

A REVIEW ON HYDRATES IN DRILLING OPERATIONS

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Abstract. Oil and gas exploration and exploitation in deep and ultradeep waters involve handling of peculiar technical problems. Gas hydrates are crystalline structures of water molecules surrounding and trapping a gas molecule, what stabilizes the reticulum, having a visual aspect of ice. The hydrate could appear in geological deposits under the sea bed, but also could occur during drilling operations, particularly during a well control procedure. A long well shutin period could result in the cooling of the natural gas and drilling fluid mixture, under high bottomhole pressure, what are favourable conditions for hydrate formation. That situation would be particularly dangerous if the crystals formation would plug the BOP and/or choke line, avoiding the kick circulation and well control operation be resumed. The knowledge of hydrates formation thermodynamics and growth kinetics, as well as the influence of inhibitors (type and concentration), should allow the development of a methodology to foresee the possibility of hydrate occurrence, to detect its presence and to prevent the problems associated with it, particularly considering safety operational issues. The objective of this work is to present and discuss the results of a comprehensive literature review about hydrate formation, experimental research in the area and reports on its occurrence in drilling operations.

Keywords: hydrate, drilling

1. INTRODUCTION

The main objective of this work is to present a literature review about gas hydrates, their molecular structure and its importance in the exploration and exploitation of oil and natural gas. Research techniques to study hydrates formation as well as their occurrence in drilling operations are also addressed.

Water is considered one of the simplest molecules abundantly found in nature. Although apparently common, its behavior could acquire peculiar aspects in some special cases, as hydrates, that are inclusion composites, where the hydrogen linking creates crystalline reticulum involving a gaseous substance, what promotes the stabilization of the solid, whose melting point can be many degrees above ice melting point. The first condition that favors gas hydrate formation is the combination of high pressures and low temperatures, easily found at sea mud line in deep and ultradeep waters. Accurate levels of the thermodynamic parameters to promote this phenomenon depend on gas composition, the presence of the stabilizing molecule of the crystalline structure, and the right amount of water or even ice.

It has been found that there were different types of hydrate lattices, which were referred to as structure I, structure II, and structure H. All the three types of lattices contain small, medium and large cavities, according to Table 1. These void spaces could be occupied by small molecules such as gaseous hydrocarbons.

Table 1. Number of water molecules and cavities for each type of hydrate structure. One cavity can hold one molecule of the stabilizing substance of the crystalline reticulum (Sinquin et al., 2004).

Structure	Water molecule	Small cavity	Medium cavity	Large cavity
I	46	2	-	6
II	136	16	-	8
H	34	2	3	1

Historically, Sir Humphry Davy, in 1811, discovered chlorine hydrate in his experiments, that he called clathrate. Since then, hydrates of other gases have been obtained and studied, with greater advancement with natural gas industry, in the 20th century. Gas hydrates may cause problems like plugging of pipes, nozzles and other equipment, what are important to consider in the design of plants and pipelines.

In hydrate research it is possible to obtain a graph of pressure versus temperature, as depicted in Figure 1, which indicates the hydrate line, or hydrate-formation curve. There is one curve for each guest molecule (like methane, ethane, propane, and so on) and depending on the type of hydrate structure. The solid formation occurs under the conditions to the left of the hydrate line, so this region must be avoided during plant operation.

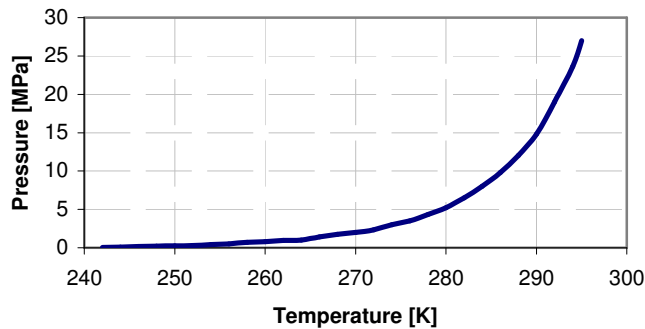


Figure 1. Hydrate line (Baptista et al., 2006).

