ANALYSIS OF GAS HYDRATES FORMATION IN A PRESSURE CELL

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Abstract. *The hydrate formation and paraffin deposition in pipes are two huge problems related to oil recovery in deep and ultra-deep water. Natural gas hydrates are compounds of small gas molecules and water and they are formed when the constituents come into contact with each other at low temperature and high pressure. In a similar way, the paraffin deposition is formed during normal operational conditions, due to heat transfer from the oil to the environment in the oil production process. The analysis of the phenomenon is extremely complex, especially when the oil temperature reaches values below the gelled temperature (GT), because the oil losses its Newtonian character and assumes an elasto-visco-plastic-thixotropic behaviour. In fact, such a phenomenon is one of the most problematic in the petroleum industry. A reliable measurement of yield stress is very important and difficult, since this value is highly influenced by shear and temperature history and also the composition of the waxy crude oils. The objective of this work is characterize an oil using a pressure cell, which enable us to take into account some rheological properties under high pressures, enough for the hydrates formation.*

Keywords: Gas Hydrates, Waxy Crude Oil, Pressure Cell.

1. INTRODUCTION

The hydrates are chemical compounds in which water molecules form capsules that are stabilized by gas molecules trapped inside "cages". In other word, hydrates are clathrate compounds in which the host molecule is water and the guest molecule is typically a gas. These gas molecules must have appropriate size to imprisonment, the most common are: methane, ethane, propane and carbon dioxide. The hydrates physically resemble ice, they are solid crystalline structures that do not flow and its formation and stabilization is facilitated by high pressure levels and low temperatures, as reported by Sloan and Koh (2007).

The hydrates are an important issue on flow assurance in the oil and gas pipelines as reported by Sinquin et al. (2004), Oliveira et al. (2010) and other authors. Typically, the oil leaves the reservoirs and enters the pipeline at a temperature ranging from 60 to 100 ℃. The temperature in very deep waters environment can achieve 4 ℃. This temperature difference generates a heat flux from the oil to the environment but, normally, at these conditions is difficult to have crystals formation. The complication arises when the passage of oil has to be stopped, which is caused for operational reasons, for maintenance of well for example. In this case, the oil is gradually cooled and at moderate pressure, hydrates form, leading to plugging of the transmission lines, causing costly production stoppages, sometimes for as long as months, while the hydrates are dissociated. The oil industry would like to maintain production processes outside the gas hydrate-formation stable range. However, if by the one side, this task is facilitated by knowledge of the thermodynamic conditions favorable to the hydrates formation, by the other, the usual temperature conditions in ultra-deep waters, associated with high pressures from the economic production demands, leads to a risk situation, because the thermodynamic conditions are into the hydrate formation region, see Sloan (2003). The strategy usually taken by the oil industry is to continue working in the thermodynamically favorable range to stability of the crystalline structure of solid hydrate. However, given the scale of the problem, the introduction of hydrate inhibitors methods is required as reported by Chen et al. (2013). Tariq et al. (2014) indicates that the adoption of these methods of hydrates inhibition can reach 15% of the total production cost.

There are different methods to prevent the problem associated with hydrates formation. For example, dehydration (since water is essential in this process); injection of thermodynamic inhibitors such as alcohols and glycols;

maintenance of the temperature outside the zone of stable hydrate using insulation or heating; use of low dosage hydrate inhibitors which can be divided into: kinetic hydrate inhibitors and anti-agglomerants agents.

Thermodynamic inhibitors of high dosage as alcohols and glycols require a high volume level injected to cause the change of thermodynamics range of hydrate stabilization. Thus, they are extremely expensive to be implemented, see Talatori and Barth (2012). Methods such as insulation and heating are also very expensive: the first requires great expenditure of material, and the second, power. Therefore, methods of injection of low-dosage inhibitors are those that currently dominate the actions to avoid blocking ducts by hydrates.

After nucleation of hydrates in different parts of the domain, there is a growth of crystalline hydrate structure that is governed by the kinetics of formation of new crystal structures attached to the old. As this process occurs in several regions, these structures are found and have a tendency to agglomerate. While low-dosage kinetic inhibitors decrease the reaction speed, governed by the kinetics of hydrate growth, low-dosage anti-agglomerants inhibitors act to hinder agglomeration of structures as explained by Jensen et al. (2011).

