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Effect of Injected Chemical Density on Hydrate Blockage Removal in Vertical Pipes: Use of MEG/MeOH Mixture to remove Hydrate Blockage

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Keywords: gas hydrate, MEG/methanol mixture, hydrate blockage removal, flow assurance

ABSTRACT:

One of the problems with natural gas production in the pipes is gas hydrate formation which can lead to blockage. Although there are options to inhibit hydrate formation e.g. thermodynamic hydrate inhibitors and kinetic hydrates inhibitors, hydrate blockage can occur in some cases, e.g. underestimation of water cut production, unplanned shut-in, inappropriate inhibitor injection method or failure of inhibitor delivery. There are a number of remediation methods for hydrate blockage removal such as depressurization, chemical injection e.g. methanol and MEG, mechanical, and thermal methods. In the case of chemical useage in vertical pipes, density plays
an important role and needs to be considered. In this work, the effect of chemical density on removing hydrate blockage in the vertical pipes was assessed using a long window rig. The use of methanol/MEG mixtures in removing hydrate blockage in vertical pipes could be more efficient than methanol or MEG alone. The results indicate that a mixture of methanol/MEG with a density of 1 g/cc could remove hydrate blockage successfully and efficiently. The hydrostatic pressure of aqueous phase due to chemical injection could be reduced by using methanol/MEG mixture, because the amount of methanol/MEG mixture required for removing plug could be less than methanol or MEG alone. In addition, ice formation during hydrate dissociation due to its endothermic nature should be taken into consideration during chemical injection.

1. Introduction

Gas hydrate is one of the flow assurance issues that can cause serious problems and blockage in pipes. Unplanned shut-in, failure of inhibitor delivery pumps or increased water content can result in hydrate formation and then hydrate blockage in pipes (Hunt, 1996; Jamaluddin et al., 1991; Kinnari et al., 2014). Several remediation options have been used to remove hydrate blockage from pipes including depressurization (Lee et al., 2009; Piemontese et al., 2015; Kashou et al., 2004; Sloan et al., 2010; Bollavaram and Sloan, 2003; Teixeira et al., 1998; Davies et al., 2006), chemical (Davalath and Barker, 1995; Lysne and Larsen, 1995), mechanical (Nepomiluev and Streletskaia, 2014; Reyna and Stewart, 2001), and thermal (Davalath, 1997; Davies et al., 2006; Loschen and Thiel, 1997; Reyna and Stewart, 2001). Although the depressurization is the most commonly used technique in the industry, it has some limitations, i.e., there is a risk of hydrate plug movement during depressurizing. In some cases, it is not possible to use depressurization e.g. in the vertical pipes and wells due to the hydrostatic head associated with the column of liquid on top of the plug. In these cases, depressurization could be
done using a pump or other techniques (Piemontese et al., 2015). Experimental Investigation of hydrate plug dissociation and its modelling using depressurization (two-sided and one-sided) and radial electrical heating were carried out by Davies et al. (Davies et al., 2006). They showed that hydrate dissociation is predominately limited by heat transfer, and the time required for hydrate dissociation depends on hydrate structure, i.e., s-II hydrates dissociate more slowly than s-I hydrates. In addition, hydrate plug removal could be time-consuming and presents safety concerns (Saleh, 2002). Therefore, all methods for hydrate plug removal need to be evaluated.

The use of chemical injection for removing hydrate blockage is an option in vertical pipes. Thermodynamic hydrate inhibitors (THIs) such as methanol (MeOH) and mono-ethylene glycol (MEG) can melt hydrates and inhibit further hydrate formation. They shift the hydrate phase boundary to a lower temperature at a particular pressure or higher pressure at a particular temperature. Selection of different THIs for hydrate blockage removal in vertical pipes needs to be considered in terms of ability to penetrate into hydrates body and melt the plug. As the density of methanol, hydrate, water, and MEG increase respectively ($\rho_{\text{MeOH}} < \rho_{\text{hydrate}} < \rho_{\text{water}} < \rho_{\text{MEG}}$), the choice of the chemical plays an important role in the vertical pipes when removing hydrate blockages. Previous work on investigation of hydrate plug removal in vertical pipes has shown the ability of MEG to penetrate into hydrate plugs (Aminnaji et al., 2017). It showed that although the amount of MEG required is more than that calculated by thermodynamic modelling due to a non-homogeneous system, the hydrate plug was eventually removed by MEG injection.