Given a pressure, the term *subcooling* is related to the temperature difference until reaching the hydrate line. The greater the subcooling effect, the better is the applied technique to avoid reaching hydrate phase boundaries. Inhibitor addition could shift the hydrate line towards lower temperatures, presenting a subcooling effect related to the type and amount of inhibitor.

Since the 1960s, naturally formed hydrate reserves have been found around the world, increasing the interest in exploring them as a methane source. The acquired knowledge indicates the potential of its use as alternative energy in the near future, stimulating the amount of research in the area. Particularly during drilling operations, hydrate formation in choke and kill lines, inside the BOP (Blow Out Preventer) and downstream valves, regulators, orifice plates, sharp bends (where turbulence accelerates hydrate formation, according to Maddox, 1989) should be better understood.

2. LITERATURE REVIEW

The review was organized in three sections: hydrate formation, experimental aspects and hydrate formation during drilling operations

2.1. Hydrate formation

Carroll (2002), Sloan (1997) and Makogon (1981) present the definition of hydrates, the conditions under which they could be formed, types of structures, methods to foresee their occurrence, limitations of the prediction techniques, review of thermodynamic models and computational packages available in the market, inhibitors, the process of dissociation, properties of hydrates, balance of phases, experimental data and use of hydrates.

A computational algorithm to foresee conditions of hydrate formation was presented by Rossi and Gasparetto (1991). It was based on the model considered by van der Waals and Platteew, in 1959, accounting for the interactions among the water molecules that form the crystalline reticulum and the gas molecules. The relations of the classic thermodynamics assisted by the statistic thermodynamics allowed to obtain the occupation fraction of the crystalline reticulum as a function of system pressure and temperature. Comparison with experimental data indicated good phenomenological description of force interactions on the molecules that formed and stabilized the crystal lattice.

Kini et al. (2004) studied hydrate growth kinetics measurements in methane plus propane structure II hydrates, probably the most common structure formed with natural gas. Although there were half as many large cages as small ones in that structure unit cell, data suggested that the large cages, filled by propane, formed twice as fast as small cages, stabilized by methane. A hypothesis based on low occupancy of small cages was presented to explain faster growth of large cages. These hydrate growth measurements could be used to improve hydrate plug prevention strategies.

2.2. Experimental aspects

The study of hydrate formation and dissociation has been performed, generally, under three kinds of experimental procedure: PVT measurements, calorimetry and rheology.

When hydrate is formed at constant volume, the pressure of the environment starts to reduce (as the gas is consumed). Because drilling fluids are opaque, it is difficult to perform a visual observation of hydrate, so the measurement of the pressure is the basic principle of the majority of the existing experimental works. The drilling fluid is placed inside a vessel of controlled volume, the PVT cell. It is pressurized and temperature is reduced until the beginning of hydrate formation, causing a sensible pressure drop and a small temperature increase. After the formation, the temperature is increased at a small rate until the hydrate totally dissociates. The intersection between the heating curve and the cooling one is the *dissociation point*. One curve pressure/temperature, that is characteristic of the thermodynamic equilibrium of hydrate in the fluid (Ebeltoft et al., 1997), can be traced repeating again this procedure for some pressures.

One of the techniques used for thermal characterization of physical-chemical transformations is the DSC - Differential Scanning Calorimetry. It consists of monitoring the heat exchange between the sample and a reference, as

function of time at constant temperature, or as function of the temperature during a heating or cooling program. Both the containers are in a thermoregulated oven. The variety of equipment basically differs in the form of measuring the heat exchanges. In summary, thermocouples indicate the difference of temperature between the two containers. The transferred heat is calculated from this temperature difference. In most complex equipment, Calvet principle is used to measure the exchanged heat. A great number of thermocouples creates a net of independent sensors that involves each container. The accurate relation between the heat flow and the electric power is obtained by calibration. According to Dalmazzone et al. (2002), this technique is easy to use and when correctly interpreted, it could determine the zone of hydrate formation. The necessary equipment is DSC device, with accessories for high pressure and temperature control, and the gas reservoir. In hydrate formation, the main limiting factors in the use of this method are the pressure levels and the agitation of the sample.

