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Experimental Investigation of a Mixture of Methane, Carbon Dioxide & Nitrogen Gas Hydrate Formation in Water-Based Drilling Mud in the Presence or Absence of Thermodynamic Inhibitors

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***Abstract*—**Gas hydrates form when a number of factors co-exist: free water, hydrocarbon gas, cold temperatures and high pressures are typical of the near mud-line conditions in a deepwater drilling operation. Subsequently, when drilling with water based muds, particularly on exploration wells, the risk of hydrate formation associated with a gas influx is high. The consequences of gas hydrate formation while drilling are severe, and as such, every effort should be made to ensure the risk of hydrate formation is either eliminated or significantly reduced. Thermodynamic inhibitors are used to reduce the free water content of a drilling mud, and thus suppress the hydrate formation temperature. Very little experimental work has been performed by oil and gas research companies on the evaluation of gas hydrate formation in a water-based drilling mud. The main objective of this paper is to investigate the experimental gas hydrate formation for a mixture of methane, carbon dioxide & nitrogen in a water-based drilling mud with or without presence of different concentrations of thermodynamic inhibitors including pure salt and a combination of salt with methanol or ethylene glycol at different concentrations in a static loop apparatus. The experiments were performed using a static loop apparatus consisting of a 2.4307 cm inside diameter and 800 cm long pipe. All experiments were conducted at 2200 psia. The temperature in the loop was decreased at a rate of 3.33 ˚F/h from initial temperature of 80 ˚F.

***Keywords*—**Hydrate formation, thermodynamic inhibitor, water-based drilling mud, salt, static loop apparatus.

I. Introduction

DRILLING for oil and gas wells involves the use of drilling mud. Drilling muds are fluids used to control formation, pressure, lubricate and cool the bit, remove rock fragments from the drilling well, and form a consolidated well cake on the sides of the hole prior to casing. These muds, which are highly viscous, are complex formulations and include such finely divided materials as ground ilmenite, bentonite, various clays, barite, lead ore, fibers, hulls, etc. in a liquid medium which may be aqueous (e.g., water or brine) or an oil (e.g., diesel oil). In general, three types of muds are currently in use: oil - based muds, water based muds and synthetic – based muds. Oil base muds are composed primarily of diesel oil or mineral oil and additives. Water – based oil consists of a base salt water or fresh water containing additives, while synthetic – based muds have oil – like base materials.

The combination of extremely cold water at the mud line and hydrostatic pressures in the 110 Bar (1600 psi) range is ideal for the formation of extremely dangerous gas hydrates [7]. Gas hydrate crystallization and dissociation, and their inhibition or promotion is of interest to a wide range of applications [1], [2], [7], [9]. Gas hydrates form when water molecules crystallize around gas molecules. The water/guest crystallization process has been recognized for several years, is well characterized and occurs with sufficient combinations of temperature and pressure. Light hydrocarbons methane-to-heptanes, nitrogen, carbon dioxide and hydrogen sulfide are the guest molecules of interest to the oil industry.

The consequences of gas hydrate formation while drilling are severe, and as such, every effort should be made to ensure the risk of hydrate formation is either eliminated or significantly reduced. Thermodynamic inhibitors are used to reduce the free water content of a drilling mud, and thus suppress the hydrate formation temperature.

Despite the potential hazards, little data have published on gas – hydrate formation with and without presence of thermodynamics inhibitors and their mixtures in drilling muds [4], [5], [6]. One research is the lack of equipment available for mud studies. The first part of this paper is the description of a high pressure static loop apparatus, gas hydrate generator recently developed at Shiraz University [3]. The remainder of the paper is a discussion of data obtained using this device on various concentrations of pure and mixtures of thermodynamic inhibitors for a water- base drilling mud used in Iran.