In the following work to evaluate THIs for hydrate blockage removal in the vertical pipes, two separate tests were carried out to assess the potential of methanol and a mixture of MeOH/MEG injection for removing hydrate plugs. The main objective of this work was investigation of THIs performance with different densities in removing hydrate blockage. In addition, the project
aimed to investigate hydrate dissociation rate, ability of THI to penetrate into bulk hydrates, the possibility of ice formation during hydrate dissociation, and possibility of movement of hydrate plugs. In the first test, methanol was injected into a system with hydrate blockage, in the second test, in order to remove hydrate blockage, a mixture of MeOH/MEG with a density of 1 g/cc was used. A comparison of three chemical injection tests with different density of injected inhibitor phase (MeOH\textsuperscript{this work}, MeOH/MEG injection\textsuperscript{this work}, and MEG (Aminnaji et al., 2017)) may give information of the role of injected chemical density in hydrate blockage removal in the vertical pipes. The results of this work are reported in this publication.

2. Experimental

2.1. Materials, and Method

The purity of MEG and Methanol used was 99.8 % and supplied by Fisher Scientific (catalog numbers E177-20 and A452-1, respectively). Deionized water was used in all experiments. The composition of the natural gas mixture used in the tests is given in Table 1. The thermodynamic hydrate phase boundary was predicted using HydraFLASH\textsuperscript{®}, a thermodynamic model developed by Hydrafact Ltd and Heriot-Watt University. The estimated percentage of water converted to hydrates (WCH %) was calculated using the method presented in previous work (Aminnaji et al., 2017).
Table 1. Composition of North Sea natural gas used in experiments.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>87.93</td>
</tr>
<tr>
<td>Ethane</td>
<td>6.00</td>
</tr>
<tr>
<td>Propane</td>
<td>2.04</td>
</tr>
<tr>
<td>i-Butane</td>
<td>0.20</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.30</td>
</tr>
<tr>
<td>CO2</td>
<td>2.03</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.50</td>
</tr>
</tbody>
</table>

2.1. Equipment

Studies were carried out using an in-house designed/built long cylindrical and windowed experimental rig with full temperature gradient control along the 1.5 meter cylindrical body of the cell (75 mm internal diameter and 6.8 litres total volume), as illustrated in Figure 1. This long windowed rig equipped with a stirrer (to encourage hydrate formation), consists of 6 sections with 6 separate jackets each connected to a bath and with 12 soda-lime glass windows (6 pairs), enabling visual monitoring of the system. The pressure at the two ends of the cell is measured by two precision Quartzdyne transducers (±0.07 bar), calibrated using a Budenberg dead weight tester. The temperature of the system is measured by 12 platinum resistance thermometers (PRT) with a measurement accuracy of ± 0.1 °C, allowing the temperature of each section to be monitored in two opposite locations. A detailed description of the experimental setup is given elsewhere (Aminnaji et al., 2017).
2.3. Procedure

To investigate the ability of different chemicals in removing hydrate blockage in vertical pipes and have comparable results with MEG injection (Aminnaji et al., 2017), a similar procedure was carried out. The long window rig was located in the vertical position and then loaded with deionized water. Then, natural gas was injected into the vacuumed cell. The cell temperature decreased to 4.5 °C to form hydrates. This temperature was chosen as it is close to seabed temperature. A long time was required to block the system completely, i.e., no pressure communication through the hydrate body. Finally, hydrate dissociation and hydrate blockage removal at constant pressure by step-wise chemical injection from the top of the cell (MeOH and a mixture of MeOH/MEG) was investigated. The system pressure was kept constant and the gas released from hydrate dissociation was removed from the top of the cell and measured by a gasometer. The volume ratio of liquid/gas in all experiments was 0.44.
3. Results and discussion

3.1. Methanol Injection

The system was loaded with 2066 g of deionized water. Natural gas (675 g) was injected into the vacuumed cell in one step. Table 2 lists more details of this test including the amount of hydrates which formed in the test. Based on pressure drop during the hydrate formation, 73 mass% of water was converted to hydrates over 30 days. Although formation of roughly 12% hydrates resulted in stirrer stoppage, i.e., this amount of hydrates blocked the system and the stirrer could not rotate, the system was not completely blocked as there was a pressure communication through the system. It suggests that it is possible to form large quantities of hydrates in the absence of any active mixing, i.e., the stirrer stopped and there was nothing (e.g. gas bubbling) to encourage the system to form hydrates by mixing the system and increasing the water/gas interface. Finally, as Figure 6 shows, the first two windows were completely blocked and pressure transducers at either end of the cell showed different values indicating complete blockage and no pressure communication through the hydrate body.