In rheological measurements, the solid particle formation inside a liquid modifies the characteristics of the flow in the rheometer, increasing the pressure drop (Sinquin et al., 2004). This is a special issue in drilling operations. The amount of hydrate will be harmful to the operation when the flow of the drilling fluid drops below a certain critical value, which will vary case by case. In laminar regime, the range of apparent viscosity is the important parameter, while in the turbulent one the friction factor has a higher influence on the pressure drop.

A special technique has been used to study hydrates in porous media with glass micromodels (Tohidi et al., 2004), which provide a unique opportunity for the observation of phase behavior in reservoir fluid systems. Several tests were conducted with methane, carbon dioxide, mixtures of both, and a natural gas to investigate the effect of fluid composition, presence or absence of free gas and the presence of nucleation sites on gas hydrate formation in porous media, as well as the effect of salt on the mechanism of hydrate formation. The results show that gas hydrate could be formed at the gas water interface or from the dissolved gas within the water phase, whereas the amount of hydrate formed in the water phase is a function of gas solubility. It was demonstrated that the formation of hydrate reduced gas saturation in the adjacent water phase, resulting in concentration gradient and gas diffusion from the surrounding water. Gas diffusion played an important role in gas hydrate growth, in particular at low degrees of subcooling, where some gas bubbles were dissolved in the water phase and transported to the hydrate forming regions.

2.3. Hydrate occurrence in drilling operations

Barker and Gomez (1989) reported two cases of interrupting the drilling process due to natural gas hydrates. The first one was in a well located at 350-m water depth offshore the United States west coast, with a sea water temperature of 280 K at the mudline. Due to a gas kick, the BOP was closed and gas hydrates had been found blocking choke and kill lines. The second case took place in the Gulf of Mexico, at 945-m water depth, 277 K, when the well was found flowing during flow check. After describing the applied procedures to solve the problem of hydrates, which had made difficult the subsequent operations, the authors arrived to some conclusions. Methods of action for the hydrate occurrence during well control operations would have to consider long shut-in periods. A previous mud circulation to maintain subsea BOP's temperature above static mudline temperature was not enough, because many hours, or even days, without wellbore circulation could allow gas in the BOP's to cool until reaching the sea bed temperature. Apparently, several hours had been necessary to block the subsea equipment. In general, gas hydrates could cause more complex problems in deepwater drilling. Despite this, it was possible to safely treat them. Both cases ended with no human accidents, uncontrolled flow or pollution.

Intending to displace the hydrate line (Figure 1) to left, Kelland et al. (1995) commented that chemical methods had been developed, related to the use of inhibitors. There are three types, the first one is thermodynamic, which involves polar and electrolytic composites that interact with molecules of water and gas, hindering the hydrate formation; the range of their applied concentration, in weight, is from 10 % to 60 % and some examples are methanol, ethylene glycol and salts. The second type is kinetic, which have effect in the chemistry of the nucleation and the growth of hydrate crystals – as function of time and stochastic processes; they are used in small concentrations, less than one per cent in weight and some examples are polymers as poli (N-vinilpirolidone) (PVP) and hidroxietilcelulose (HEC). The last class of inhibitor is anti-agglomerator, which prevent the agglomeration of crystals, so the solids are carried without blocking the flow; they also are added in low concentrations, less than one per cent in weight and some examples are polymers (polyacrylamides), surfactants (alquilfeniletóxilatos), polisaccharides (xanthan, Arabic and karaya gum), bile acids (glycocholic acid), alkyl glycosides (alkyl- β -D-glycopyranosides). In order to prevent hydrate formation, in small or medium size fields, the insulation of the tubing or the application of thermodynamic inhibitors are usual methods. Another technique performs the heat of the pipe, either by hot water jacket, or by an electric resistance involving the tube. Kinetic inhibitors and anti-agglomerators have been more attractive from the economic point of view, in comparison to the thermodynamic ones. Moreover, their application in the shutin stage can also be advantageous. New types of inhibitors could reduce the costs of the product itself, transport and equipment aspects of injection, pumping and storage, besides making possible the improvement of environmental requirements. Experimental tests in high-pressure sapphire cell have been carried out, to analyze the kinetic and anti-agglomerator inhibitor action, not based on fugacity, which was the method used by other researchers, but on the chemical potential, evaluated from measures of driving force. The kinetic ones delayed the formation of the crystal, but they did not present the anti-agglomerator effect. Anti-agglomerator additive, applied to an oil based mud, inhibited the agglomeration of crystals during and after