II. Materials

The materials used for the experiments are a water-based drilling mud which was donated by National Iranian Oil

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Company as an aqueous phase, carbon dioxide from Aboghadare Chemical Co. with 99.95% purity, methane gas from Erish Gas Gostar Chemical Co. with 99.95% purity, nitrogen gas from Aboghadare Chemical Co. with 99.9% purity as the hydrate former and the water distillated twice. In the experiments with presence of thermodynamic inhibitors, the inhibitor is typically (such as pure salt and a combination of salt with methanol or ethylene glycol) injected into the static loop as an aqueous solution to produce the desired weight percent concentration of inhibitor in the aqueous solution.

III. Experimental Apparatus and Procedure

The static loop system was a pilot - scale apparatus used to conduct hydrate formation for a water–based drilling fluid in the presence or absence of the thermodynamic inhibitors. The system consisted of a main closed – loop pipeline and high pressure screw pump. The temperature of the loop was controlled using a glycol – water bath circulator. A simplified schematic diagram of the static loop apparatus used in this experimental study is shown in Fig. 1. The flow line was made of 316 grade stainless steel with a 2.4307 cm inside diameter and 800 cm in length. The loop was monitored with 2 temperature sensors (100 ohm platinum resistance thermometers or PT-100, T1 and T2) and 3 pressure indicators (two Bourdon gauges, P1 and P2, and one Rosemount pressure drop transmitter, DP1) arrayed around the loop. The gas injection rate is monitored by means of a Rosemount pressure drop transmitter and an orifice plate. The pressure of the static loop is maintained at a constant value during the experimental runs by means of a regulator and gaseous mixture make-up. The accuracy of the pressure gauges and temperature measurements is estimated to be +/- 10 psi and +/- 1K, respectively.

To prevent the contents of the loop from impurities contained in the gas, a line filter was installed. A temperature bath is used for cooling the entire loop made of stainless steel, with thermocouples placed inside the loop to measure the actual temperature of the mud sample. For each test, 4000 mL of mud is placed inside the vessel, which is then pressurized using a mixture of methane, carbon dioxide & nitrogen gases, once the cell has been pressurized, typically to 2200 psi, the cell is cooled at a rate of 3.33 ˚F per hour. During the cooling process, the pressure inside the cell naturally decreases. When conditions inside the cell become critical, gas hydrate crystals begin to form. The gas-hydrate generator described in this paper can operate at temperatures from 80 to 32 ˚F and pressures up to 2200 psia. The circulator temperature baths are cooled by circulating a coolant (ethylene glycol) through separate refrigeration units.

Mud was injected from the above valve into the static loop apparatus. The system temperature is lowered at a rate of 3.33 ˚F /hr and the pump is off. The initial system temperature is usually set at 80 ˚F. At the beginning of an experiment, the temperature and pressure in the static loop apparatus follow a constant-volume, cooling line on a pressure versus temperature plot (Figs. 4, 5). When the thermodynamic conditions for hydrate formation are reached as a consequence of supercooling of the system, the pressure decreases more sharply indicating the enclosure of gas in a hydrate structure (Figs. 4, 5). When the gas hydrates form, the temperature of system slowly increases (Figs. 2, 3).

IV. Results and Discussion

In this work, a high pressure pilot scale apparatus was set up. The experiments were then carried out for a mixture of 26% methane, 27% nitrogen and 47% carbon dioxide in the presence or absence of the thermodynamic inhibitors including pure salt and a combination of salt with methanol or ethylene glycol at different concentrations at initial temperature and pressure of 80˚F and 2200 psia, respectively. In the experiments of gas hydrate formation in the presence of the thermodynamics inhibitors (pure salt, glycol and methanol and their mixtures), the inhibitor is typically injected into the loop as an aqueous solution to produce the desired weight percent concentration of inhibitor in the solution. During an experiment, the data acquisition system scans the pressure and temperature of the static loop every 60 s. As a matter of the fact, two methods were employed to detect the onset of gas hydrate formation in the pipeline. The first method relies on the fact that gas hydrate formation is an exothermic reaction. As a result of gas hydrate formation, a temporary exothermic peak occurs in the pipeline temperature (see Figs. 4, 5), the second method utilizes an increase in the pressure drop as an indication of the appearance of the first nuclei of gas hydrates (see Figs. 2, 3, 6, 7).