Figure 2 shows that 30 mass% methanol could dissociate all hydrates of this system (if the system is homogeneous). Therefore, methanol was injected in three steps, as listed in Table 3 (18, 26, and 30 mass% MeOH in total). Figure 6 (Window 3) shows that dyed injected methanol was located on the top of the hydrates body and couldn’t penetrate to the hydrate plug due to its lower density. Therefore, only some of those hydrates which were contact with methanol at the interface of methanol/hydrate bulk dissociated. Figure 3 indicates that the hydrate dissociation rate in the first few hours of the first injection was very high and then gradually decreased. The main reason is that there was no mixing in the system. Another reason could be dilution of the methanol, i.e., in fact, the fresh water which came from hydrate dissociation diluted the methanol
and reduced its effectiveness. However, fresh methanol couldn’t penetrate through aqueous phase due to its lower density.

**Table 2.** Details of gas injection including amount of gas injected, calculated percent water converted to hydrate 30 days after the beginning of the experiment of the methanol injection test.

<table>
<thead>
<tr>
<th>No.</th>
<th>Amount of gas</th>
<th>Liquid mole fraction</th>
<th>WCH%</th>
<th>No. of days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>675 g</td>
<td>36.7 mole fraction</td>
<td>0.76</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

**Table 3.** Details of methanol injection into the long windowed rig.

<table>
<thead>
<tr>
<th>No. of injection</th>
<th>Type</th>
<th>Mass / g</th>
<th>Volume / cc</th>
<th>Total Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>methanol</td>
<td>516</td>
<td>651</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>methanol</td>
<td>203</td>
<td>256</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>methanol</td>
<td>200</td>
<td>252</td>
<td>30</td>
</tr>
</tbody>
</table>

**Figure 2.** Hydrate phase boundary for natural gas system with different amount of methanol and operating condition.
As shown in Figure 3, the effect of methanol gradually diminished after the first injection and then hydrate dissociation stopped, so more methanol, 26 and 30 mass%, was injected. These two methanol injections were not able to dissociate hydrate as Figure 3 doesn’t show any increase in pressure/gas volume curves after the last two injections. Although the total methanol concentration in the system after the last methanol injection was 30 mass% the system was still blocked, even though, Figure 2 shows that this amount of methanol should dissociate all hydrates in this system. The main reason for this is the lower density of methanol compared to water and hydrate. Basically, the fresh water which is associated with hydrate dissociation prevents methanol from penetrating into the hydrate plug due to its lower density. Dilution of methanol, non-homogeneous methanol distribution/concentration in the absence of any active mixing in the system, localized low temperature, and localized compositional variations could be the other reasons for the aforementioned behavior of methanol in removing and dissociating of gas hydrates in a vertical pipe.

Data acquisition system recorded reduction of temperature in the hydrate-methanol contact zone during hydrate dissociation and recorded some low temperature as much as -2 °C. This sub-zero temperature indicates the possibility of ice formation during hydrate dissociation. The system temperature in each section of the rig during the methanol injection is shown in Figure 4.
Figure 3. Volume of gas from hydrate dissociation at standard conditions, percentage of dissociatedhydrate, and pressure response due to methanol injection versus time. The pressure build-up due to methanol injection was calculated based on the volume of methanol injected considering the volume of gas released due to hydrate dissociation. Use the line with the open circles for both hydrate gas dissociation and percentage of dissociation hydrate axes.
Figure 4. Temperature profile for the different sections of the rig during methanol injection.

As methanol was not able to remove hydrate blockage, it was decided to depressurize the system. The main aim of this work was to promote hydrate dissociation. This could be achieved by keeping the system farther away from the hydrate phase boundary. Depressurization was done in three steps by removal of gas from the top of the cell. The system pressure at the top of the hydrate plug decreased from 79 to 65, 59, and 34 bara as shown in Figure 2. Figure 5 shows the pressures at above and below the hydrate plug during the depressurization. It shows that hydrates didn’t dissociate in the first two depressurizations as the system pressure at the top of the cell didn’t increase.

