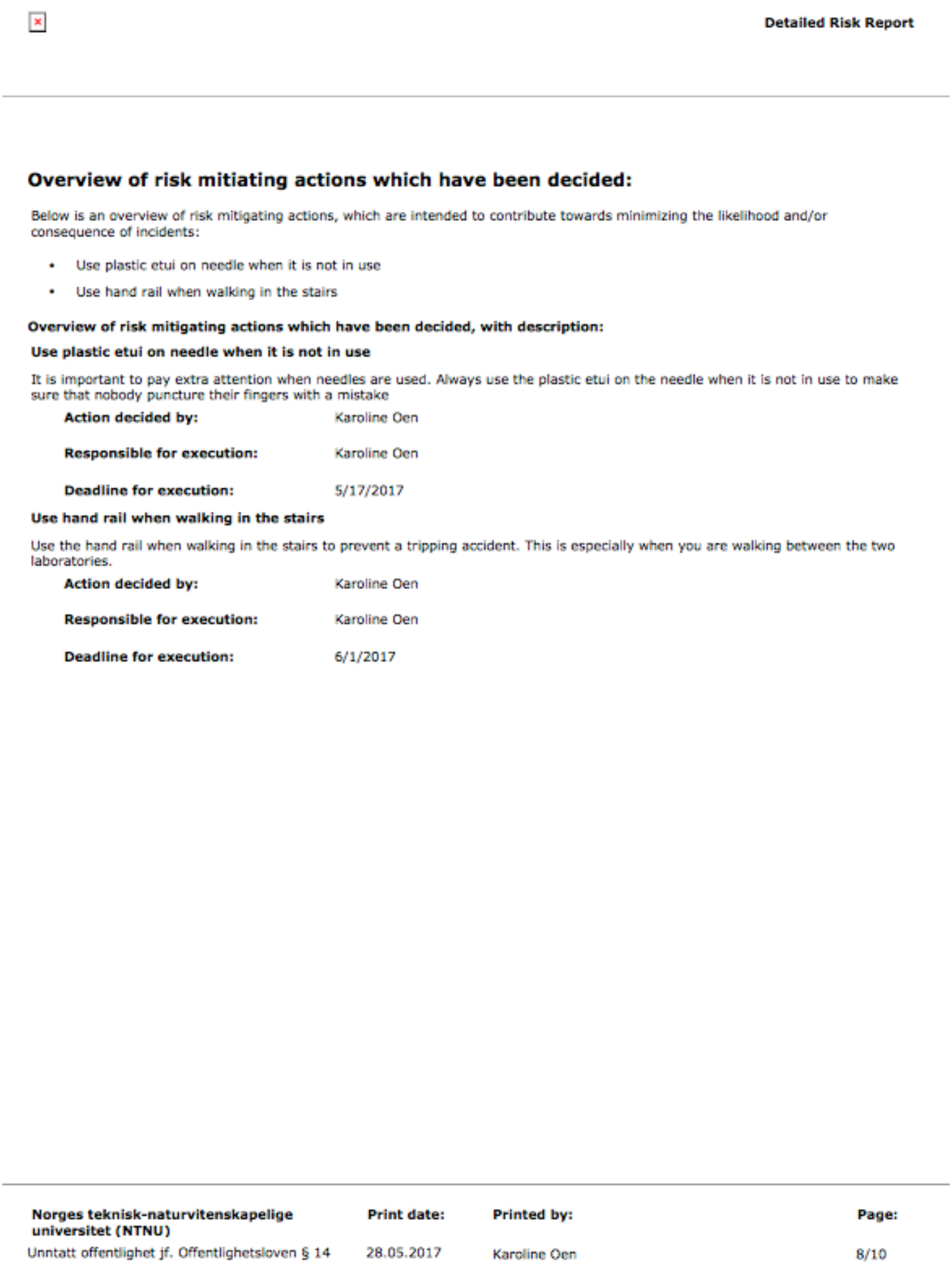

Detailed Risk Report

Overview of risk mitiating actions which have been decided:

Below is an overview of risk mitigating actions, which are intended to contribute towards minimizing the likelihood and/or consequence of incidents:

- Use plastic etui on needle when it is not in use
- Use hand rail when walking in the stairs

Overview of risk mitigating actions which have been decided, with description:

Use plastic etui on needle when it is not in use

It is important to pay extra attention when needles are used. Always use the plastic etui on the needle when it is not in use to make sure that nobody puncture their fingers with a mistake

Action decided by: Karoline Oen

Responsible for execution: Karoline Oen

Deadline for execution: 5/17/2017

Use hand rail when walking in the stairs

Use the hand rail when walking in the stairs to prevent a tripping accident. This is especially when you are walking between the two laboratories.

Action decided by: Karoline Oen

Responsible for execution: Karoline Oen

Deadline for execution: 6/1/2017

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Detailed view of assessed risk for each hazard/incident before and after mitigating actions

Hazard: Usage of needles

Incident: Puncture my finger with a needle

Likelihood assessment (common to all consequence areas)

Initial likelihood: Likely (3)

Reason: It is easy to puncture the finger if you don't pay enough attention.

