



25th ABCM International Congress of Mechanical Engineering
October 20-25, 2019, Uberlândia, MG, Brazil

COB-2019 - 1156

HYDRATE FORMATION IN NON-EMULSIFYING SYSTEMS UNDER SHUT-IN AND RESTART CONDITIONS

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Abstract. *Hydrate formation and blockage in oil and gas flowlines is one of the concerns in offshore operations, specially in shut-in and restart conditions. In order to increase insight into the hydrate formation and accumulation mechanism under transient condition, experiments were performed using a visual rocking cell with a multiphase system (water + gas and water + gas + oil). Two different gas were tested (pure methane and gas mixture of methane + propane). Also, different driving force and liquid loading were tested in order to evaluate the hydrate formation behavior at transient condition. The experiments showed that hydrate morphology was highly influenced by the subcooling. Moreover, the hydrate formation with two phase system resulted in a highly porous hydrate, while experiments with three phase system resulted in hydrates with different morphology, depending on the subcooling.*

Keywords: *clathrate hydrate, flow assurance, rocking cell, shut-in, restart*

1. INTRODUCTION

Clathrate hydrates are non-stoichiometric compounds, composed by water molecules organized as regular polyhedrons and stabilized by gas molecules inside the cavities (Sloan and Koh, 2008). Thermodynamic conditions, such as high pressure and/or low temperature and phase mixing, could favor the hydrate formation. The interest in gas hydrate has increased in the last decades, especially in oil/gas industry, one of the concerns of this sector is to avoid agglomerations of hydrates, which can block pipes, reducing productivity, damaging equipment and affecting safety in oil wells and pipelines. In oil drilling and production activities in deep and ultra-deep water there are favorable conditions for hydrate plug formation, especially during shut-in and restart operations. Long period of shut-in may favor the risk of hydrate formation upon the restart due to the heat loss to the ambient seabed temperature. The fluids can enter in the hydrate formation zone, which upon restart, could result in rapid hydrate formation, which can lead to a hydrate blockage.

Some variables can influence the dynamics of hydrate formation and agglomeration in transient conditions, for example, the fluids properties, amount of water cut, memory effect, driving force, time of shut-in, emulsion stability and shear/mixing at restart. Hydrate mechanisms associated with hydrate formation, deposition and accumulation can be studied in different apparatus, for example: high pressure cell coupled to a rheometer (Charin & Sum, 2017), flowloop (Srivastava et al., 2017) and rocking cell. (Straume et al., 2016; Straume et al., 2018). The rocking cell oscillation could create a flow regime, which could be compared to slug flow pattern as pipelines and risers might be subjected to slug flow depending on reservoir fluids, pipe geometry and flow conditions. Also, the rocking cell could reproduce different conditions, such as temperature, pressure, gas mixture, water cut, liquid loading, pipe inclinations, flow velocities that may be useful to identify the phenomena involving hydrate formation and accumulation—depending on the parameters studied.

This work is an effort to understand the dynamic of hydrate formation, breakage and agglomeration during shut-in and restart conditions. Experiments were performed in a high-pressure rocking cell with visual capabilities with two phase (water + gas) and three-phase system (water + gas + oil). Different subcoolings, gases, liquid loadings and water cuts were tested to evaluate the effect of these parameters on hydrate formation in transient condition.

2. EXPERIMENTAL SECTION

2.1 Experimental apparatus

Figure 1 represents the apparatus setup. The experiments were performed in a rocking cell with eight polycarbonate windows (three windows in the front side, three windows in the rear side, one window in the left side and one window in the right side). There were two cooling chamber (in the upper wall and in the lower wall) connected to a chiller to control the temperature of the cell. The pressure was controlled by the syringe pump. Also, the gas consumption was measured based on the volume variation of the pump which can be converted to volume of hydrate. The rocking cell was surrounded by air conditioning in order to control the temperature outside the cell and to avoid any water vapor condensate in the windows of the cell. Different pipe inclinations (5° - 30°) and different oscillation velocities could be set up. There were nine temperature sensor installed in different positions in the rocking cell to measure the upper wall surface, in the gas phase and in the lower wall surface. All experiments were documented by images and the phenomena could be observed throughout the experiments.