Finally, in the last depressurization, the pressure difference between the ends of hydrate blockage increased to 47 bara (pressure at top and bottom of cell were 34 and 81 bara respectively). This high-pressure difference caused hydrate plug movement. As a result, the hydrate plug moved up and the system became turbulent and mixed intensely. As shown in Figure 5, the bottom pressure
decreased immediately and both pressures at top and bottom of the cell became the same after a few hours indicating hydrate blockage removal.

Although the hydrate plug was removed, all hydrates didn’t dissociate as Figure 5 shows increase of the system pressure after hydrate blockage removal. This plug movement mixes the system efficiently and methanol was distributed in the system causing hydrate dissociation. The pressure, therefore, increased very fast due to this hydrate dissociation. Figure 6 shows that the dyed methanol was distributed through the system after the last depressurization, in the first three windows, indicating the homogeneous system.

![Figure 5. Top and bottom pressures of the long windowed rig during depressurization-methanol injection test.](image)
Figure 6. Hydrate formation and dissociation, hence hydrate plug removal during methanol injection at 4.5 °C and ~81 bar. (a) no hydrate present, (b) blocked windows with hydrates before methanol, (c) 18 mass% methanol, (d) 26 mass% methanol, (e) after depressurizing to 34 bar.

3.2. Hydrate blockage removal using a mixture of methanol/MEG in vertical pipes

A mixture of methanol and MEG with a density of 1 g/cc which is equal to water density was used to remove hydrate blockage. This mixture could penetrate into the hydrate plug, i.e., the density of hydrates is lower than 1 g/cc. However, the possibility of hydrate reformation due to
produced fresh water from hydrate dissociation could be minimized by adjusting the chemical density to 1 g/cc.

The same procedure for hydrate formation and blockage removal was carried out. The cell was loaded with 2066 g of deionized water and 598 g of natural gas. Details of natural gas which was used and the amount of hydrates formed in this test are listed in Table 4. As with the previous test, the stirrer was stopped due to roughly 12 mass% hydrate formation. 65 mass% of the water was converted to hydrates over 30 days, and the system became completely blocked as indicated by a lack of pressure communication through the hydrate bulk. The different required amount of hydrate causing blockage in these two tests indicates that complete blockage of the system may occur with different amounts of hydrate. In reality, the amount of hydrates required to block the system completely, e.g. no pressure communication, is much more than the amount of hydrates required to prevent fluid movement in pipes. As mentioned, in these two tests, roughly 12 mass% hydrates resulted in stirrer stoppage, potentially preventing fluid movement in pipes. There are many factors could affect the pipeline blockage due to hydrate formation e.g. amount of hydrates, subcooling temperature, hydrate growth rate, gas composition, and pipe diameter.

Software calculation shows that 36 mass% of methanol/MEG mixture with a density of 1 g/cc could dissociate all hydrates in this system, Figure 7. Following hydrate blockage, the methanol/MEG mixture was injected stepwise. Details of chemical injections are given in Table 5. The measured gas volume produced from hydrate dissociation and pressure response due to chemical injection and hydrate dissociation are plotted in Figure 8. The system temperature for each chemical injection is shown in Figure 9.

Figure 8 shows that hydrate dissociation rate shortly after each injection was high due to hydrates coming into contact with the undiluted methanol/MEG mixture. The results show that
dilution of chemical with fresh water produced from hydrate dissociation causes reduction of dissociation rate and ultimate cessation. However, results show that the hydrate dissociation rate during methanol/MEG mixture injection is higher than MEG injection (Aminnaji et al., 2017) or methanol injection alone (this work). The reasons for this difference could be the presence of methanol and MEG simultaneously with a density of 1 g/cc.

**Table 4.** Details of gas injection including amount of gas injected, calculated percent water converted to hydrate after 30 days, from the beginning of the experiment-methanol/MEG injection test.

