1. INTRODUCTION

A five-year national project was initiated by Korea Gas Corporation (KOGAS) R&D Division in the year 2000 with the sponsorship of the Ministry of Commerce, Industry and Energy (MOCIE) of Korea. This project focuses on the exploration of natural gas hydrate for East Sea of Korea, the characterization of natural gas hydrate, and development of utilization technology for natural gas hydrate. This study was performed as one of the project. Hydrates are solids resembling ice in appearance, which are consist of a gas molecule surrounded by a cage of water molecules. Because of containing a large amount of methane, hydrates have been considered as a future energy resource. However, the formation of hydrates in the oil and gas pipelines has been a serious problem for a long time [1, 2]. The formation of hydrates in a pipeline is common in seasonally cold or sub-sea environments with low temperatures and high pressures. In particular, hydrate blockages becomes a real menace to flow assurance in inadequately protected flowlines.

Hydrates may exist far above the freezing point of water, and hence they can cause plugging of pipelines and nozzles. Also, they may cause many difficulties in deep water drilling platform because they could block mud line, choke, and blow out preventer (BOP) [see figure 1]. For over 160 years hydrates remained a mere scientific curiosity. Their importance to the oil and gas industry was realized in the early 1930's when Hammerschmidt discovered that the solid compounds, which frequently plugged the gas transmission lines during cold weather, were not ice but hydrates [4]. It has been discovered under which conditions hydrates could form and how to prevent hydrate formation by the use of chemicals. During the recent years, the quest for long-distance transport of untreated or partly treated pipelines has caused an increased interest in the area of hydrate formation, hydrate crystallization, and hydrate mitigation [5, 6]. Recently published field experiments showed that hydrate blockage could form more readily in under-inhibited systems than in systems completely without inhibitor [7]. On the basis of this experience, under-inhibited systems appear to be more likely to cause hydrate problems than systems completely without inhibitor. Consequently, the amount of the inhibitor in the pipeline must be maintained at such a level that hydrate formation will not be encountered.
In this study, the visualized pipeline experimental apparatus, which is called KOGAS flow loop system has been set up in order to find the methane hydrate equilibrium conditions and formation conditions. Methanol, an inhibitor, was also used to investigate of the inhibitor performance. This study shows an experimental phenomenon of the potential problems associated with hydrate formation and deposition in pipelines and how to prevent hydrate formation and to remove hydrate blockage.

2. Experimental apparatus and procedure

The experiments were carried out in a lab-scale high pressure flow loop. It consists of a main closed flowline and high pressure vane pump contained within a water bath. The temperature of the loop is controlled with refrigerating bath circulator which the temperature can be varied between 248.15 and 383.15 K. The flowline consists of 316 grade stainless steel with the size of 1.575 cm inside diameter and 400 cm long. Fluid inside the loop can be observed by 20 cm long transparent view pipe made by polycarbonate. A high pressure view pipe (up to limit 15 MPa) is located at downstream of the pump. Flow is provided with a high pressure vane pump driven by a 1 hp motor having a variable speed drive. The pump can provide up to 12 liter/min. The loop is monitored with 6 temperature sensors and 6 pressure transmitters arrayed around the loop. 100 ohm platinum resistance temperature detectors are used to measure the temperature in the loop and the accuracy of the temperature measurement is within ± 0.1 K. The pressure of the system is controlled with high sensitive pressure regulator. To measure the system pressure, the calibrated pressure transmitters are used, and the accuracy of its measurement is within ± 20 KPa. In order to prevent the contents of loop from drafting backward and to remove impurities contained in gas, the check valve and line filter are installed. For measurements of gas consumption needed to hydrate formation, mass flow meter is equipped in front of gas inlet line. The methane gas used in the experiments is high purity grade (99.95%), and the water is distilled twice. Methanol also is high purity grade (99.8%) of DC Chemical Co. All data are automatically recorded and monitored with the data acquisition system, which is called
DaqBook. Pressure, temperature, and flow rate can be recorded and the loop can be operated in the constant pressure, constant volume, or constant temperature modes.

