STUDY OF HYDRATES IN DRILLING OPERATIONS : A REVIEW

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Abstract. Natural gas hydrates formed in drilling operations are of increasing concern to petroleum engineers as the search for oil and gas moves to deep and ultradepth waters, where low temperatures and high pressures are found. Solutions for the problem of hydrate formation in these areas demand large amounts of capital and operating expenses. Furthermore, gas release near the surface during hydrate decomposition may create a dangerous well-control situation. Hydrate formation could begin in an area of little or no circulation, such as choke and kill lines, or near the blowout preventers. Researches have been carried out on the thermodynamic conditions (pressure, temperature and composition) necessary for gas hydrate formation. Different experimental apparatus and methods have been used for screening potential inhibitors. Laboratory data are useful to improve theoretical models in a continuous development. This article intends to review these issues, discussing the state-of-the-art knowledge on hydrate formation in drilling operations.

Keywords: hydrate formation; inhibitors; drilling; deep water; well control

1. INTRODUCTION

The petroleum industry has been challenged to develop oil and gas fields in increasingly deeper waters, where particular environmental conditions such as low temperatures and high pressures are encountered. As a consequence, hazards to drilling operations from gas hydrates have to be considered with greater emphasis. Despite this serious problem, which could result in a blowout situation, little data have been published on gas hydrate formation in drilling muds.

Hydrates are inclusion compounds, within which small gas molecules are trapped to form a lattice of water molecules. The hydrate crystals can remain stable within a certain range of temperature and pressure. The solid structure is kept thermodynamically stable through van der Waals interactions between the water molecules forming the cages and the gas molecules inside them. Naturally formed hydrate reserves have been of global interest because of their potential impact on energy issues, global climate change, continental margin slope stability and petroleum industry hazards. In the latter case, hydrate formation risks which are specific to drilling operations are well-bore collapse, uncontrolled gas release and blowouts, besides flow problems. Generally, the operating conditions are maintained away from the hydrate formation region controlling the heat transfer, by means of heating or thermal insulation, and using additives as inhibitors.

There are at least three types of known structures of hydrates, named as S-I (Structure I), S-II and S-H, as depicted in Figure 1.

In structure I, containing 46 water molecules, there are eight cavities, two small ones with twelve pentagonal faces, and six large ones, with twelve pentagonal faces and two hexagonal faces. This is formed with light components such as methane, ethane or carbon dioxide.

Structure II, with 136 water molecules, has twenty four cavities, sixteen small ones with twelve pentagonal faces, and eight large ones, with twelve pentagonal faces and four...
hexagonal faces. These large cavities, larger than those in S-I, might accommodate molecules such as propane or butane, which do not fit in the cavities of structure I.

The third type of structure, S-H, presents 34 water molecules and is constituted of six cavities, three small ones with twelve pentagonal faces, two small ones with three squared faces, six pentagonal faces and three hexagonal faces, and one large cavity composed of twelve pentagonal faces and eight hexagonal faces. Structure H is formed by heavy molecules, such as cycloalkanes, but a support gas, such as methane, is required in order to stabilize the reticulum.

The small cavity of structure I has a different equivalent radius than that of structure II or structure H. Even low concentrations of propane generate structure II, the most common type of hydrate. Structure H, which is stabilized by molecules larger than n-butane, could be found in petroleum reservoir fluids, as studied by Tohidi et al. (2001). It is possible that these two types of structures, and even all three together, coexist.

In this way, different types of gas are able to form hydrates. The gas that can be normally found in a well-control situation is natural gas, so the hydrates could be formed as types S-I, a body-centered cubic lattice, or S-II, a diamond lattice. However, a kick of light hydrocarbon fluids could contain intermediate hydrocarbon molecules, theoretically permitting S-H hydrate formation.

The hydrate formation mechanism comprises two main stages: nucleation and growth. In the first stage, small nuclei are formed demanding an induction time. Then these aggregates exceed a critical size, when the growth stage begins. The use of thermodynamic inhibitor disrupts the hydrogen bondings within the water phase, acting in the nucleation stage. Kinetic and anti-agglomeration inhibitors can delay the formation time. So, one could prevent hydrate formation by operating outside the hydrate zone, or allowing the nucleation but inhibiting the aggregation. In this case, hydrates could be transported as slurry.