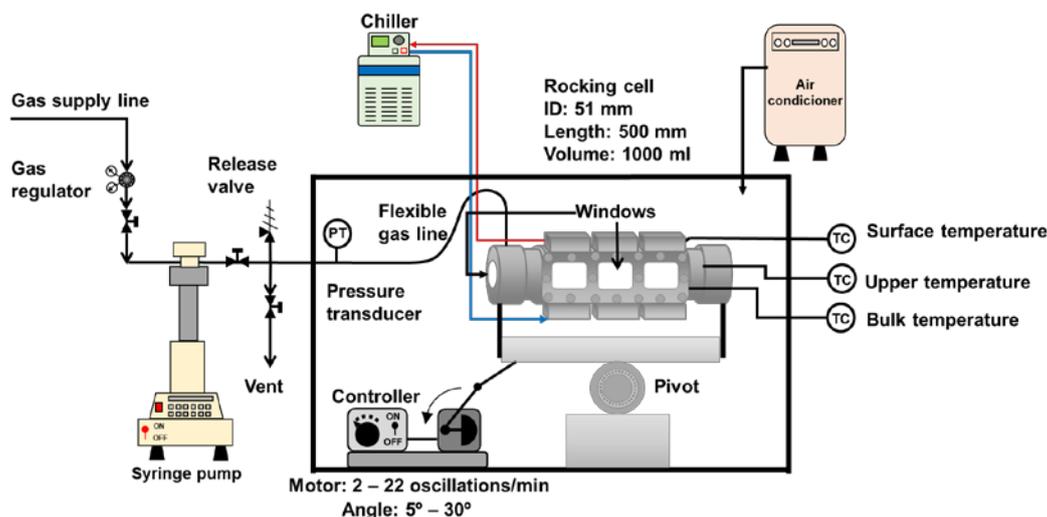


Figure 1 Schematic view of the rocking cell

Before the experiments, the cell is cleaned and air drying. All the liquids were admitted in the cell by weight under atmospheric conditions. Then, the syringe pump was set to the desired pressure. The two phase experiment was performed with 20% of liquid loading and the three phase experiments were performed with 50% of liquid loading and 10% of water cut. The cell is cooled down from an initial temperature of 20°C until the desired temperature. All experiments were performed using the isobaric method, at 70 bar.

Initially, the rocking cell was oscillated in order to promote gas solubility into the liquid phase at an amplitude of $\pm 20^{\circ}$. After the gas saturation step, the system was cooled until the desired temperature. The cooling step was performed at lower oscillation velocity ($2.06 \text{ oscillation} \cdot \text{min}^{-1}$) to avoid the hydrate formation at this step. When the desired temperature was reached, the oscillation was stopped, simulating the shut-in. The system was kept at the quiescent condition for a few hours and after this shut-in period, the oscillation was settled in 11.25 revolutions per minute, simulating the restart. The hydrate formation can be observe in this step, right after the restart. Once the system had achieved the steady-state, a second shut-in and restart were performed, in order to observe the hydrate slurry behavior upon the restart, in the presence of hydrates.

3. RESULTS AND DISCUSSIONS

Experiments with two phase (blue dye water + methane – Fig. 2) and three phase (blue dye water + yellow dye mineral oil + methane – Fig. 5, Fig. 6 and Fig. 7) were performed. The liquid phases were dyed in order to increase the contrast between the phases, improving the images analysis. The amount of dye used was insignificant, and then any interference due to the addition of the dye (for instance, superficial tension) was neglected. Figure 2 shows the images

from the experiment with two phase (water and methane), 20% of liquid loading, 7.5 °C of subcooling, 70 bar, 11.25 oscillation.min⁻¹ and 20° of pipe inclination. Figure 2(a) shows the side view, while Fig. (2) (b)/(c)/(d) show the front view. After the saturation and the cooling step, the first shut-in was done. The system was kept at quiescent condition for about 17 hours. Then the first restart was done. Figure 2(i) shows the beginning of the first restart step. The water-gas interface was clearly defined at this moment. After around one and half hour, the hydrate started to form at the gas-water interface (region with the high concentration of solubilized gas), shown in Fig. 2(ii). The fast hydrate growth could be seen in Fig. 2(iii) that shows the hydrate formed after 10 minutes from hydrate formation onset. From this moment until the end of the experiment, the hydrate morphology did not change and any free water phase could be observed. After 17 hours from hydrate formation onset, the gas consumption was ceased, suggesting the maximum water was converted to hydrate. In order to observe the hydrate slurry behavior, a second shut-in and restart were done and any hydrate morphology was observed.