Another approach is the analysis of the rheological material in the presence of hydrate crystals. This complementary approach has a positive feature in a practical point of view, as to understand the mechanical response of the material that allows establishing the appropriate conditions for its flow. To discern the impact of the action of low-dosage inhibitors in the rheology of paraffinic oil, it is necessary to know the rheology of the parent compound, before the hydrate-formation. Thus, this parent compound can be taken as a reference and the performance of high-dosage inhibitors can be measured from the point of view of its mechanical response.

The goal of the present work is to rheologically analyze the gas hydrate formation in a rheometric geometry, through a pressure cell. With this device, it is possible to study the emulsion under low, medium and high pressure and several temperatures.

2. EXPERIMENTAL PROCEDURE

The measurements were made with a commercial rheometer Haake Mars II, manufactured by Thermo Scientific, Germany. The geometry used is a concentric cylinders PZ35 for pressure cell, as illustrated in the Fig. 1.
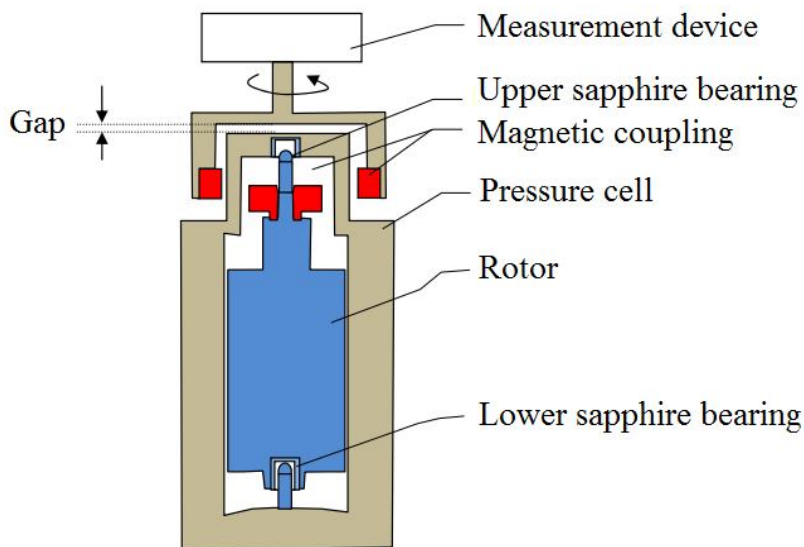

Figure 1. Geometry PZ35 for Pressure Cell.

The device consists of two parts. The outer part, which is composed by the cylinder base of the pressure cell and the magnetic coupling, and by the measuring geometry (rotor), which is supported by two sapphire bearings, located at top and bottom within the pressure cell. The rotor drive is done by the magnetic field created by the two magnets, indicated in red in the Fig. 1. The inner magnet is located at the top of the measuring geometry, while the external magnet is coupled to the measuring head of the rheometer.

Compressed air is supplied by an oil-free compressor. It is used to lubricate the bearings of the measuring head, allowing it to rotate with minimum friction. The sample temperature control is done through a thermostatic bath type Thermo Haake Phoenix II P1-C50P model, also provided by Thermo Scientific. All experiments are automatically controlled and the results are extracted with the aid of HAAKE RheoWin (version 1.3) program. The gas (CO_2) used to pressurize the cell and which is required for forming the hydrate is stored in a pressure cylinder. The same is conducted to the pressure cell as illustrated in Fig. 2. The pressure desired for the experiment is regulated through a series of

valves. The cell supports up to 400 bar pressures. The amount of sample used for each test is 50 ml, which is deposited between the rotor and the inner wall of the pressure cell.