As can be seen in Figs. 2- 5, The slope of the pressure versus time curve after hydrate begins to form is much steeper for the mud without using the thermodynamic inhibitors. Thermodynamic inhibitors can also increase the induction time of gas hydrate formation and decrease the temperature of exothermic peak formation. For example, as shown in Table I, the induction time for the gaseous mixture in fresh drilling mud during hydrate formation is 5 hr. The addition of 5, 10 and 12.5 wt% pure Nacl delayed the induction time to 5.5, 7.5 and 8.5 hrs, respectively, whereas the addition of 5 wt% Nacl +5 wt% MeoH and 10 wt% Nacl + 10 wt% MeoH delayed the induction time to 8 and 10.5 hrs, respectively. Thus, the addition of 10 wt% Nacl + 10 wt% MeoH in the fresh drilling mud increases the induction time of gas hydrate formation about 2.1 times more compared to that without using the inhibitor.

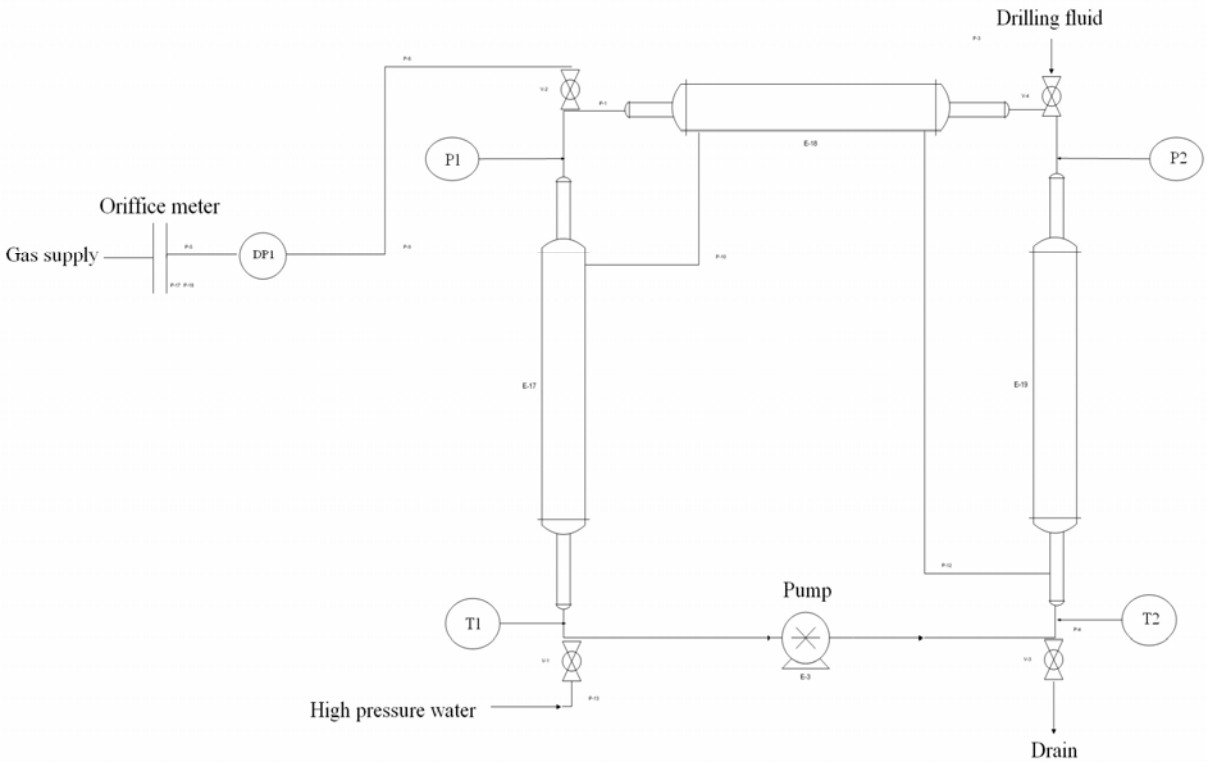


Fig. 1 Process diagram at a pilot scale for a static loop apparatus
T1 and T2: Temperature gauge, P1 and P2: Pressure gauge and DP1: Pressure drop gauge