Before starting the experiments, the entire system is evacuated to at least 758 mmHg vacuum for several minutes to remove any foreign gases. Next, the required volumes of the distilled water are pumped into the flow loop, and methane gas is charged to the loop. The pressure in the loop is raised above the expected equilibrium pressure to form hydrates and the contents of the loop are then cooled at constant rate until the pipe is plugged by hydrate. As soon as hydrates were formed, the loop pressure is reduced by methane gas entrapped hydrates. When the formation of hydrate in the system is completed, the system temperature is increased to decompose hydrates. In this process, the system temperature is increased slowly, allowing sufficient time for equilibrium to be achieved. It is noted that the temperature should be slowly increased because of possibilities to measure wrong equilibrium condition. In order to start an experiment for investigating the inhibition effect of methanol, the loop is set at 6.87 MPa and cooled at a constant pressure under gas/liquid flow regime. During the cooling process, the temperature at which the onset of hydrate formation occurs is determined and corresponds to the so-called the temperature of formation. To measure inhibitor performance, methanol concentration is used in the range of 2, 4, 6, 8, and 10 wt %. The temperature in the loop is decreased at a rate of 2.2 K/h from initial temperature of 290.15 K until the pipe is plugged by hydrate. Data are recorded automatically at 10-second intervals. Recorded variables are the loop internal temperature, loop pressure, and gas consumption rate. For the tests carried out in this work, the quantity of water in the loop is a volume of 400 ml.

3. EXPERIMENTAL RESULTS

In order to investigate hydrate formation in pipelines, the equilibrium conditions of methane hydrate were measured from the experimental works. Figure 2 is a pressure-temperature trace that describes the hydrate formation/dissociation process. After pressurization of the system with gas, the experiment starts at point A (8.27 MPa, 291.75 K). The curve A-B is the cooling curve, where a slight decrease in gas pressure is observed. This decrease is considered to be a result of gas cooling and gas dissolving in water. This interval is described as being the nucleation region by Sloan and several researchers [10-12]. The curve B-C is presents the continuous and rapid growth taken place, and solid hydrate phase becomes massive enough to plug pipe. A rapid hydrate growth is accompanied by a catastrophic pressure drop in the constant volume pipeline due to the encapsulation of gas molecules in the hydrate cluster. Hydrate formation stops at Point C. The curve C-E represents the dissociation region, where the system is being warmed up and the hydrates are decomposed into the liquid and vapor phases. Point E (7.93 MPa, 284.35 K) is the equilibrium point where all the hydrate particles were disappeared. Beyond point E, we can see no more hydrate particles. These experiments to measure equilibrium conditions were performed in various pressures and temperatures. The obtained results were consistent with the results published by Sloan [10], as can be seen in Figure 3.
The thermophysical properties of hydrate formation and decomposition processes are extremely important in hydrate problems of pipeline. In this study, enthalpy change in the dissociation process was analyzed based on the measured equilibrium results. The enthalpy of dissociation may be determined from the univariant slope of the phase equilibrium line using the Clausius-Clapeyron equation.

\[
\frac{d \ln P}{d (1/T)} = -\frac{\Delta H}{ZR},
\]