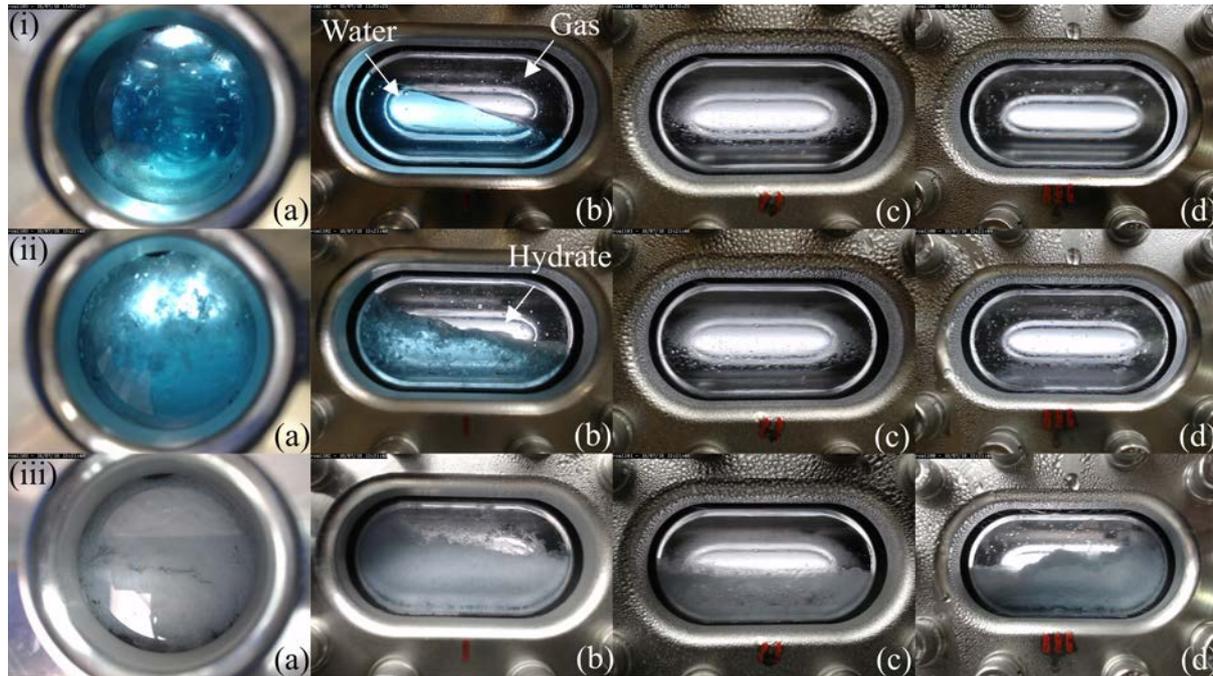


Figure 2 (i) Restart; (ii) hydrate formation onset; (iii) 10 minutes after hydrate formation onset. (a) Side view; (b)/(c)/(d) front view. System: distilled water + methane. Liquid loading: 20 vol%, 70 bar, 2 °C (subcooling of 7.5 °C), 11.5 oscillation.min⁻¹, 20° of pipe inclination.

Figure 3 represents the temperature (blue line) and the hydrate fraction (red line) over time, Fig. 4 represents the temperature (blue line) and the water converted (red line) over time. Both graphs are the data from the images showed in Fig. 2. Each dashed line represents the transition between the steps. First, the system was cooled until the desired temperature was achieved, followed by the first shut-in. After that, the system was restarted and hydrates started to form. Consequently, hydrate fraction and water converted to hydrate started to increase. After 10 minutes from hydrate formation onset, the hydrate morphology did not change, but the gas consumption still increased, indicating that the free water in the hydrate porous was slowly converted to hydrate. The hydrate formation decreased the mass transfer rate water-gas, explaining the slow water conversion. The second shut-in was performed after the steady-state was achieved, which means that the maximum amount of hydrate was formed and the hydrate fraction and water converted were constant. Then, after a few hours, the system was restarted again and the experiment was finished when the steady-state was achieved again. The hydrate fraction and the hydrate morphology remained constant during the second shut-in and restart.