hydrate formation, and the oil acted as the continuous phase to carry crystals. An inhibitor must interact with the fluid, that is, it should be studied in which applications the inhibitor could be applied and the chemical effect must act over a certain range of concentrations, in case of some amount being accumulated in one portion of the pipeline. Some inhibitors showed a concentration limit for its action, above which the activity was stabilized or even decreased. The highest temperature, about 373 K, could not hinder the inhibitor solubility, and the viscosity should not difficult its application. Finally, there must be chemical compatibility with other composites such as corrosion or wax formation inhibitors, besides agreement with the legislation regarding toxicity and pollution. In conclusion, the kinetic inhibitors have had limited application, perhaps a temperature variation of only 10 K of subcooling. The anti-agglomerator could solve this problem, however its action depends on the hydrocarbon fluid composition, the brine concentration and the water presence. A new inhibitor generation could surpass these difficulties, always considering reduction of costs and environmental aspects.

According to Ebeltoft et al. (1997), drilling mud using salts and polymers had been applied in Gulf of Mexico, North Sea and Brazil. They presented experimental measurements with hydrate phase equilibrium in twenty-five, including two new drilling fluid formulations. In Gulf of Mexico, it was usual to prevent hydrate formation with highly saline drilling muds, however, in Norway, at extreme water depths or very low temperatures, that thermodynamic inhibition was not enough. Kinetic inhibitors, together with the thermodynamic, had revealed more efficiency. The authors concluded that the most common drilling mud used in deepwater, had been the systems of 20 % to 23 % NaCl, in weight, together with polymers, because, based on the weight, the NaCl was the most effective one, followed by KCl, CaCl_2 , NaBr, Na-Formate and $\text{Ca}(\text{NO}_3)_2$. Besides, Na-Formate increased the degree of inhibition of the NaCl, but it had the tendency to precipitate at low temperatures and high concentrations. Synthetic fluids with 30 % of CaCl_2 had not formed hydrates; however, when the concentration was reduced to 15 %, the precipitation happened. Among the tested glycols, ethylene glycol had the best performance. These experiments showed that organic phase of the synthetic fluid slightly reduced the hydrate equilibrium temperature; on the other hand, at the same time, it increased the rate and the amount of hydrate formation due to higher solubility of the gas. Finally, regarding the two new formulations, without solids, the first one did not form hydrates while the second one demonstrated a subcooling effect of 25 K.

Palermo et al. (2004) discussed self-inhibition based on natural surfactants, which has been investigated and field-observed. Experiments have demonstrated the capabilities of appropriate flow conditions to restart operations in the hydrate domain. Petrobras experience in Campos Basin has shown that crudes have natural surfactants compounds that strongly stabilize water-in-oil emulsions. This behavior will reflect on hydrate-oil stability and may explain why no hydrate plugging has been reported in production flowlines even during shutdowns and restart operations. Based on field experience and pilot loop tests, authors have reviewed hazards associated with different operational conditions inside the hydrate domain without conventional prevention methods.