It is necessary to determine with precision the thermodynamic conditions for hydrate formation, as a function of the gas and mud composition. This is represented by a hydrate line, in a pressure versus temperature graph, as showed in Figure 2, for a methane and water system.

Drilling fluids are complex mixtures with several functions. One may particularly cite
well cleaning, transportation of solids to the surface, development of hydrostatic pressure, cooling and lubrication of machinery mobile parts, to name a few. During a circulation stop, as a result of periodical shutdowns, or after a gas kick, the mud temperature could reach values within the hydrate zone. Hydrate formation could then cause the drilling mud to lose its rheological properties, hence affecting the flow. In the worst scenario, solid plugs could completely interrupt the flow of fluids.

Another issue arising after hydrate plugs are formed refers to estimating how long it would take in order to dissociation occurs, by means of depressurization, heating or action of chemical additives. Rapid gas release deriving from hydrate crystals dissociation could result, under uncontrolled circumstances, in destruction of the rig equipment, because of the high amount of gas inside the solid. One cubic meter of hydrate could liberate 170 cubic meters of gas. Also, there is the risk of the plug velocity, when it is pushed out of the line.

In view of this, the main objective of this article is to present a comprehensive literature review about hydrate formation in drilling operations, covering reports on laboratory assays, inhibitors, thermodynamic and experimental models, providing information for the better understanding of problems in the petroleum industry.

2. LITERATURE REVIEW

Lai and Dzialowski (1989) investigated 23 drilling mud formulations, presenting laboratory-derived equilibrium temperature and pressure data. A gas hydrate generator was described, which could operate at temperatures from 268 K to 300 K and pressures up to 41 MPa (5950 psi). Mud and gas were introduced into a closed cell equipped with pressure and temperature sensors. Rocking mechanisms could keep the fluids agitated. Gas hydrate formation was monitored by direct temperature and pressure measurements of a constant-volume system, instead of visual inspection, because drilling muds were opaque. The authors discussed some calculus to estimate the salt concentration required to inhibit hydrate formation, or even slow down the reaction rate. Tubing flow tests were conducted to simulate plugging and clearing of choke or kill lines. The pressure to break through a plugged line was of particular interest. Tests confirmed the well control problems with hydrates encountered in the field, so they suggested there was a need to develop better drilling fluids.

The option of oil-based mud, instead of water-based, could help to control the formation of gas hydrates, as pointed out by Grigg and Lynes (1992). Initially, it was believed that oil-based mud could be used without concern about the formation of gas hydrates. They made experimental PVT tests, with two equipments, a blind cell and a windowed cell, from 3 MPa (450 psi) to 31 MPa (4500 psi). Both apparatus had a mixing system because gas hydrate formation is a surface phenomenon. Four systems were tested: pure water, 20 wt. % CaCl$_2$ brine, oil-based mud with 20 vol % water and oil-based mud with 20 vol % brine. A synthetic natural gas mixture was used. The cooling and heating rates, for a series of experiments, were selected at 1.7 K/h. Upon reduction of the rate to 0.06 K/h, the formation temperature was lowered and the precision improved. On the other hand, this increased the test time on a system from
one day to weeks. The authors concluded that addition of dissolved solids into the aqueous phase affected surface activity and gas solubility, and then reduced the gas hydrate formation temperature. The effects caused by the dissolved salts in the brine and the oil phase were additive.

Kotkoskie et al. (1992) explained that it was necessary to determine the highest possible temperature at which hydrates could be stable for a given pressure and gas composition. This was the dissociation point, determined by cooling the test fluid during contact with a gas sample, thereby forming hydrates, and slowly heating it until the last hydrate crystal disappeared, inside a PVT cell. They made a series of experimental tests, with several fluid mixtures. The results of a typical experimental run are depicted in Figure 3.

In figure 3, point A represents the initial pressure and temperature conditions of the test. Line CC shows the isochoric cooling period, from point A to point B. The authors found that twenty-four hours at the constant temperature $T_B$ was a reasonable period of time to form an appreciable amount of hydrates and produce a significant pressure drop, $\Delta p$, from point B to C. After the holding period, the system was heated to its original temperature, following the line HC. Heating was enough to allow the system to be at or near equilibrium, particularly in the neighborhood of the dissociation point D, where the heating curve rejoined the cooling curve. This pressure/temperature pair was characteristic of the thermodynamic equilibrium of gas hydrate in the gas and mud studied, corresponding to their dissociation point. A typical run of this kind of experiment lasted between 60 and 80 hours. When the pressure at point B ($P_f$) is attained, hydrate formation first becomes apparent and the total pressure drop produced ($\Delta p$) is an indication of the amount of gas encapsulated in the hydrate lattice. The authors concluded that hydrate formation in drilling mud was determined by the salt concentration present in the aqueous phase and that the sum of the drilling mud constituents, other than salt, tended to promote hydrate formation slightly.