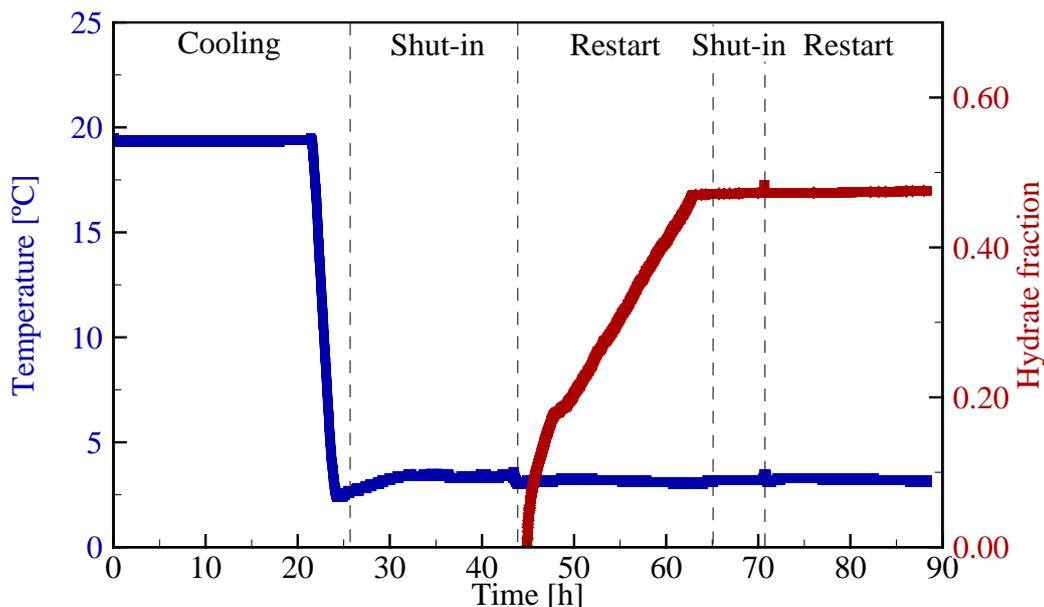


Figure 3 Temperature and hydrate fraction over time. System: distilled water + methane. Liquid amount: 20 vol%, 70 bar, 2 °C (subcooling of 7.5 °C), 11.5 oscillation.min⁻¹, 20° of pipe inclination.

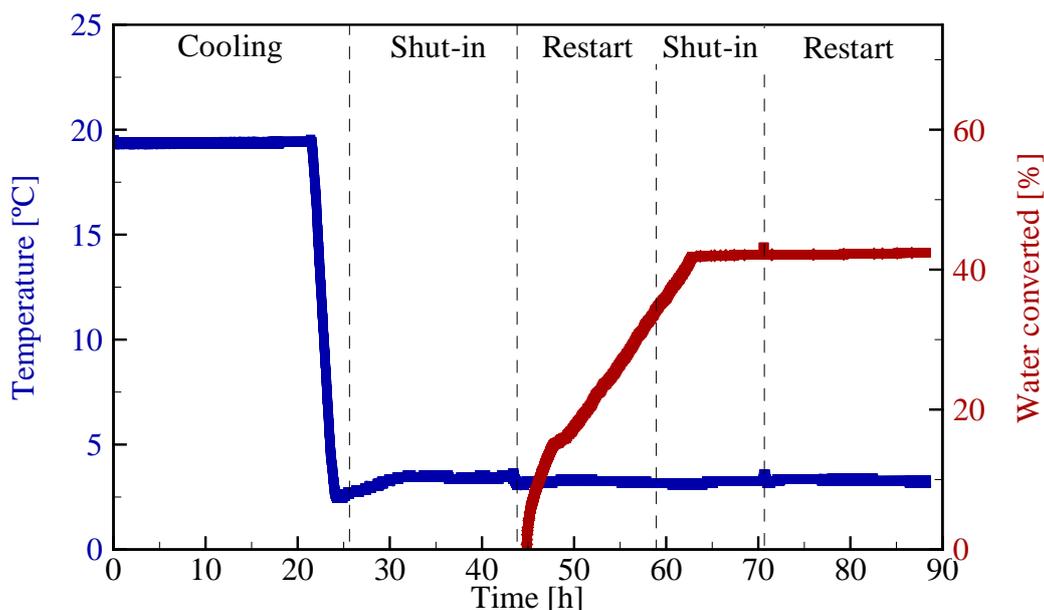


Figure 4 Temperature and water converted over time. System: distilled water + methane. Liquid amount: 20 vol%, 70 bar, 2 °C (subcooling of 7.5 °C), 11.5 oscillation.min⁻¹, 20° of pipe inclination.