A thermodynamic analysis was performed by Baptista et al. (2006), about hydrate formation in drilling operations. Both sea water and drilling mud, have a certain amount of salts in their composition. Inhibitors, as salts and alcohols, diminish the system free water quantity. So, it is important the knowledge of how salt inhibitors could prevent hydrate occurrence. It was analyzed a system of three phases named alpha, H and G. In the first phase, alpha, there was free water, with solubilized inhibitors. This phase could be solid, liquid or gaseous, but the authors only focused in liquid phase. The second phase, H, represented the lattice of water molecules. The last phase, G, was composed by methane. Non ideal liquid phase was considered by Debye-Huckel activity coefficient, while hydrate phase was studied by statistical thermodynamics of van der Waals and Platteew. Fugacity calculation of gas phase was obtained with Peng-Robinson equation. They tested salt inhibitors such as sodium chloride, potassium chloride and calcium chloride, in several concentration and combination, showing a good agreement between theoretical and experimental data.

A general equation capable of predicting hydrate inhibition effect of various salts and organic additives was developed by Østergaard et al. (2005). The correlation requires inhibitor concentration, pressure of the system and, if known, the dissociation pressure of the fluid in the presence of distilled water at 273 K. They studied hydrate phase boundaries for methane and seven natural gases in the presence of various single inhibitors, covering nine electrolyte solutions and six organic inhibitors, which may be available to the reservoir and drilling fluids. It was analyzed the effect of pressure, hydrocarbon fluid composition, inhibitor and ionization.

Botrel (2001) presents a discussion about some procedures, as to flush choke and kill line circuit with a water free fluid, in order to avoid or to mitigate the problem. A different well control method consisted in mixing, at BOP's level, the circulating mud with an Additional Flow Rate fluid of lower density and rheological properties. Density and rheological properties of the mixture entering the choke line were lowered compared to the original drilling mud properties and induced a decrease of the hydrostatic head and friction losses inside the choke line. Once formed, hydrates are difficult to remove, because it takes around twice more heat to dissociate hydrates than to melt ice. The addition of chemical inhibitors in the formulation of drilling mud is only partially effective, therefore, a sound strategy to prevent and remedy hydrate incidents during drilling operations must be implemented. The possibility of hydrate formation involving nitrogen gas and the water content of hydraulic control fluid inside subsea accumulators was also discussed. Among some remedial action, one could list external heating, internal heating, de-pressurization, chemical dissociation and mechanical removal.

Barros Filho et al. (2004) explained hydrate problems in the case of a well located in the coast of the state of Sergipe, Brazil, with water depth of 1164 meters. After testing the interval 3674-3682 meters, during the withdrawal of the electric cables, there was a problem at 1257 meters of depth, near to the submarine tree, due to hydrate formation that, besides immobilizing the cable, hindered the reverse circulation and consequently the withdrawal of the column. The lines were depressurized and the column of liquid exerting hydrostatic pressure on the hydrate was removed, through the use of flexi tube, in order to modify the conditions of hydrate formation, promoting the dissolution of the plug. Although uncommon, the use of flexi tube with the presence of the electric cable in the column increased the operational flexibility. The injection of methanol and butilglicol contributed considerably for the success of releasing the test column, with possible predominance of butilglicol, due its higher density and tendency to keep in contact with the hydrate plug. The removal of hydrate was done with the help of depressurization of the column with nitrogen and linear paraffin circulation on the plug through flexi tube, each technique carried out simultaneously to injection of methanol and butilglicol through chemical line and drilling mud above of the BOP.

3. DISCUSSION

In order to face the challenge of studying hydrate formation in drilling operations, it was necessary to understand the history of this compound, since its discovery until nowadays, when there are some reports about incidents related to this phenomenon. After analyzing its characteristics and the particular conditions to promote its formation, the next step was to choose the adequate experimental equipment to perform tests in laboratory. Among them, three techniques were identified: PVT cells, calorimetric method and rheological measurements. Ideally speaking, each one could extend the work of the other, with their advantages and disadvantages. Much more experimental data are expected by the researchers to improve the safety and decrease the costs of drilling operations, because there still is a surprising lack of available data in literature.