Different thermodynamic models found in the literature could solve the multiphase equilibrium, based on an equation of state. Edmonds et al. (1996) employed the Soave-Redlich-Kwong (SRK) equation of state, which appears to give more accurate fugacity values for natural gases than the Peng-Robinson equation. According to the authors, the liquid densities calculated by SRK equation should be corrected using the Peneloux volume shift method. In order to model the properties of water and hydrate inhibitors, they used the Huron-Vidal mixing rule to determine an excess Gibbs energy. The hydrate phase was modeled with van der Waals and Platteew model with all parameters determined specifically for this case by the authors. The developed model should be simple to use, requiring as input no more than a typical ion analysis table from a laboratory report. The model represented the ionic components in water by a single salt pseudo-component in the equation of state. Other salts were handled on a sodium chloride equivalent basis. It was assumed that the salts remained in the aqueous liquid phase and therefore the relative amounts of the salts did not change, so none of the salts crystallizes out of solution. The action of inhibitors was indirect in that they did not enter

![Figure 3. Pressure versus temperature plot for a typical hydrate formation test.](http://www.portalabpg.org.br/bjpg)
the hydrate phase, and did not alter its properties, but modified the thermodynamic characteristic of the fluid phases, in particular the aqueous liquid phase. Inhibitor lowered the fugacity of water thereby reducing its tendency to form hydrates.

Some techniques to remove a hydrate blockage from the choke and kill lines, as radial heat tracing, pipe warm-up and hot water circulation through coiled tubes, were examined by Yousif et al. (1997). The feasibility of radial heat tracing in a deepwater offshore environment was analyzed by a mathematical formulation of the energy balance. They determined the sensitivity of the melting process to such parameters as heat flux, hydrostatic pressure over the plug, insulation thickness and quality (thermal conductivity). This option could be viable to either melt a hydrate plug or to keep the choke and kill lines warm enough not to form hydrates. The required heat flux to heat the choke and kill lines to a preset target temperature above the mud line temperature was calculated. The results showed that the bulk of the heat energy was consumed in raising the temperature. Another computer model was developed to study the method of hot water circulation from the surface through coiled tubing. The authors analyzed the sensitivity of the melting process to the water circulation rate, pipe insulation and the inlet water temperature. It was necessary to insulate the choke and kill lines in order to make this option as energy efficient as desired.

Dalmazzone et al. (2002) compared some results of equilibrium points, obtained from two techniques. The first one was the more classical, such as measurements of pressure variation versus temperature, at constant volume. The second was Differential Scanning Calorimetry, DSC, a rapid and sensitive technique, broadly used in the characterization of any kind of phase change. It allows the measurement of the heat transfer as a function of time, temperature and pressure, hence permitting the detection of any phase transitions. They tested various aqueous media including pure water, high-concentration calcium chloride solutions and water-in-oil emulsions. From a thermodynamic point of view, there were no measurable differences between bulk solutions and emulsions. From a kinetic point of view, due to the considerable surface area between the two phases, the emulsions allowed the formation of much higher amounts of hydrate than the solutions, regardless of the stirring level. Further work was needed to apply the DSC technique to a complete drilling mud in order to test the kinetic and thermodynamic effects of solid particles on hydrate formation and stability.

Several correlations to predict the hydrate point suppression have been proposed, with an improvement over the Hammerschmidt’s equation, but only few of them could work for complex systems, including inhibitors. Ameripour (2005) developed correlations applicable to a range of temperatures up to 305 K and pressures up to 83 MPa (12,000 psi). The capability of these correlations were tested for aqueous solutions containing electrolytes such as sodium, potassium and calcium chlorides lower than 20 wt %, and ethylene glycol, triethylene glycol and glycerol lower than 40 wt %, since the use of higher amounts of these inhibitors was neither practical nor economic; in addition, these correlations may not be appropriate in some cases with high concentration of inhibitors. Knowing the gas composition, the inhibitors concentration and either temperature or pressure of the system, a user could calculate the hydrate formation pressure or temperature.