Experiments with three-phase system were performed using different gas phases (pure methane and gas mixture 92 mol% methane + 8 mol % propane) and different subcoolings (7.5 °C and 18 °C). Two different clathrate structures were studied (sI – pure methane – and sII – gas mixture). All experiments were performed at constant pressure (70 bar), in an uninhibited system. The liquid loading inserted into the rocking cell was 50 vol% related to the total volume of the cell and the water cut used was 10%. The mineral oil and water phases formed a shear-stabilized dispersion, which the phases easily separate right after the mixing was ceased.

Figure 5 (i / ii / iii / iv) shows images from the experiment using pure methane and subcooling of 7.5 °C. The experiment started with the gas saturation into the liquid phase – Figure 5 (i). Due to the high affinity between the gas and liquid hydrocarbon phase, the gas readily dissolved into the oil phase. Next, the set point temperature of the chiller was changed from 25 °C to 2 °C at low oscillation rate in order to avoid hydrate formation. Then, the system was kept at quiescent condition for several hours, simulating the shut-in. The next step was the first restart. Figure 5 (ii) shows the system behavior after few seconds upon the restart. It was possible to see the hydrate formation started at the water-oil

interface. Figure 5 (iii) shows the images obtained 15 minutes after hydrate formation onset. It is possible to observe some hydrate deposition and small hydrate balls formed. After 3 hours from hydrate formation onset, as shown in Fig. 5 (iv), an single hydrate ball was formed. In the field, this behavior could plug the pipeline and induce an accident. In the second shut-in and restart any changes in terms of the hydrate morphology were observed.

The maximum hydrate fraction obtained in this experiment was around 0.10 and the maximum water converted was around 80%.