Another important issue is the use of inhibitors, which can be divided in three categories, thermodynamic, kinetic and anti-agglomerator. The most widely used are the first ones, probably because the knowledge from the experience dealing with snow and ice. Unfortunately, they have less effectiveness at high pressure and low temperature. Besides, the necessary amount of these substances is very large, which is expensive. This fact leads to enhancement of the research looking for another kind of inhibitor, improving the technology on this area.

About hydrate formation in drilling in deep and ultradeep waters, only a few publications of field cases were found in literature, despite the great probability of this phenomenon occurrence in that area of exploitation. When someone detects a hydrate formation, it must be encouraged to do a report about the conditions, pressure, temperature, mud composition and so on, providing a development of the procedures adopted to solve the situation.

Making a theoretical study, thermodynamic models of hydrate formation need gas composition as an entry data. The relative amount of methane, ethane, propane, n-butane, i-butane and non-hydrocarbons, specially hydrogen sulfide, carbon dioxide and nitrogen, as well as their solubility, should be taken into account.

There are two ways in order to propose an equation for hydrate curve. Based on thermodynamic studies or fitting experimental data. The use of computer programs makes fast and better the analysis of the parameters involved in hydrate formation. So the crew could have the necessary information to make the right decision in a short time.

A relevant aspect about hydrate formation in drilling operations is related to gas solubility. When gas enters into the well, it could be totally miscible in the liquid phase. It depends on pressure, temperature and gas composition. In this case, there would be possibility for gas molecule to stabilize a water reticulum, at gas water interface or among the dissolved gas within water phase (Tohidi et al., 2004). Consequently, the user must consider the right amount of each gas to determine hydrate phase boundaries, when applying software for calculations. The precise composition of gas and liquid phase is an important entry data for a correct software prediction. Solubility is a key topic in deep and ultradeep waters drilling because in this case, synthetic oil-based mud may be more indicated than water-based mud. As Silva (2004) concluded in her work, methane solubility in synthetic oil-based mud must not be ignored.

Finally, study of hydrate formation needs local temperature, inside the pipe, as input, and this is a very difficult measurement and/or prediction. In this way, it is also necessary to develop a system of temperature measurement.

4. RESEARCH PLANNING

Initially, it is necessary to choose the gas phase and the test fluid. In a prospective methodology, based on PVT measurements, in this case, the option could be methane or natural gas and water, aqueous salt solutions or drilling muds as the liquid phase.

For this investigation work, the following experimental apparatus, showed in Figure 2., will be built. A 300-cm³ autoclave cell is filled with test fluid. In order to understand the process, the cell pressure and temperature must be measured and recorded to get the hydrate phase boundaries, as in the Figure 1. A 500-cm³ gas bottle, with 6,88 MPa (1000 psi), is connected to the cell and should permit feeding the gas, through a valve that is open, carefully, until reach the pressure determined by the desired gas-liquid ratio (for example, 4,83 MPa (700 psi)). Closing the valve, the system of liquid plus gas, with constant volume and composition, will be ready for the test. After having the calculated amounts

of methane and test fluid inside the cell, a special pump could be used to get higher pressures, for instances, up to about 34,5 MPa (5000 psi). The pressure rating needs to simulate the expected value in the subsea environment, to anticipate field conditions, so the limit pressure could be upgrade in the future. The cell is immersed in a water and ethylene glycol solution, inside an acrylic chamber, to simulate the low temperatures. The cooling equipment has capability to provide solution constant temperature set from 268,15 K up to 333,15 K.

