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STUDY OF HYDRATE 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 goes to deep and ultradeep waters, where low temperatures and high pressures are found. Solutions about the problem of hydrate formation in these areas demands large amounts of capital and operating expense. Furthermore, the liberation of gas 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. The water needed for crystal formation could come out from the drilling mud, changing its flow properties. Several researches have been studied 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, which are divided in three types: thermodynamic, kinetic and anti-agglomerator. 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 about hydrate formation in drilling operations.

Key words: hydrate, drilling.

1. INTRODUCTION

The petroleum industry is facing up to develop oil and gas fields in increasingly deeper water, where there are particular environmental conditions such as low temperatures and high pressures, so the hazards to drilling operations due to gas hydrates have greater emphasis. Despite this serious problem, which could result in a blowout situation, little data have been published on gas hydrate formation in drilling mud.

Hydrates are inclusion compounds, where small gas molecules are trapped inside 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 type interaction 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, specific in drilling operations, hydrate formation risks are, besides the problems with the flow, wellbore collapse, uncontrolled gas release and blowouts. Generally, the operating conditions are kept out of 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 sI (structure I), sII and sH, as depicted in Figure 1:

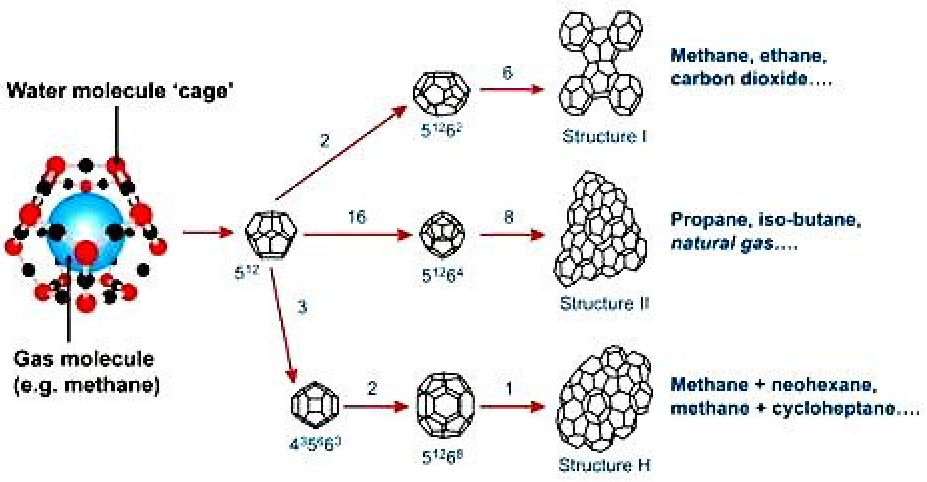

Figure 1. The gas hydrate structures (www.pet.hw.ac.uk).

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

Structure II has twenty four cavities, sixteen little with twelve pentagonal faces, and eight large, with twelve pentagonal faces and four hexagonal faces, These large cavities, greater than that in sI, could receive molecules such as propane or butane, which do not insert in large cavities of structure I.

The third type of structure, sH is constituted by six cavities, two small with three squared faces, six pentagonal faces and three hexagonal faces, three medium cavities with twelve pentagonal faces, and one large cavity composed of twelve pentagonal faces and eight hexagonal faces. This structure H is formed by heavy molecules, such as cycloalkanes, but it is necessary a support gas, as methane, in order to stabilize the reticulum.

The small cavity of structure I has a different equivalent radius than in structure II, and also, it is not the same as medium cavity in structure H. Even low concentration of propane results in 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 co-exist two types of structures and even all the three together.

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 the natural gas, so the hydrates could form in types sI, a body-centered cubic lattice, or sII, a diamond lattice. But a kick of light hydrocarbon fluids could contain intermediate hydrocarbon molecules, theoretically permitting sH hydrate formation.

Hydrate formation can be divided into two steps: nucleation and growth. In the first stage, small nuclei are formed that demands an *induction time*. Then these aggregate exceeds a critical size, when growth begins. The use of thermodynamic inhibitor disrupts the hydrogen bonding within the water phase, acting in nucleation step. Kinetic and anti-agglomerator inhibitors can delay the formation time. So, one could prevent hydrate formation by operating outside 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 of hydrate formation, as a function of the gas and mud composition. This is a *hydrate line*, in a pressure *versus* temperature graph, as depicted in Figure 2.

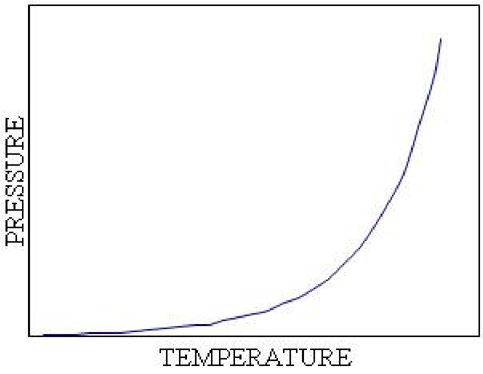

Figure 2. Hydrate line.