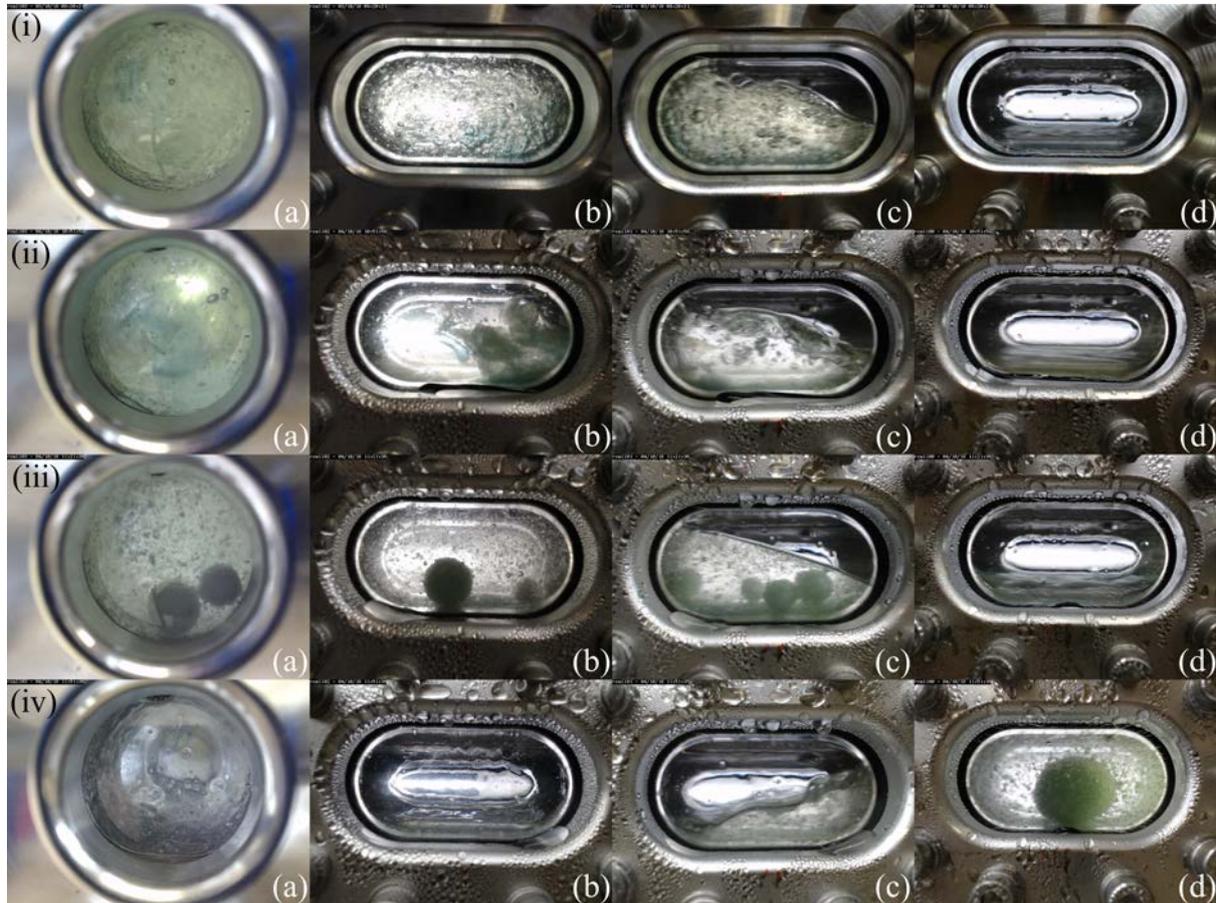


Figure 5 (i) Saturation; (ii) hydrate formation onset; (iii) 10 minutes after hydrate formation onset. (a) Side view; (b)/(c)/(d) front view. System: distilled water (10% water cut) + methane. Liquid amount: 50 vol%, 70 bar, 2 °C (subcooling of 7.5 °C), 11.5 oscillation.min⁻¹, 20° of pipe inclination.

Figure 6 shows imagens from the experiment using the gas mixture (C₁/C₃) and subcooling of 18 °C. Figure 6 (i) shows the first shut-in in the experiment. Figure 6 (ii) shows the system behavior upon the restart and Fig. 6 (iii) shows the hydrate formation, observed right after the restart. Figure 6 (iv) shows the images obtained 15 minutes after hydrate formation onset was detected. At this time, it is possible to see the differences between the experiment showed previously, with methane and subcooling of 7,5°C. In the highest subcooling (18 °C), it was formed a hydrate slurry instead of small hydrates ball as observed in the smallest subcooling (7.5 °C). After 3 hours from hydrate formation onset, as shown in Fig. 6 (v), a dispersed hydrate slurry was formed. At this point, with the lower subcooling, a hydrate ball was formed, as shown in Fig. 5 (iv). The maximum hydrate fraction obtained in this experiment was around 0.08 and the maximum water converted was around 70%.



Figure 6 (i) First shut-in; (ii) first restart; (iii) hydrate formation onset; (iv) 15 minutes after hydrate formation onset (v) 3 hours after hydrate formation onset; (vi) second shut-in; (vii) second restart. (a) Side view; (b)/(c)/(d) front view. System: distilled water (10% water cut) + gas mixture. Liquid amount: 50 vol%, 70 bar, 2 °C (subcooling of 18 °C), 11.5 oscillation.min⁻¹, 20° of pipe inclination.

Figure 7 shows imagens from the experiment using the gas mixture (C₁/C₃) and subcooling of 7.5 °C. Figure 7 (i) shows the images obtained 5 minutes after hydrate formation onset was detected. After 3 hours from hydrate formation onset, as shown in Fig. 7 (ii), it was observed hydrate deposition and also a small hydrate ball was formed. The maximum hydrate fraction obtained in this experiment was around 0.035 and the maximum water converted was around 27%.