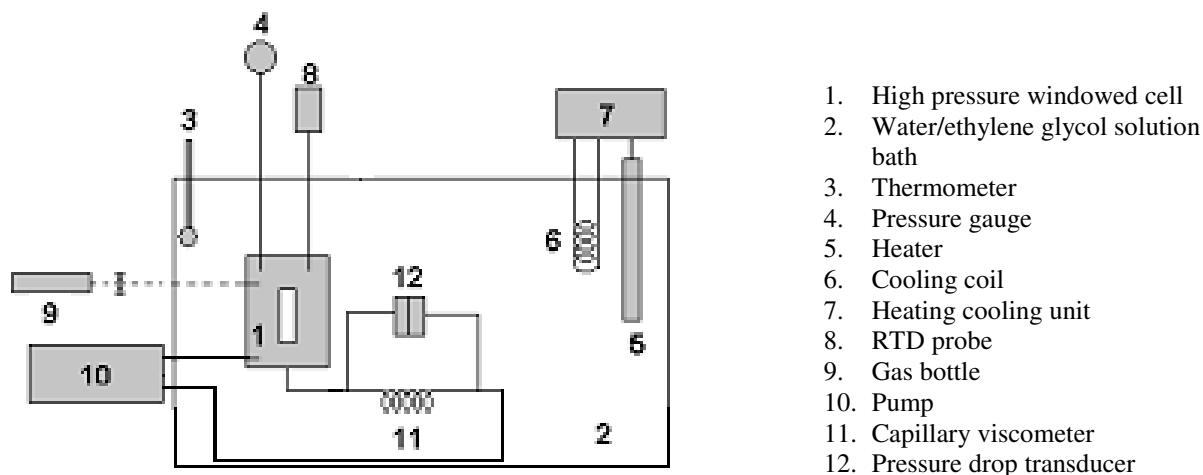


Figure 2. Schematic apparatus for hydrate formation tests.

To start the experiment, the temperature must be set to a value slightly above the expected hydrate point. The thermal equilibrium may be obtained, when the cell temperature equals to the bath one. Then, the cooling rate must be set to about 1,5 kelvin per hour, a reasonable rate for hydrate nucleation. For a visual static observation, through the window one could note the solidification phenomena observing the interface between gas and liquid. If the fluid test is opaque like drilling muds, then the hydrate formation should be monitored exclusively by measuring pressure. Besides this pressure and temperature study, it is worth to have a capillary viscometer connected to the cell, for evaluating the changes in the viscosity data during the hydrate formation, in a very small flow.

Once formation has begun, growth may be quite rapid. It is important to obtain some measurements about the growth velocity, controlling the time of the experiment. It is expected that hydrate take longer time to form in mixtures than in pure water and this difference should be greater at lower pressures, because some substances, as salt, may have a function as inhibitor.

Some experiments could analyze the effects of the addition of inhibitors such as sodium chloride, calcium chloride, glycerol, polymeric solutions and so on.

After the formation of a solid block, it is possible to start a heating process and the dissociation time could be studied, besides the effectiveness of some techniques, as the addition of methanol, for example.

In the literature, there are several equations determined by fitting experimental data, calculating the pressure or temperature of hydrate formation, as a function of gas and drilling mud compositions. Their results could be used to compare and adjust the tests. In addition, a modeling investigation could be conducted, based on an equation of state, generating a predictive thermodynamic model, validated against experimental data.

Once this methodology is implemented in a laboratory, it will permit to obtain experimental and theoretical data for various mud systems and gases, studying the effect of several factors on the equilibrium point and reaction rate. Then, it should help the development of better drilling fluids to significantly inhibit or even prevent hydrate formation in drilling offshore wells.

5. CONCLUSIONS

In this work we discussed the importance of hydrate formation in drilling operations, pointing out what these solids are, some techniques used to analyze them and specific problems related to drilling mud. Among several challenges faced in offshore Brazilian oil and gas exploration, there is great probability of gas hydrate occurrence during deep and ultradeep water drilling operations. This is due to favorable conditions of high pressures, low temperatures and the presence of water in drilling mud, or in the formation, and gaseous hydrocarbons from the vicinity nearby the well. There should be special concern to prevent the dissociation in natural hydrate reserves, during drilling operations, when these interventions could cause severe damages to formation. Even more interesting is to develop a methodology to foresee hydrate formation, considering the composition of gas and drilling mud, solubility and expected pressure and

temperature profiles, and optimize techniques to deal with the occurrence of the phenomenon. If the crystallization of the solid happens, equally important are the procedures to locate and remove it, taking in consideration the economic, technical, safety and environmental parameters. Research on this subject will contribute to continuous development of petroleum technology.

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