Our waxy crude oil extracted from the pre-salt well was supplied by the Brazilian Oil Company (Petrobras). Initially with 10% of water, it was dehydrated by the gravitational method of the volumetric flask. The residual water content was then measured by Karl Fischer titration technique indicating 0.3%. This dry oil is used as a reference for all our experiments. The dry oil was mixed with brine, the latter was made with deionized water and 5% of salt. All the samples studied in the present work have a concentration of 30% water-in-oil emulsion. The emulsions were prepared rigorously following the procedure described below: Initially the oil and the deionized water were heated to 80 ℃ in closed bottles for 1h. After that, the samples were cooled down spontaneously at the room temperature. Finally, when the samples reached the ambient temperature, they were mixed manually, and subsequently, with the aid of a blender in a turbulent flow (speed and stirring time also were controlled in the different samples) to obtain the emulsion. Before deposited the prepared sample in the geometry of the pressure cell, it was stirred again manually for 3 minutes.
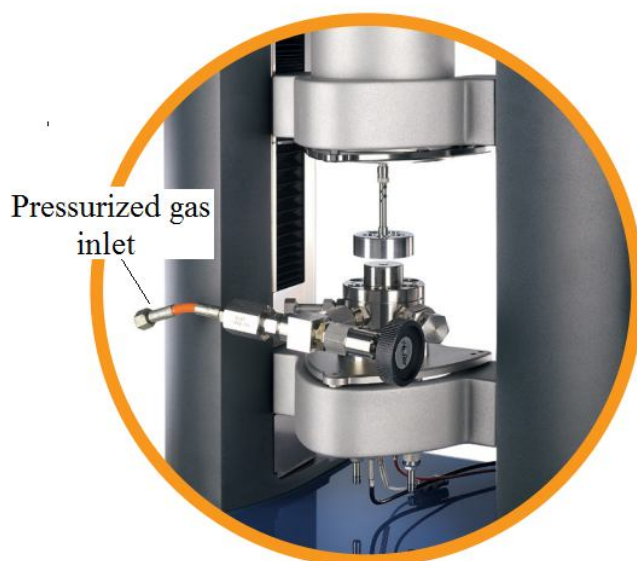

Figure 2. Inlet of pressurized gas to the cell.

3. RESULTS AND DISCUSSION

Figure 3 shows the viscosities of dry oil and emulsion varying with a temperature for a period of time. This experiment was conducted to see how the sample behaves under the effect of pressure. The final temperature, which is desired to analyze the gas hydrate formation, was maintained constant for a long period of time. The shear stress used in the test was always constant, 200 s^{-1}. Initially the temperature was reduced from 20 °C to 4 °C, causing the increase in viscosity at the beginning in the curves. In the Fig. 3, the solid red line indicates the temperature variation over time. Regarding the depressurized samples, the viscosity of the emulsion achieved higher values than for the dry oil. This result is probably because the effects of droplet size, in the case of the emulsion, are lessened at the time of the mixture preparation. Usually, size effects are due to significant colloidal interaction between particles. Decrease in particle size means increase in surface area and thus an increase in the viscosity. For a more detailed understanding, see Barnes (1994).

As expected, the viscosity of pressurized emulsion is less than the viscosities of the unpressurized samples. That is, the pressure in the emulsion reduced its viscosity, since the gas interact with the liquid molecules. This is essential for hydrate formation. As already mentioned, the single small guest molecules are encaged by hydrogen-bonded water cavities.
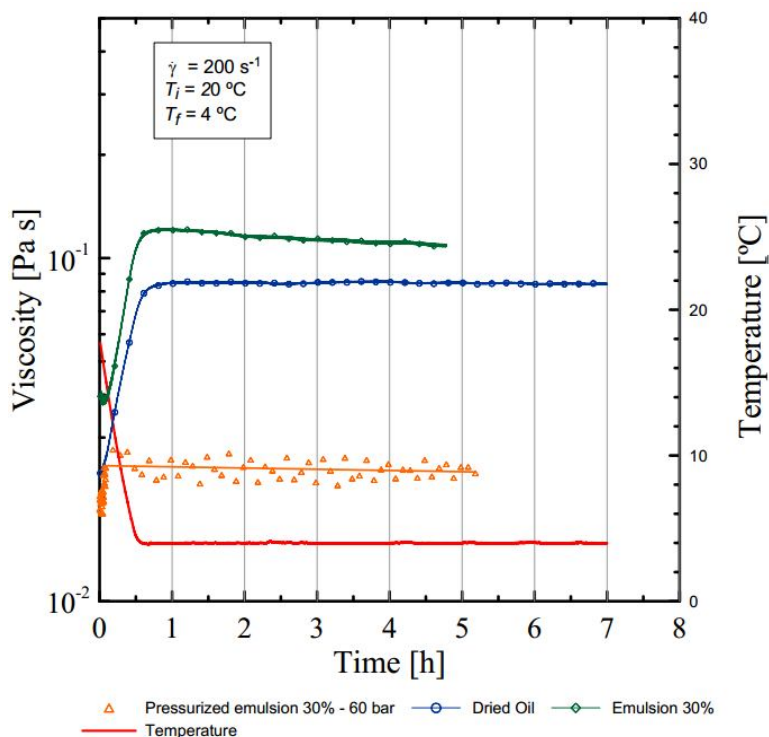
Figure 3. Viscosities varying with temperature and time for pressurized and unpressurized samples.

