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STUDY OF HYDRATE FORMATION IN TRANSIENT CONDITIONS

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Abstract. *In an oil and gas production, it is common transient operation involving shut-in and restart and at these conditions there is a high probability of hydrate formation. When the flow in the pipe stops, the fluids start cooling down due to the heat transfer with the subsea environment. If the shut-in takes enough time for the fluids reach the hydrate formation temperature, the restart could result in rapid hydrate formation and even form hydrate plug. In this study, we simulate transient operations by performing a series of experiments in a high pressure rheometer to determine the conditions that can result in favorable and unfavorable restart conditions. The system tested are mineral oil, water and gas. The rheometer allows for precise control of the impeller rotation and measures parameters such as the torque, which can be correlated with an apparent viscosity. Tests were performed to understand and identify which conditions hydrate plugs form or flowable conditions results with the restart. The results from these tests can contribute to our understanding of hydrate formation and agglomeration, as well as correlate the condition that hydrate plug can form in a shut-in and restart process.*

Keywords: *gas hydrate, transient condition, rheometer.*

1. INTRODUCTION

Gas hydrates are non-stoichiometric compounds, composed by water and gas, formed under conditions of low temperature and/or high pressure. The water molecules interconnected through the hydrogen bonds are responsible for the formation of the crystalline structure with free cavities that allow the occlusion of light hydrocarbons molecules (Sloan and Koh, 2008). Hydrate is one of the most challenges in flow assurance in the petroleum industry.

The petroleum industry adopts some strategies to avoid the hydrate formation (thermodynamic inhibitor, for instance) or let the hydrate in flowable conditions (anti-agglomerant inhibitor). Salt and alcohol are thermodynamic inhibitors that shift the equilibrium curve, requiring higher pressures and lower temperatures to form hydrates (Sloan and Koh, 2008). The disadvantage of using thermodynamic inhibitors is the need for large volumes of inhibitors in the oil fields. The methanol costs for the petroleum industry to inhibit hydrate formation is around \$ 740,000/day. Low – dosage inhibitors can be divided into kinetics and antiagglomerants and the cost to the oil industry is around \$350,000/day (Creek et al. 2011).

In general, the formation of hydrate plugs is not related to normal production (flow) operations due to the design aimed at flow assurance (Sloan et al., 2011). Transient operations, such as in the case of a scheduled or emergency shutdowns, can result in conditions with a higher potential for hydrate plugs formation. Cooling of the stagnant fluid in the line due to thermal exchange with the seabed may cause the pressure and temperature conditions to enter in the formation zone. During start-up of the line, the shearing caused due to the flow and the increased pressure can contribute to the rapid formation of hydrate plugs. Knowing the parameters that influence the formation of hydrates and

the involved phenomena are important to develop and improve techniques of inhibition of hydrate plug formation in transient regime.

This work is focused on identifying which conditions hydrate plugs form or flowable conditions results with the restart. Experiments were performed using high pressure cell coupled with the rheometer, using three phases: water phase, oil phase and gas phase. It was analysed the influence of variables such as pressure, temperature and rotational speed after a simulation of long period of shut-in.

2. EXPERIMENTAL PROCEDURE

The experimental apparatus (Figure 1) was composed by an Isco pump (b) for maintaining the pressure along the experiment and pressurize the cell, the rheometer (Discovery Hybrid Rheometer – 2 from TA Instruments - d) which was responsible for torque measurements, a chiller (c) for temperature control and the computer for data acquisition. The experiments were performed using a high pressure cell coupled with a rheometer. The operating pressure cell was up 100 bar and the maximum volume was 35 ml. The impeller used was custom made with 1 mm of gap from outer vane to the cell wall. The geometry of the impeller can influence the experiments results. The ideal impeller is one that avoid accumulation of hydrate at the wall and in the middle section and is able to provide good mixing in the system.