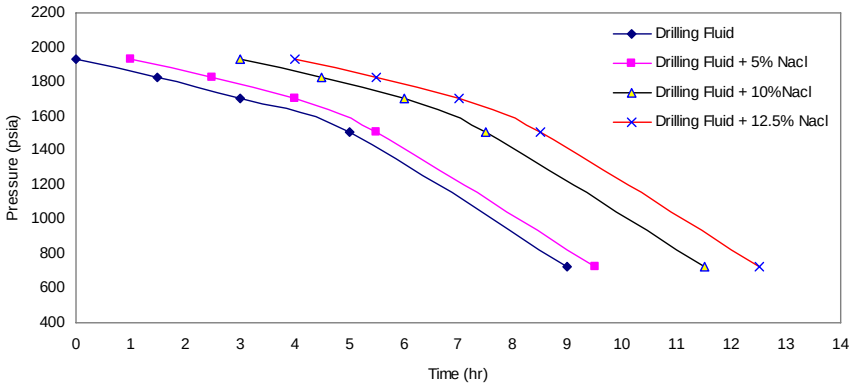


Fig. 2 The history curve of pressure and time in the process of gas hydrate formation in a static loop apparatus

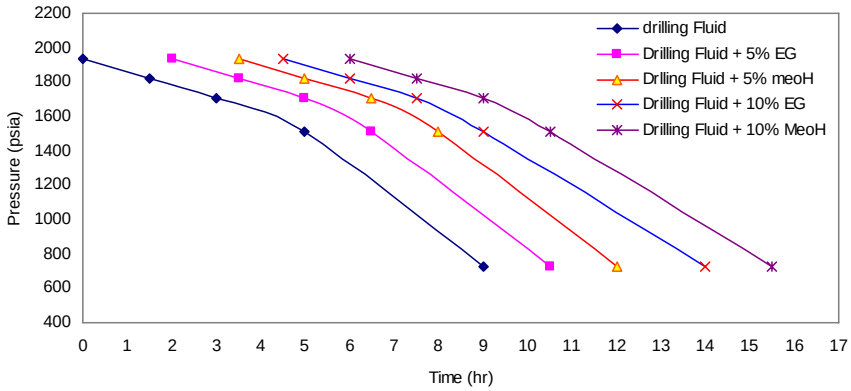


Fig. 3 The history curve of pressure and time in the process of gas hydrate formation in a static loop apparatus

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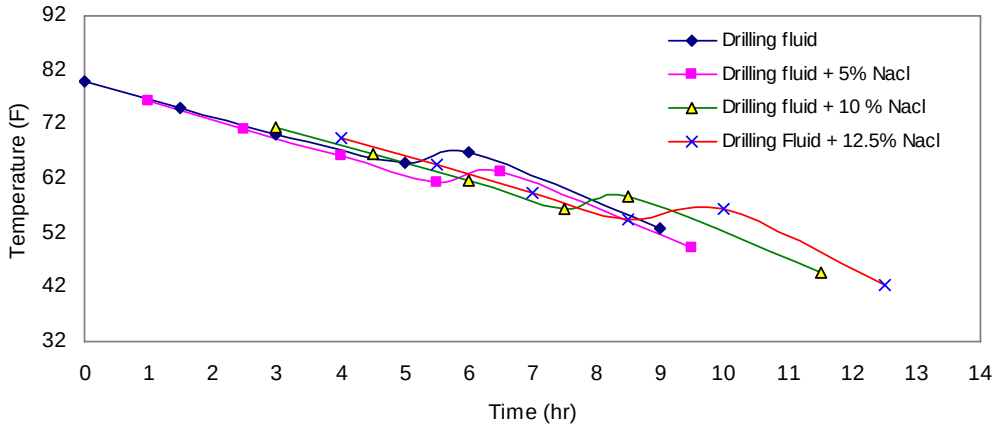