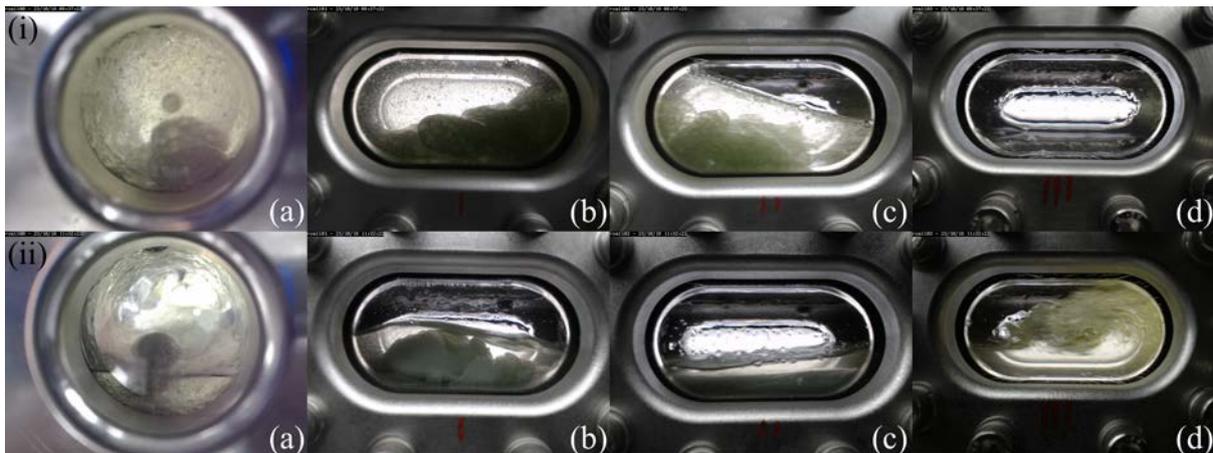


Figure 7 (i) 5 minutes after hydrate formation onset (ii) 3 hours after hydrate formation onset. System: distilled water (10% water cut) + gas mixture. Liquid amount: 50 vol%, 70 bar, 12.5 °C (subcooling of 7.5 °C), 11.5 oscillation.min⁻¹, 20° of pipe inclination.

As observed in Fig 5 and Fig 7, experiments with same subcooling but different gas phase formed hydrate with similar morphology, as hydrate deposition and the formation of the hydrate ball. However, the experiments with different subcooling and same gas composition (Fig. 6 and Fig.7) showed hydrate with different morphology. While the higher subcooling formed hydrates dispersed and in a flowable condition, the lower subcooling formed hydrate deposits. These results indicate the high influence of the subcooling in the hydrate morphology.

4. CONCLUSIONS

The hydrate formation behavior at transient condition with different water cut, gas phase (methane and methane + propane) and liquid loading were studied in order to identify the phenomena at shut-in and restart condition. Understanding the mechanism of hydrate formation and agglomeration during transient conditions may help to develop strategies to avoid and let the hydrate slurry in flowable conditions.

In all experiments performed in the rocking cell, the hydrate formation was induced to occur during the restart. The experiments with two and three phase systems resulted in hydrate with different morphologies. This behavior should be due to the mass transfer limitation, imposed by the hydrate formation. Upon the restart it was observed the fast hydrate formation, especially in the three phase system (oil, water and gas). The hydrate formation started at the water-oil interface and depending on the subcooling, two hydrate morphologies were observed:

- (1) The highest subcooling promoted a dispersed hydrate, which means hydrate in flowable condition. This result indicated that the high subcooling favors the formation of small and dry hydrates. Some phenomena, such as agglomeration, deposition, sloughing bedding and hydrate plug did not occur when dry hydrates are in system, due to the lack capillarity effect.
- (2) The lowest subcooling promoted an agglomerated hydrate, similar to a hydrate ball, which could be associate to hydrate plug. A slow hydrate formation rate and slow water conversion were expected with low subcooling, favoring the agglomeration and the plugging.

More experiments should be done to evaluate the influence of other parameters, such as pipe inclination and oscillation.

5. ACKNOWLEDGEMENTS

The authors would like to thank the support of CENPES/PETROBRAS, PRH-10 ANP and UTFPR.

6. REFERENCES

- Charin, R.M., Sum, A.K., 2017. "Steady-state and transient studies of gas hydrates formation in non-emulsifying oil systems". *Energy Fuels*, Vol. 31, p. 2548-2556.
- Sloan, E. D. & Koh, C., 2008. *Clathrate hydrates of natural gases*. Taylor and Francis Group, Boca Raton, FL, 3rd edition.

- Srivastava, V., Majid, A. A. A., Warriar, P., 2017. "Hydrate Formation and transportability investigations in a high-pressure flowloop during transient shut-in/ restart operations". *Offshore Technology Conference*, OTC-27849-MS, Houston, Texas, EUA.
- Straume, E.O., Kakitani, C., Salomão Jr., L.A.S., Morales, R.E.M., Sum, A.K., 2018. "Gas hydrate sloughing as observed and quantified from multiphase flow conditions". *Energy Fuels*, Vol. 32, p. 3399-3405.
- Straume, E.O., Kakitani, C., Merino-Garcia, D., Morales, R.E.M., Sum, A.K., 2016. "Experimental study of the formation and deposition of gas hydrates in non-emulsifying oil and condensate systems". *Chemical Engineering Science*, Vol. 155, p. 111-126.

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