Figure 4 depicts a typical viscosity behavior of the sample when a gas hydrate is formed. The shear rate and pressure were always constant throughout the experiment, 200 s^{-1} and 60 bar, respectively. Initially, the temperature t_i was kept constant at 80 °C for 8 h for the dissolution of gas in the emulsion. Then, it was continuously reduced at a rate of 0.01 °C/min until a value of 4 °C is achieved; consequently, an increase in the viscosity after 10 h of experiment was observed. This final temperature t_f, was maintained constant during the rest of the experiment. Hydrate formation is evidenced by the sharp increase in the viscosity, that happen approximately 80 h after starting the test, indicating that local crystals have been agglomerated in a domain region forming a crystal lattice.
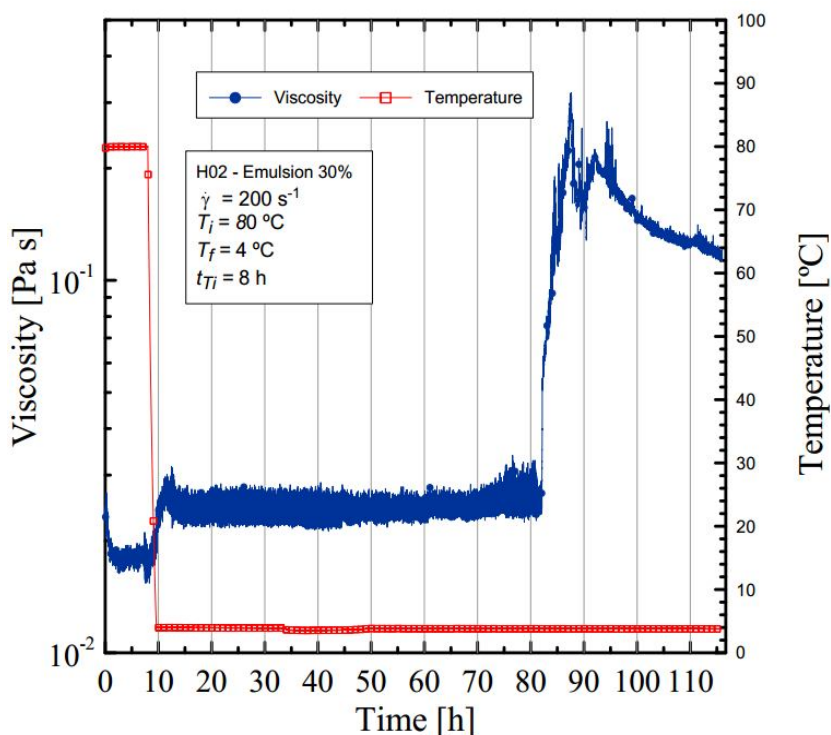

Figure 4. Typical illustration of viscosity behaviour in hydrate gas formation.

4. FINAL REMARKS

The main results show the behavior of the viscosity of the samples as a function of the experimental time. The viscosity increases abruptly when the hydrate is formed. Although there are explanations for the formation of the crystal structures of hydrates, there are many variables that affect the rheology, such as the composition of the oil, the water content, the way to mix oil and water, the historical of temperatures and pressures imposed on the material, besides of the efficiency of low-dosage inhibitor. Variables that will be tested in future experiments.

5. ACKNOWLEDGEMENTS

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