<table>
<thead>
<tr>
<th>No. of gas injection</th>
<th>Amount of gas</th>
<th>Liquid mole fraction</th>
<th>WCH %</th>
<th>No. of days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g mole</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>598</td>
<td>32.5</td>
<td>0.78</td>
<td>65</td>
</tr>
</tbody>
</table>

**Table 5.** Details of methanol/MEG injection into the long windowed rig.

<table>
<thead>
<tr>
<th>No.</th>
<th>Density g/cc</th>
<th>Type</th>
<th>Mass / g</th>
<th>Total / g</th>
<th>Volume / cc</th>
<th>Mass %</th>
<th>Total Mass% (relative to aqueous phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>MeOH</td>
<td>56.4</td>
<td>200</td>
<td>200</td>
<td>2.5</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MEG</td>
<td>143.6</td>
<td></td>
<td></td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>MeOH</td>
<td>56.4</td>
<td>200</td>
<td>200</td>
<td>4.6</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MEG</td>
<td>143.6</td>
<td></td>
<td></td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>MeOH</td>
<td>56.4</td>
<td>200</td>
<td>200</td>
<td>6.9</td>
<td>23.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MEG</td>
<td>143.6</td>
<td></td>
<td></td>
<td>16.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>MeOH</td>
<td>56.4</td>
<td>200</td>
<td>200</td>
<td>7.9</td>
<td>27.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MEG</td>
<td>143.6</td>
<td></td>
<td></td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>MeOH</td>
<td>56.4</td>
<td>200</td>
<td>200</td>
<td>9.2</td>
<td>32.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MEG</td>
<td>143.6</td>
<td></td>
<td></td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>MeOH</td>
<td>56.4</td>
<td>200</td>
<td>200</td>
<td>10.4</td>
<td>36.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MEG</td>
<td>143.6</td>
<td></td>
<td></td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.9</td>
<td>MeOH</td>
<td>41.4</td>
<td>100</td>
<td>111</td>
<td>11.3</td>
<td>38.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MEG</td>
<td>58.6</td>
<td></td>
<td></td>
<td>27.3</td>
<td></td>
</tr>
</tbody>
</table>
In terms of mass%, methanol shifts the hydrate phase boundary to lower temperature and higher pressures compared to MEG. The primary reason for the difference by mass is that MEG has a much higher molecular mass, so less moles per gram. They should be much more comparable if mole% is used, i.e., in fact, a quick model freezing point check suggests MEG is more inhibiting per mole. That could be down to it having two OH groups per CH₂ group, so more polar / more attractive to water in terms of hydrogen bonding. Certainly, the industries do injection based on volumes, and by volume, methanol is better than MEG in terms of inhibition, i.e., there are more moles per volume in methanol. Therefore, the mixture of methanol/MEG could be more efficient for hydrate dissociation if it is based on mass%. The evidence of system temperature reduction during hydrate dissociation for different injection (methanol, MEG, and methanol/MEG) confirms this. The temperature reduction of the system for MEG and methanol injection were 4 °C (from 1 °C to -3 °C, (Aminnaji et al., 2017)) and 6.5 °C (from 4.5 °C to -2 °C) respectively. It does suggest that methanol is stronger than MEG in terms of hydrate dissociation if a same mass% chemical is used. A further clue may be gleaned from the temperature reduction in the case of methanol/MEG injection. The temperature reduction for the methanol/MEG injection during hydrate dissociation was 8.5 °C (from 4.5 °C to -4 °C) which is higher than the previous cases, so the density could be a second reason for the effectiveness of methanol/MEG mixture in hydrate dissociation. It is notable that, ice formation is possible in all cases during hydrate dissociation.

Although methanol is better than MEG at dissociating hydrate (if the same mass% of chemical is used), it doesn’t have an ability to penetrate and remove hydrate blockage in vertical pipes due to its density. Therefore, using a mixture of MEG/methanol can increase the efficiency of hydrate
blockage removal using chemical injection in the vertical pipes. However, as the density of methanol/MEG mixture and produced fresh water are the same, the possibility of hydrate reformation in the upper section reduces. In addition, the hydrostatic pressure of injected chemical in the vertical pipes could be reduced by injection of MEG/methanol rather than MEG alone, i.e., MEG/methanol is stronger than MEG at shifting the hydrate phase boundary to lower temperature and higher pressure (if a same mass% chemical is used), hence less MEG/methanol mixture is required to remove hydrate blockage from the system.
Figure 7. Hydrate phase boundary for natural gas system with different amount of THI, i.e., injected chemical consists of methanol and MEG so that its total density is 1, and operating condition.
Figure 8. Volume of gas from hydrate dissociation at standard conditions, percentage of dissociated hydrate, and pressure response due to methanol/MEG injection versus time. The pressure build-up due to injection was calculated based on the volume of methanol/MEG injection considering the volume of gas released due to hydrate dissociation. Use the line with the open circles for both hydrate gas dissociation and percentage of dissociation hydrate axes.