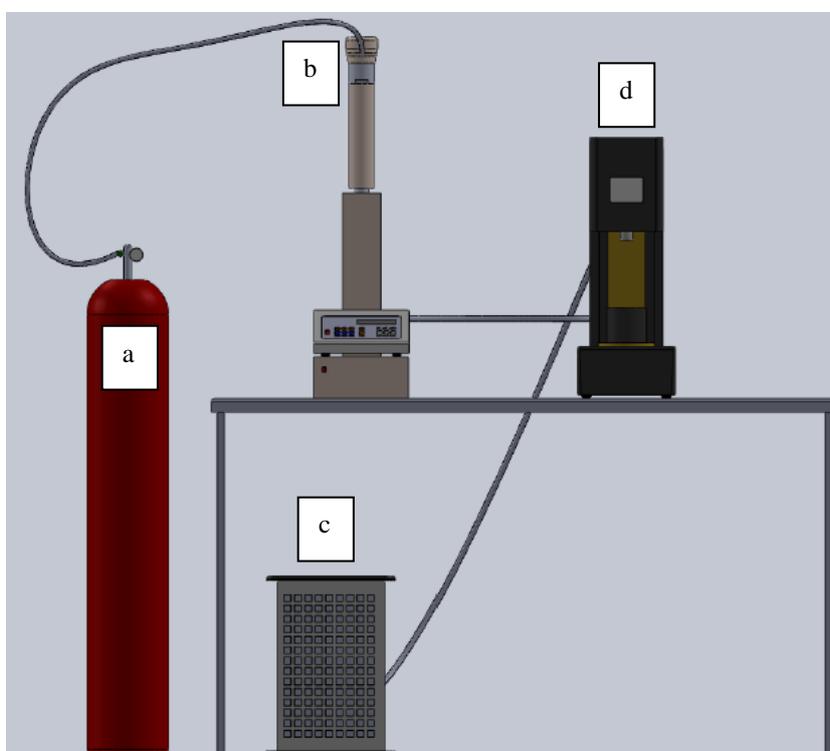


Figure 1. Schematic of the experimental setup.

Due to the design of the impeller used in the experiments and the high rotational speed, the measured viscosity was undefined. In order to find a correlation between torque measured from the rheometer and the apparent viscosity from the mixture, a calibration was made using standard silicone oil with known viscosity. The measured torque of the silicone oils was done under the same conditions as for the hydrate forming experiments, including the liquid volume and rotational speed. This calibration was performed using four silicone oils with different viscosities. This calibration was the same used by Charin and Sum (2017).

The experiments were performed using three phases: deionized water, mineral oil 70T and a gas mixture (methane 92.7 mol% and propane 7.3 mol%). The liquid loading was 25 ml with 10% of water cut and the experiments were performed using the isobaric method by monitoring the torque and volume remaining at the pump response with the changes in the temperature.

The experiment started with the rheometer calibration with the cell empty. Then the liquids were loaded and the gas was injected into the cell up to the desired pressure. After verifying the absence of gas leakage, the experiment was started at 25 °C. The gas was saturated in the liquid phase after some hours and then the temperature was set to some temperature below the equilibrium temperature. The hydrate formation was detected with the suddenly increase in torque, however, the torque value quickly decreased and after some hours the torque remained steady and the mixing was stopped. The system was restarted after few hours and the system behavior was observed by the torque data. When

the system was reached steady state, the experiment have finished. It was performed experiments with different pressures, subcooling and changing the rotational speed along the hydrate formation. The results are showed in Section 3.

3. RESULTS AND DISCUSSION

Figure 2 shows a typical result from transient experiment with hydrate. The experiment consists of several stages: (a) the gas saturation in the liquid phase; (b) cooling: the temperature was decreased up to desired subcooling. Hydrate formation: it was observed a suddenly increase in torque, (c) shut-in, (d) restart.

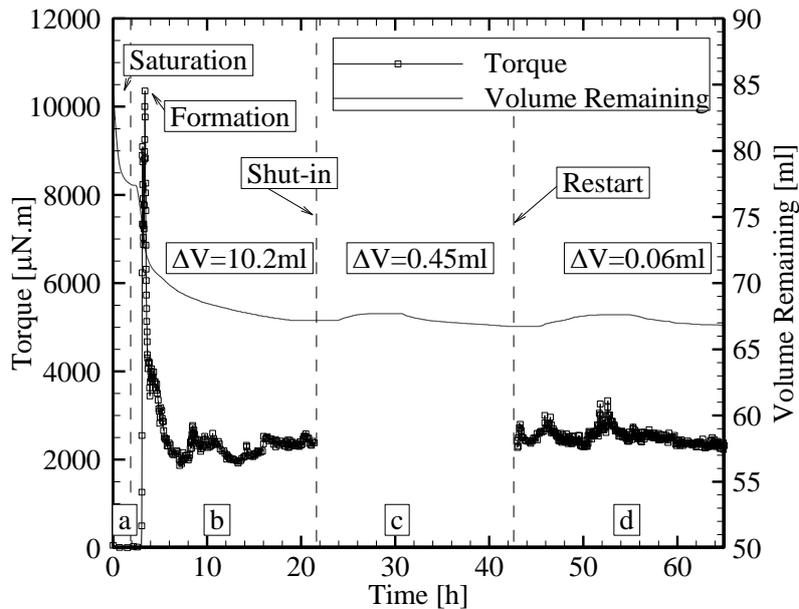


Figure 2. Typical experiment showing the stages: saturation, cooling, hydrate formation, steady state, shut-in and restart.