Fig. 4 The trend curves of temperature obtained in the experiment for mixture gas hydrate formation in a static loop apparatus

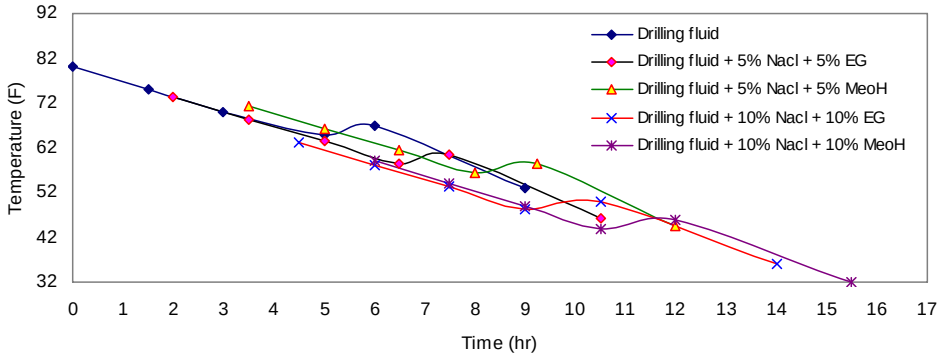


Fig. 5 The trend curves of temperature obtained in the experiment for mixture gas hydrate formation in a static loop apparatus

TABLE I
SUMMARY OF HYDRATE FORMATION CONDITIONS WITH ADDED PURE SALT AND MIXTURE OF SALT WITH METHANOL OR ETHYLENE GLYCOL

Composition	Hydrate Formation Temperature (°F)	Hydrate Formation Pressure (psia)	Induction Time (hr)
Fresh drilling fluid	67	1550	5
Fresh drilling fluid + 5 wt % Nacl	63.2	1550	5.5
Fresh drilling fluid + 10 wt% Nacl	58.5	1550	7.5
Fresh drilling fluid + 12.5 wt% Nacl	56.5	1550	8.5
Fresh drilling fluid + 5 wt % Nacl + 5 wt% EG	60.4	1550	6.5
Fresh drilling fluid + 5 wt % Nacl + 5 wt% MeoH	58.4	1550	8
Fresh drilling fluid + 10 wt % Nacl + 10 wt% EG	50	1550	9
Fresh drilling fluid + 10 wt % Nacl + 10 wt% MeoH	46	1550	10.5

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Comparison results between the effect of experimental temperature reduction upon the pressure variation for the gaseous mixture during the gas hydrate formation in the presence of 5, 10 and 12.5 weight percent Nacl are shown in Fig. 6. Similarly, the effects of experimental temperature reduction upon the pressure variation for the gaseous mixture during the gas hydrate formation in the presence of a combination of salt with two thermodynamic inhibitors including MeoH and glycol (5 wt% Nacl + 5 wt% MeoH, 5 wt% Nacl + 5 wt% EG, 10 wt% Nacl + 10 wt% MeoH and 10 wt% Nacl + 10 wt% EG) are ploted in Fig. 7.