Hydrate blockage was removed after the 6th chemical injection (36 mass% mixture of methanol/MEG with a density of 1 g/cc). As shown in Figure 10, hydrate blockage was removed from windows 1 and 2 at this stage and both pressure transducers at top and bottom of the cell showed the same pressure. Although the most of the hydrates dissociated and hydrate blockage removed, there were still some hydrates at the top of the aqueous phase, window 3 in Figure 10. These hydrates could be from hydrate reformation or pre-formed hydrates, i.e., pre-formed hydrates could detach from hydrates body during hydrate dissociation and then move up, at the
top of the aqueous phase, due to being less dense. As the previous results show that methanol, MEG, and methanol/MEG with a density of 1 g/cc are not able to dissociate these remaining hydrates, it was, therefore, decided to inject a mixture of methanol/MEG with a density of 0.9 g/cc. Its details are listed in Table 5. The density of methane hydrate is roughly approximated 0.91-0.94 g/cc at 273.15 K and 25.1 atmospheres (Sloan Jr and Koh, 2007). This mixture of Methanol/MEG was injected with different color, violet (the previous mixture of methanol/MEG was red). Figure 10 shows that this mixture could dissociate all hydrates in window 3 which didn’t dissociate by injection of methanol/MEG mixture with a density of 1 g/cc. It indicates that density is the most important factor in selection of chemical (MEG, methanol, and methanol/MEG mixture) for remove hydrates in vertical pipes.

Figure 9. Temperature profile for the different sections of the rig during MEG/methanol injection.
Figure 10. Hydrate formation and dissociation, hence hydrate plug removal during MEG/methanol injection at 4.5 °C and ~80 bara. (a) no hydrate present, (b) blocked windows with hydrates before methanol/MEG injection, (c) 8.8 mass% chemical*, (d) 16.2 mass% chemical*, (e) 23 mass% chemical*, (f) 27.9 mass% chemical*, (g) 32.6 mass% chemical*, (h) 36.7 mass% chemical*, (i) 3 mass% chemical†.

* Injected chemical consists of methanol and MEG so that its total density is 1.

† Injected chemical consists of methanol and MEG so that its total density is 0.9.
## 4. Conclusion

Work to assess the effect of THI density on hydrate blockage removal in the vertical pipes and whether methanol/MEG mixture has advantages over methanol or MEG alone has been undertaken with a natural gas system. Based on the findings, the following can be concluded:

1. Methanol injection can only dissociate those hydrates which contact with methanol at the top of the hydrate plug, and there is no penetration into the bulk of hydrates.

2. The mixture of methanol/MEG with a density of 1 g/cc is a better option for dissociating and removing hydrates in the vertical pipes, i.e., hydrate dissociation rate is higher than in the case of methanol or MEG injection alone and the methanol/MEG mixture can remove hydrate blockage effectively.

3. The amount of chemical required for injection in terms of mass% could be reduced by injection of methanol/MEG mixture. This also results in a reduction of hydrostatic pressure during chemical injection.

4. Hydrate reformation as a result of water generated due to hydrate dissociation could change the location of the blockage. In addition, those hydrates which are detached from the hydrate plug can move up and block the system.

5. A mixture of methanol/MEG with a density of 0.9 g/cc can dissociate those hydrates which are at the top of the aqueous phase.

6. The non-homogeneous THI-water system indicates that the mixing due to diffusion and gas release/bubbling from hydrate dissociation and depressurization is not very efficient.
7. Sub-zero temperature and ice formation are possible due to endothermic nature of hydrate dissociation.

8. Density of injected inhibitor needs to be considered in terms of its effectiveness in hydrate blockage removal in the vertical pipes.

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ABBREVIATIONS

THIs, thermodynamic hydrate inhibitors; WCH, water converted to hydrates; MEG, monoethylene glycol; MeOH, methanol.

REFERENCES


Highlights

- Hydrate blockage removal improvement in vertical pipes using a MEG/MeOH mixture.
- The importance of density of injected inhibitor in hydrate blockage removal in vertical pipes.
- The possibility of ice formation during hydrate dissociation.