where \( P \) is the equilibrium pressure, \( T \) is the equilibrium temperature, \( \Delta H \) is the heat of dissociation, \( Z \) is the gas compressibility factor, and \( R \) is the universal gas constant. If the gas compressibility factor does not change rapidly, this equation can be used to calculate the heat of dissociation from commonly available (\( P, T \)) data. However, this equation is hard to apply to mixed guests of more than two components. Figure 4 shows the slope of linear equation which is plotted as logarithmic pressure versus reciprocal temperature. The slope of this line is equal to the left-hand-side of the Clausius-Clapeyron equation. Through this method, the estimated dissociation heat value of methane hydrate is 56.43 kJ/mol and is compared with several reported experimental values [13-15] determined by calorimeter listed in table 1. As shown this table, the good agreement between the estimated value and measured values showed that the estimated value of \( \Delta H \) is acceptable for the hydrate melting process when experimental value is not available.
Methanol injection has been used effectively to keep hydrates from forming as well as to release hydrate plugs restricting or stopping gas flow [16, 17]. Methanol is used as a means of preventing hydrate plugging or freezing in offshore hydrate control operations. The experiments were carried out to investigate the effects of concentration of methanol on the hydrate formation and inhibition processes. All the tests were performed at 6.87 MPa and 0.44 m/s. Figure 5 shows formation temperature and methanol concentration at the onset of hydrate formation. As the methanol concentration increases, the formation temperature decreases linearly. Figure 6 shows the experimental data for hydrate formation point and the predicted equilibrium curve with different amount of methanol. The equilibrium curve was predicted using the methanol calculated by CSMHYD. CSMHYD is a computer program developed by Sloan at Colorado School of Mine in 1984 and widely used to estimate hydrate equilibrium conditions in oil and gas industry. The program used the method of van der Waals and Platteeuw for the hydrate phase, and Soave-Redlich-Kwong equation of state for the fluid phases. In Figure 6, it can be known that formation points are shifted toward low temperature for increased methanol concentration in 6.87 MPa set pressure. Figure 7 shows the gas consumption after the onset of hydrate formation. All the concentration of methanol showed more gas consumption than that obtained with pure water. Particularly, aqueous solutions of 4, 6 wt % of methanol showed considerably higher rates and more amount of hydrate formation than pure water. This means that aqueous solutions of methanol had a decreased formation temperature from 1.2 K to 4.2 K but actually they were used as promoter after the onset of hydrate formation. Therefore these results show that the amount of the inhibitor in the pipeline must be maintained at such a level that hydrate formation will not be encountered.

Table 1: Comparison of dissociation heat values for methane hydrate

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H$ (kJ/mol)</th>
<th>Remark</th>
</tr>
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<tbody>
<tr>
<td>This study</td>
<td>56.43</td>
<td>Indirect method</td>
</tr>
<tr>
<td>Handa</td>
<td>54.19</td>
<td>Exp. data at 273.15 K</td>
</tr>
<tr>
<td>Lievois et al.</td>
<td>54.77</td>
<td>Exp. data at 273.15 K</td>
</tr>
<tr>
<td>Kang et al.</td>
<td>56.84</td>
<td>Exp. data at 274.15 K</td>
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Figure 4: Plot of logarithmic pressure vs. reciprocal temperature

$$\ln(P) = -7986.793 * \left( \frac{1}{T} \right) + 30.161$$
5. CONCLUSION

To investigate the plugging phenomena of hydrates in a pipeline environment, the experimental study was conducted. As such, the following conclusions are drawn:

1. The methane hydrate equilibrium conditions were measured by using the constant volume experiment. The experimental results were compared with the published experimental results, and found to be good matches.

2. As a result analyzing enthalpy change based on the measured equilibrium results, dissociation heat of methane hydrate was estimated in 56.43 kJ/mol. The result was consistent with several reported
experimental values determined by calorimeter. The dissociation heat of methane hydrate predicted through equilibrium data and using the Clausius-Clapeyron equation are comparable with calorimeter values.

3. Inhibition experiments have been conducted using the methanol to inhibit hydrate formation in a pipeline. As the result, methanol had lower formation temperature than pure water but it was used as promoter to enhance the rate and amount of hydrate formation after the onset of hydrate formation.

These works can provide the predicting techniques of the hydrate plugging phenomena and hydrate control techniques by the inhibitor in the sub-sea pipeline system as well as flowlines of natural gas production system. Specifically, the results of this study can be applied to the selection of the prevention criteria and method of hydrate formation.

6. REFERENCES