In their work, Baptista et al. (2006) reported a thermodynamic analysis determining state conditions necessary for gas hydrate formation in drilling operations, with electrolyte inhibitors. They theoretically modeled the gas phase, considered as only methane, calculating the fugacity value with the Peng-Robinson cubic equation of state. By modeling the liquid phase, the water activity was determined considering two situations. In the first one, without inhibitor, it was assumed that there was no soluble component, and the liquid phase was pure water, therefore the activity value equals one. In the second case, with addition of inhibitor, a non-ideal liquid mixture is formed with water, demanding a methodology for activity calculation, which was provided by the Debye-Hückel model. For the hydrate phase, they followed the van der Waals and Platteew statistic thermodynamic model, establishing that the condition for equilibrium was reached.
when the chemical potential of water in the liquid phase was equal to that in the hydrate phase. Applying the Gibbs-Duhem equation, the authors presented an implicit equation to calculate pressure, solved by an iteration process. The probability for gas molecule to be trapped inside the reticulum was determined based on Langmuir gas adsorption constants. The comparison between the results of the computer algorithm with experimental data, obtained in the literature, showed good agreement, for mixtures with and without inhibitors.

3. DISCUSSION

In the literature, there are few laboratory experimental data of hydrate formation in drilling muds, maybe because these tests take long time or require special apparatus. Typical experimental results were shown in Figure 3. The experiment starts at point A and mixing of the fluids should be continuous, while temperature changes should be gradual so that gas-liquid equilibrium is maintained. In this way, temperature slowly lowers towards point B, where hydrate begins to form. From this point on, drastic pressure drop is observed due to gas molecules being encapsulated into the hydrate crystal structure. This solidification phenomenon is not necessarily an isothermal process, and depends on the gas and liquid composition, meaning that point C might have a different temperature than point B. As a matter of fact, hydrate formation is an exothermic phenomenon. The dissociation point, D, is the true thermodynamic hydrate formation point, instead of point B, because the process is time-dependent. If the cooling had been slower, point B would be closer to point D, but tests could not run slowly enough to maintain the thermodynamic equilibrium at each temperature, and then cooling and heating lines are slightly separated. The relative effectiveness of kinetic inhibitors could be evaluated by comparing the time taken for the system to move from point D to point B, at constant cooling rate.

Low dosages of inhibitors are preferable due to the great amount of drilling mud in a specific activity. Therefore, the use of kinetic and anti-agglomeration compounds tends to increase. Laboratory testing continuously develops novel and better samples, by carrying out studies on their compatibility with the drilling mud components and evaluation of kinetic plus thermodynamic inhibitors combinations. During the flow, precipitation of any component should not happen, whist specific density, viscosity, corrosivity, flammability and toxicity aspects should be taken into account.

The majority of data found in the literature is for methane hydrate, so it would be interesting to perform more tests with other gases, especially natural gas, frequently found in drilling operations. However, even for methane only, the collection of data from different sources revealed that the experimental data were not mutually consistent.

3. CONCLUSIONS

Researches on hydrate formation are more developed in gas-producing areas, especially in deepwater fields, because, in this case, the seabed ambient pressure and temperature conditions fall in the hydrate zone, and the probability of hydrate occurrence is high. Increasingly deeper offshore oil recovery also generates extended gas hydrate problems with regard to the drilling muds used. Large amounts of methanol and glycol are currently used, in addition to salts such as sodium and calcium chloride, which cause important difficulties in terms of density adjustment, corrosion and toxicity. This scenario must be changed by the development of the knowledge about low-dosage inhibitors, especially some polymers, improving the environmental and economic aspects.

In drilling operations, the particular characteristics of the mud composition must be taken into account. In fact, the hydrate problem discussed here is slightly different than when examining hydrates formed in natural reservoirs or when investigating producing and transporting systems. Gas solubility in the mud
components plays an important role in the studies of hydrate formation, because this is an interfacial phenomenon, whereby free gas is trapped into a solid reticulum.

Therefore, continuous efforts are necessary to develop the understanding of the equilibrium conditions for hydrate formation in drilling operations, mainly in deep and ultradeep waters, where they become a major concern.

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