Likelihood after actions: Likely (3)

Reason:

Consequence assessments:

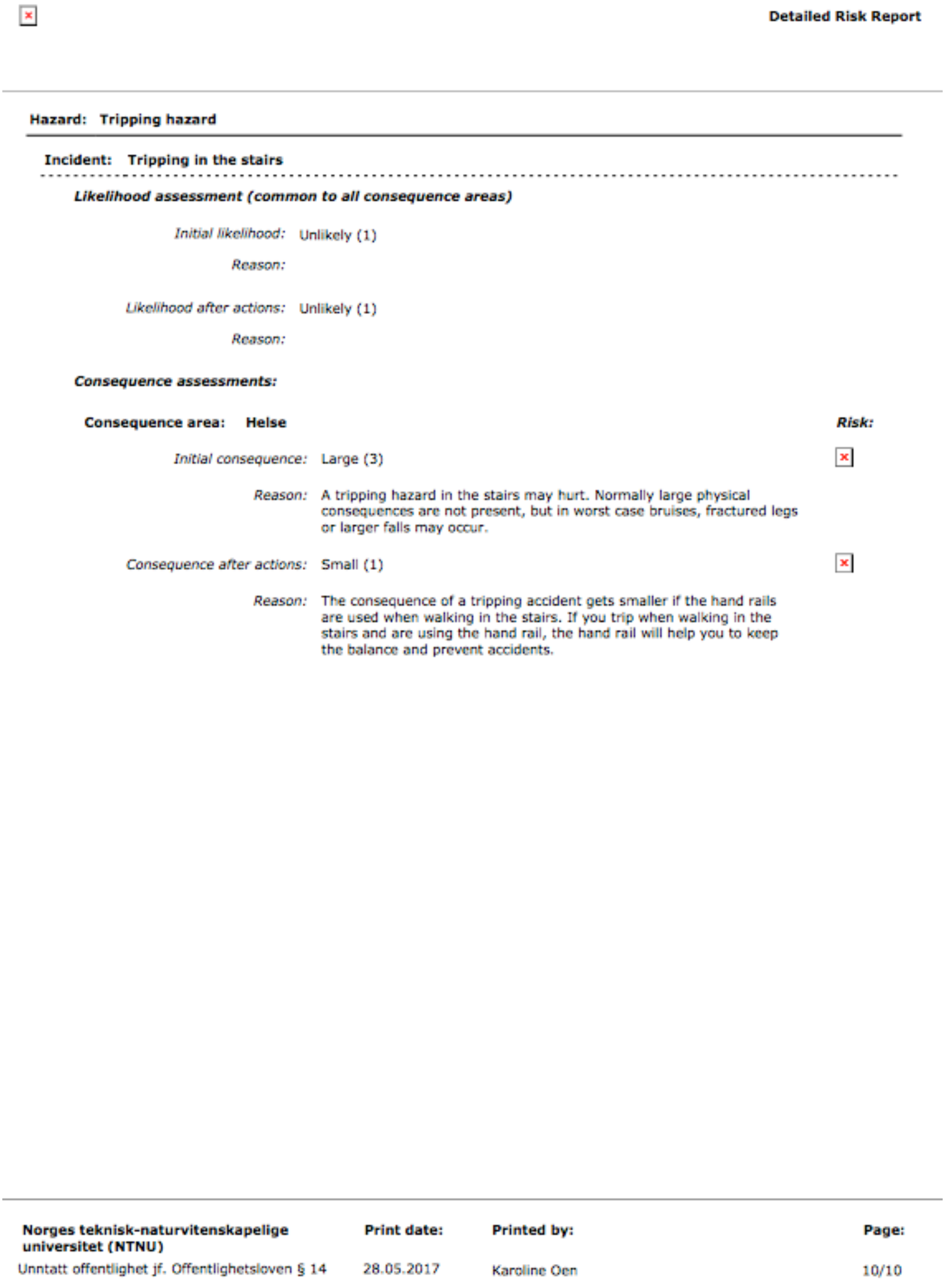
Consequence area: Helse ***Risk:***

Initial consequence: Small (1)

Reason: You can get a small puncture in the finger. Most likely can only a adhesive bandage be used to prevent bleeding and infection. No hazardous chemicals are used in the experiments. Gloves may be used to protect the fingers.

Consequence after actions: Small (1)

Reason: No hazardous fluids were used. The needle was clean and the etui was used when samples were not taken.



Detailed Risk Report

Hazard: Tripping hazard

Incident: Tripping in the stairs

Likelihood assessment (common to all consequence areas)

Initial likelihood: Unlikely (1)

Reason:

Likelihood after actions: Unlikely (1)

Reason:

Consequence assessments:

Consequence area: Helse ***Risk:***

Initial consequence: Large (3)

Reason: A tripping hazard in the stairs may hurt. Normally large physical consequences are not present, but in worst case bruises, fractured legs or larger falls may occur.

Consequence after actions: Small (1)

Reason: The consequence of a tripping accident gets smaller if the hand rails are used when walking in the stairs. If you trip when walking in the stairs and are using the hand rail, the hand rail will help you to keep the balance and prevent accidents.

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Appendix D Nomenclature

Clathrate - when a compound, e.g. a gas molecule, is physically enclosed inside the crystal structure of another.

Clathrate hydrate - a structure that consists of water molecules that encloses gas molecules within the cavities. Hydrate is often used for clathrate hydrate.

Colligative property – properties of solutions that only depend on number of molecules dissolved in the solute, and no other properties of the dissolved molecules.

Hydrate - a chemical compound that contains water molecules.

Hydration free energy, G_{hyd} - the free energy needed to dissolve a substance in the aqueous phase

Hydration number, n - number of water molecules per guest molecule.

M - 10^6.

o.e. – oil equivalent

Specific gravity of gas - molar mass of the gas divided by molar mass of air

Subcooling, supercooling - Temperature decrease from the equilibrium temperature.

Supercooled water - Water below its freezing point in a liquid state.

Supersaturation - liquid [solvent] contains more dissolved solute than can be ordinarily dissolved at that temperature.