Drilling fluids are complex mixtures that have several functions as clean the well, carrying solids to the surface, provide a hydrostatic pressure, cool and lubricate mobile parts, among others. During a circulation stop, caused by a shut in period, or after a gas kick, the decrease of mud temperature could reach until values inside hydrate zone. Hydrate formation could result the drilling mud to lose its rheological properties, affecting the flow. In worst case, the solid plug could totally block the fluid movement.

Another issue, after formed a hydrate plug, is estimating how long it would take for dissociation, by means of depressurization, heating or chemical additives. A rapid liberation of gas when hydrate crystals dissociate could result, if not controlled, in destruction of the rig equipment, because there is a great amount of gas inside the solid. One cubic meter of hydrate could liberate one hundred seventy cubic meters of gas. Also, there is a risk about the velocity of the plug, when it is pushed out of the line.

The main objective of this article is to present a comprehensive literature review about hydrate formation in drilling operations, covering references of laboratory tests, inhibitors, thermodynamic and experimental model providing information for understanding the problem in petroleum industry.

2. LITERATURE REVIEW

Lai and Dzialowski (1989) investigated 23 drilling mud formulations, presenting laboratory-derived equilibrium temperature and pressure data. For the authors, little data had been published on gas hydrate formation in drilling mud because of the lack of equipment available for mud studies. 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 a visual inspection, because drilling mud were opaque. They 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 a choke or kill line. The pressure to break through a plugged line was of particular interest. The 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 for 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. It was used a synthetic/natural gas mixture. The cooling and heating rate were chosen about 1.7 K/h (3 °F/h). Slowing the rate to 0.06 K/h (0.1 °F/h), the formation temperature was lowered and the precision improved. This increased the test time on a system from one day to weeks. They 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, in hydrate research, it is necessary to determine the highest possible temperature at which hydrates can be stable for a given pressure and gas composition. This is the *dissociation point*, which is determined by cooling the test fluid during contact with a gas, then forming hydrates, and slowly heating until the last hydrate crystal disappears, inside a PVT cell. They made a series of experimental tests, with several fluid mixtures. The results of a typical experimental run are in Figure 3.

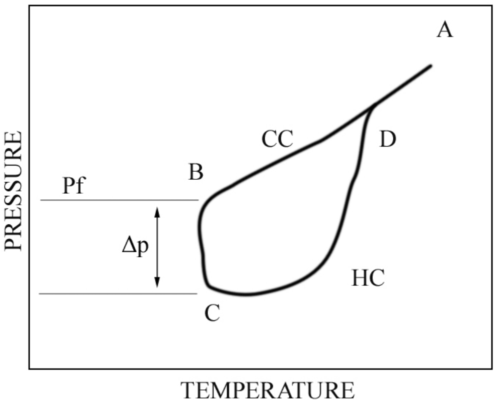

Figure 3. Temperature versus pressure, from Kotkoskie et al. (1992).

In this figure, point A represented the pressure and temperature conditions of starting the test. Line CC shows the isochoric cooling period, from point A until B, where the temperature was held constant. They found that twenty-four hours at constant temperature, T_B , was a reasonable time to form an appreciable amount of hydrates and a significant pressure drop, Δp, from point B to C. After the holding period, the system was heated to its original temperature, following the line HC. Heating was slow to allow the system to be at or near equilibrium, particularly in the neighborhood of the dissociation point, where the heating curve rejoined the cooling curve, in point D. This couple pressure/temperature was characteristic of the thermodynamic equilibrium of gas hydrate in the gas and mud studied, their dissociation point. A typical run of this kind of experiment lasted from 60 to 80 hours. The pressure at point B, Pf, was where hydrate formation first became apparent and the total pressure drop, Δp, was 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), chose Soave-Redlich-Kwong (SRK) equation of state that appears to give more accurate fugacity for natural gases than Peng-Robinson equation. These cubic equations of state are suitable for engineering calculations. The tendency of the SRK equation to calculate poor liquid densities was addressed by correcting them 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 were modeled with the 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 of 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 that 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 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 hydrate.

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 tube, 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 mudline 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 point, obtained from two techniques. The first one was the more classical, such as measurements of pressure variation versus temperature, at constant volume, PVT, and the second was Differential Scanning Calorimetry, DSC, a rapid and sensitive technique, broadly used for the characterization of any kind of phase change. It allowed the measurement of heat transfer as a function of time, temperature and pressure and thus detected phase transitions. They carried out experiments at atmospheric pressure and high-pressure gas hydrates. It was 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 of interface between the two phases, emulsions allowed the formation of much greater amounts of hydrate than solutions, independently of any agitation. Further work was needed to apply DSC method 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 Hammerschmidt´s equation, but only few of them could work for complex systems including inhibitors. When the aqueous phase is a mixture of electrolytes and alcohols, the statistical thermodynamic type models need to be simplified. Such correlations intend to allow field engineers to obtain a quick estimate of the hydrate point suppression of a specific drilling mud. Ameripour (2005) developed correlations applicable to a range of temperatures up to 305 K (90 °F) 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. From gas composition, 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 operation, under the action of electrolyte inhibitors. They theoretically modeled the gas phase, considered as only methane, calculating fugacity with Peng-Robinson cubic equation of state. Modeling liquid phase, water activity was determined considering two situations. In the first one, without inhibitor, assuming there was no soluble component, the liquid phase was only water, so activity was equal one. In the second case, with inhibitor addition, it formed a non-ideal liquid mixture with water, demanding a methodology for activity calculation, which was chosen Debye-Hückel model. For hydrate phase, they followed van der Waals and Platteew statistic thermodynamic, where the condition for equilibrium is reached when water chemical potential in liquid phase is equal to water chemical potential in hydrate phase.