Webb et al. (2014) attribute the accentuated increase of the viscosity due to the response to the conversion of liquid water into solid particles of hydrate, and also by the dissolution and depletion of the gas in the oil phase, by the agglomeration of the solid particles and by capillary connections. The viscosity drop shortly after the peak that indicated the hydrate formation due to the alignment of the particles in the flow (Quemada, 1978, Webb et al., 2014).

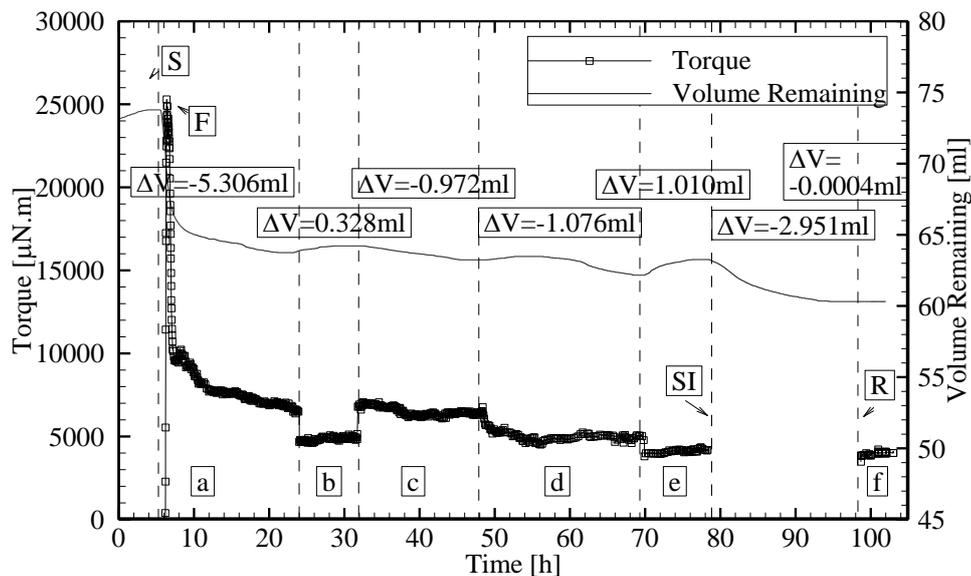


Figure 3. Torque/volume remaining versus time – (S) Saturation; (F) Formation; (SI) Shut-in; (R) Restart. Rotational speed: (a) 200 rpm; (b) 100 rpm; (c) 200 rpm; (d) 300 rpm; (e) 200 rpm; (f) 200 rpm.

Experiments varying rotational speed were performed and it was observed a change in torque at the transition of the rotational speed (Figure 3). The change in rotational speed occurred when the steady state was observed in the torque measurements. The purpose of this test was to observe the interference of the stirring in the crystalline structure of the hydrate. The sequence of rotational speeds used in the experiment was: (a) 200 rpm; (b) 100 rpm; (c) 200rpm; (d) 300 rpm; (e) 200 rpm, shut-in and restart (f) 200 rpm. The data obtained from this experiment show that the rate of rotational can influence the structure of the hydrate. By modifying the rotational speed from 200 rpm to 100 rpm and returning to 200 rpm (a → b → c), it is possible to notice that even with the decrease of the rotational speed, there was no change in the torque values when returning the speed rotational speed for 200 rpm. In terms of viscosity, it may mean that there was no change in viscosity with the decrease of the rotational speed.

However, by modifying the rotational speed to 300 rpm (c → d → e) it is possible to note that the torque values in step "e" do not return to the same values in step "c". This fact could mean that the increase in the rotational speed caused the hydrates to break down and therefore the torque values in step "e" decreased. Camargo et al. (2000) observed the same behavior. In the restart (step f), no variation in torque values was identified. This suggest the breakage of the hydrate structure should be due to the increase of the shear.