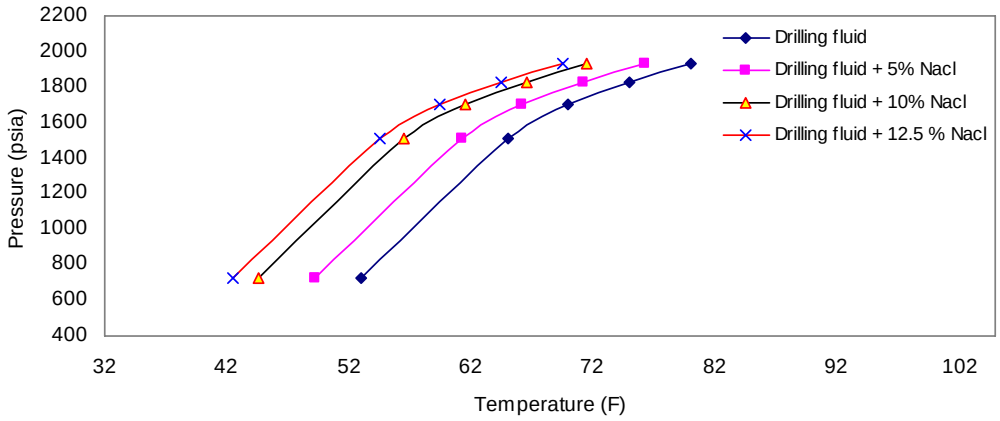


Fig. 6 The history curve of pressure and temperature in the process of gas hydrate formation in a static loop apparatus

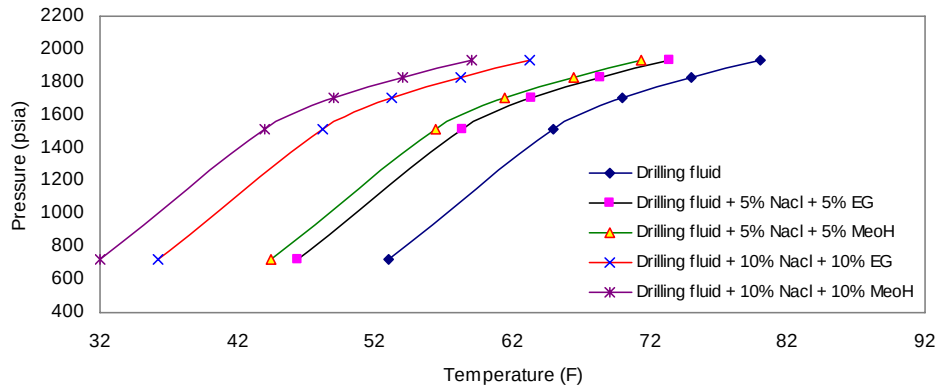


Fig. 7 The history curve of pressure and temperature in the process of gas hydrate formation in a static loop apparatus

TABLE II
SUMMARY OF TEMPERATURE SUPERVISION WITH ADDED PURE SALT AND MIXTURE OF SALT WITH METHANOL OR ETHYLENE GLYCOL

Nacl (wt%)	EG (wt%)	MeoH (wt%)	ΔT in hydrate formation temperature (F)
0	0	0	0
5	0	0	3.8
10	0	0	8.5
12.5	0	0	10.5
5	5	0	6.6
5	0	5	8.6
10	10	0	17
10	0	10	21

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Summary of the temperature supervision in gas hydrate formation temperature after adding salts and inhibitors is shown in Table I. The results obviously determined that the best effect in gas hydrate formation temperature supervision related to the 10 wt% Nacl + 10 wt% MeoH with the 21˚F among the other ratios of salts and MeoH and glycol were tested in this work. General speaking, it is seen that the induction times in the presence of mixtures of Nacl and MeoH are longer than the others. As can be seen in Table II, for example the injection of 10 wt% Nacl and 10 wt% EG decreases 17 ˚F in the temperature of gas hydrate formation. These results were shown that the fresh drilling mud tends to have a shorter time during the gas hydrate formation.

V. Conclusion

In this work, the experimental data points of the gas hydrate formation for the gaseous mixture (26% methane, 27% nitrogen and 47% carbon dioxide) in the presence or absence of the thermodynamic inhibitors (pure salt and a combination of salt with EG or MeoH at different concentrations) were measured by a static loop apparatus. The effect of pressure and temperature on the gas hydrate formation conditions in the presence or absences of the thermodynamic inhibitors were also investigated. The presence of the thermodynamic inhibitors caused an increase in induction time. In all experiments, when comparing the induction time during the hydrate formation for the gaseous mixture in the presence of EG and MeoH as inhibitors, it is seen that the induction times in the presence of MeoH are longer than those with EG. In addition, the combination of 10 wt% Nacl and 10 wt% MeoH with 21 °F reduction in gas hydrate formation temperature is the best mixture of the inhibitors among pure salt and the other combinations of salt with MeoH or EG.

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