Applying Gibbs-Duhem equation, the authors presented an implicit equation for pressure calculation, solved by 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 literature, showed a good agreement, for mixtures with and without inhibitors.

3. DISCUSSION

In the literature, there are few laboratory experimental data of hydrate formation in drilling mud, maybe because these tests take long time or need special apparatus. A typical experimental result is pictured in Figure 3, the experiment starts at point A and a 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 in direction to point B, where hydrate begins to form. From this point, the pressure drop is drastic due to gas molecules are encapsulated into the hydrate crystal structure. This phenomenon of solidification is not necessarily an isothermal process, because depending on gas and liquid composition, point C could have a different temperature than point B. Actually, hydrate formation is an exothermic reaction. 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 for maintaining thermodynamic equilibrium at each temperature, and then, cooling and heating lines are slightly separated. The relative effectiveness of kinetic inhibitors could be evaluated comparing the time from point D to point B, for a constant cooling rate.

Due to the great amount of drilling mud, low dosage inhibitors are preferable so the use of kinetic and anti-agglomerant tends to increase. Laboratory testing continuously develop new and better samples, including studies about compatibility with drilling mud components and evaluation of kinetic plus thermodynamic inhibitors combinations. During the flow, precipitation of any component should not happen, while specific density, viscosity, corrosivity, flammability and toxicity aspects must be taken into account.

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

The drilling mud must be adequately inhibited against hydrate formation. If hydrate start to form, it is necessary to detect this event prior to hydrate build up. For this kind of monitoring, it is possible to use special devices such as acoustic, flow monitor and viscosity measurements, for example.

4. CONCLUSIONS

Research on hydrate formation is more developed in producing gas area, especially in deepwater fields, because in this case, the seabed ambient conditions of pressure and temperature are in the hydrate zone, and the probability of hydrate occurrence is high. Increasing deep offshore oil recovery also has extended gas hydrate problem to drilling mud area. Large amounts of methanol and glycol are currently used, in addition of salts as sodium and calcium chloride, which cause important difficulties 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, we have to take into account the particular characteristics of the mud composition. So, the hydrate problem has a slight difference from the studies of hydrates formed in natural reserves or in producing and transporting system. Gas solubility in the mud components plays an important rule in the studies of hydrate formation, because this is an interface phenomenon, where the free gas is trapped into the solid reticulum.

It is necessary a continuous effort to improve the understanding of the equilibrium conditions for hydrate formation in drilling operations, mainly in deep and ultradeep water, where they become a major concern.

5. ACKNOWLEDGEMENTS

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Internet site: http://www.pet.hw.ac.uk/research/hydrate/hydrates_what.htm

ESTUDO DE HIDRATOS EM OPERAÇÕES DE PERFURAÇÃO: UMA REVISÃO

Resumo: A formação de hidratos de gás natural em operações de perfuração é de crescente interesse dos engenheiros de petróleo, à medida que a procura por óleo e gás vai para águas profundas e ultra-profundas, onde baixas temperaturas e altas pressões são encontradas. A solução dos problemas de formação de hidratos nessas áreas exige grandes quantias de capital e despesas de operação. Além do mais, a liberação de gás próximo à superfície, durante a decomposição do hidrato pode criar uma situação perigosa de controle de poço. O hidrato pode começar a se formar em áreas de pouca ou nenhuma circulação, como as linhas de *choke* e de matar, ou próximo ao BOP. A água necessária para a formação do cristal pode ser proveniente do fluido de perfuração, alterando suas propriedades de escoamento. Muitas pesquisas têm sido feitas sobre as condições termodinâmicas (pressão, temperatura e composição) necessárias para a formação de hidratos de gás. Diferentes aparatos experimentais e métodos têm sido utilizados para pesquisar potenciais inibidores, que são divididos em três tipos: termodinâmicos, cinéticos e anti-aglomerantes. Dados laboratoriais são imprescindíveis para aprimorar modelos teóricos em um contínuo desenvolvimento. Este texto pretende fazer uma revisão desses assuntos, discutindo o estado-da-arte sobre a formação de hidratos em operações de perfuração.

Palavras-chave: hidrato, perfuração.