To calculate the amount of hydrate formed in each experiment, the following parameters will be used: variation of the volume of the pump, temperature and pressure measured during the experiment. The calculations will be carried out using three softwares: (1) Phase Equilibria (PE): used to calculate the molar fraction in the equilibrium of each component in each of the phases, (2) Refprop: used to calculate the properties of the mixture, as specific mass and compressibility factor and (3) CSMGem: used to calculate hydrate property as specific mass and hydration number.

Figure 4 shows the subcooling results as a function of the hydrate volume fraction. At higher pressure and subcooling, it is possible to observe a higher amount of hydrate formed. On the other hand, analysing the results of the experiments performed at 42 bar, it was observed that for the higher subcooling (14.5°C) it did not imply a higher hydrate formation. For pressure of 42 bar and subcooling of 10,0 °C was obtained the highest value of hydrate volume fraction between the tests performed with the same pressure. In addition, it was not possible to restart the test, because the necessary torque exceeded the limit of the rheometer (0.2 N.m) During the shut-in, no variation in pump volume was observed, which may be an indication that there was no hydrate formation during the shut-in, however, agglomeration may have occurred. Hydrate crystals may have rearranged then the torque needed to restart the experiment exceeded the equipment limit. According to Sakemoto et al. (2010) and Kishimoto et al. (2012) the dominant factor that affects the morphology of the crystals is the subcooling. It means, the higher the subcooling, the smaller the size of the crystals.

The experiment performed at 42 bar and subcooling at 6 °C required the use of the memory effect of the water to form hydrate in the desired subcooling, because with at this subcooling, it was not possible to form a hydrate. Therefore, initially hydrate was formed with subcooling of approximately 14 ° C, then, dissociated and hydrate was formed again with the desired subcooling. It is possible to notice that even using the memory effect of water, the hydrate volume fraction remained lower in relation to the other tests performed with the same pressure, but with higher subcoolings.

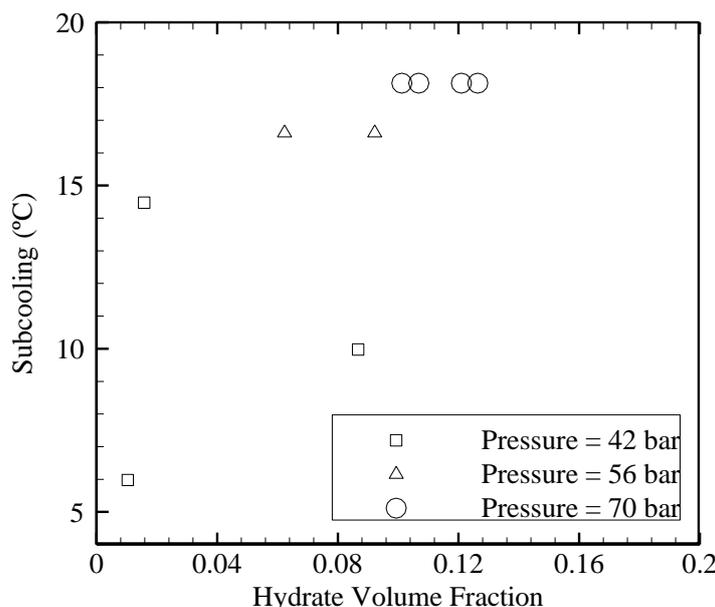


Figure 4. Summary of the results. Hydrate volume fraction versus subcooling.

Performing experiments with different pressure and temperature had the purpose to evaluate the influence of the driving force in the hydrate formation. Based on the experiments performed in this work, they should suggest that the subcooling could influence the morphology of hydrate, forming more porous hydrates at lower subcoolings.

4. CONCLUSIONS

Predicting the hydrate behavior during a shut-in and restart process can avoid some issues like hydrate plug formation and the blockage of the line. In this work, it was focused on studying the behavior of hydrate formation in transient condition using a high pressure cell coupled with a rheometer. It was observed the influence of the subcooling in the restart, it means that the subcooling could change the morphology of hydrate and influence the hydrate porosity. Also, it was observed that the increase in the rotational speed may cause the breakage of the hydrate structure due to the increase of the shear. More experiments are necessary with different fluids and conditions of pressure and subcooling to confirm the same behavior observed will be observed as well.

5. ACKNOWLEDGEMENTS

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