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Gas Hydrate Formation and Accumulation in Non-Emulsified Oil/Water Systems under Pseudo-Flow Conditions

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Abstract

Hydrate formation and accumulation throughout the flowline is one of the main concerns during deep water oil and gas production operations. It may cause production impairment or pipeline blockage, leading to revenue losses and threatening the system's structural integrity. Hydrate formation and accumulation were therefore investigated as a gas-hydrate-oil-water system in a high-pressure rock-flow cell with visual inspection capabilities to understand the primary mechanism involved in the process of hydrate accumulation in multiphase flow conditions. Several experiments were carried out, varying the subcooling, the liquid loading, the water cut, the flow conditions, and the temperature gradient inside the cell. Footage was obtained throughout the experiments. The analyses of the flow conditions after and before the hydrate formation were compared to understand the effect of hydrodynamics on the process of hydrate accumulation at the bottom with a flowing liquid phase; (2) all the liquid in the system gets trapped inside the porous hydrate structure accumulated mainly at the bottom of the line; (3) wave effect is the primary mechanism leading to hydrate deposits at the upper region of the line and (4) hybrid region with hydrates agglomerates at the bottom and upper hydrate deposits.

Keywords

Flow assurance; gas hydrate; hydrate deposition

Introduction

Hydrate formation in offshore operations has been avoided through heating, insulation and injection of thermodynamic inhibitors. However, these approaches are ineffective, and the costs involved are high. Therefore, the industry has been moving from hydrate avoidance toward hydrate management strategies, thus allowing hydrate formation while preventing its accumulation. Consequently, a solid understanding of the mechanism leading to hydrate accumulation in multiphase flow conditions is critical to safely implementing hydrate management strategies.

Understanding how multiphase flows behave in the presence of solid particles is an important part of flow assurance studies. Laboratory efforts have been made to replicate the operational field conditions faithfully¹⁻⁵.

Experiments were carried out in a rock-flow cell apparatus to understand the thermo-hydraulic conditions affecting hydrate formation and accumulation in flowlines. The experimental setup allows the simulation of different multiphase flow conditions and captures the phase distribution in the flowlines.

The hydrodynamic of the system before the hydrate formation onset demonstrates to be an important condition for understanding the process of hydrate accumulation. The dispersion of the phases, capillary force, shear, hydrate particle-particle contact-time and subcooling seem to influence the process of hydrate accumulation. Four different hydrate accumulation processes were identified depending on the flow conditions. Phenomena such as hydrate agglomeration, wall deposition, sloughing and washing were also identified.

Methodology

The experimental system is composed of a dataacquisition system, a rocking cell with eight windows made of polycarbonate (three on each frontal side and one at each end), air conditioning for external cooling, two chillers (one for the upper wall and another for the bottom wall of the cell) and a motor for oscillating the cell. The cell has nine temperature sensors (three in the upper wall, three in the bottom wall and three inside for measuring the gas phase) and a pressure transducer. Cameras were installed close to the windows to allow footage of the experiments.

The liquid displacement in the rock-flow cell apparatus is gravity-driven, contrasting with the differential pressure-driven displacement of the flowlines. Although the flow conditions in the rock-flow cell apparatus do not correspond exactly to the flowline shear conditions, it captures the phase distribution in the flowlines, which is key to understanding the thermo-hydraulic conditions affecting flow assurance problems. Figure 1 shows the experimental setup.



Figure 1. Schematic view of the rock-flow cell apparatus.

Experimental Procedure

After appropriately cleaning the cell, fresh water and mineral oil were admitted at the desired liquid loading (LL) and water cut (WC) conditions. The gas mixture was admitted right after, pressurising the cell up to 70 bar. The experiments were performed at a constant oscillation rate between 06 to 18.75 rpm, with the cell at an inclination angle of $\pm 20^{\circ}$. This set of conditions creates a gravity-driven flow comparable to a stratified wavy flow pattern in a pipeline. The rock-flow cell was left oscillating for about one hour at a constant temperature to guarantee the liquid phase saturation with the gas mixture. When the pressure stops decreasing due to the liquid/gas solubility, the data acquisition begins, and the experiment starts.

The liquid loading ranged from 40% to 80% v/v, whereas the water cut from 20 to 70% v/v. A gradient temperature inside the rocking cell wall was forced by varying the bottom wall temperature as an attempt to stimulate upper wall deposition and simulate heat

transfer conditions on the seabed. The bottom wall temperature was changed from 4°C to 10°C, whereas the upper wall temperature was kept at 4°C. All the experiments were performed under isochoric conditions.

Materials

The systems studied were composed of distilled water as the aqueous phase, mineral oil as the oil phase and a mixture of 74.7 ± 0.2 mol% methane and 25.3 ± 0.2 mol% ethane as the gas phase. Because the sample fluids were colourless, they were dyed to contrast the phases better. The aqueous phase was blue-dyed, and the oil phase yellow-dyed. The gas mixture was chosen because its components are found in natural gas and form hydrate structure II⁶. The mineral oil's specific gravity, composed mainly of saturated and aromatic hydrocarbons, is 0.838 g/ml at 25°C. The hydrate equilibrium temperature of the system at 70 bar is $17.2^{\circ}C^{7}$.

Results and Discussion

The hydrate formation and accumulation in freshwater, oil and gas systems were assessed by investigating the influence of water cut, liquid loading, subcooling and temperature gradient inside the pipeline under different flow rate conditions. Other flow conditions were observed depending on the volume of the liquids poured into the cell and the oscillation rate. Still, the predominant flow pattern in all experiments before the onset of hydrate formation was stratified wavy flow (SW). The flow conditions before the beginning of hydrate formation are summarised in Figure 2, considering the liquid loading and water cut parameters based on the footage taken during the experiments.



Figure 2. Illustration of a gas-oil-water flow map in the rock-flow cell before the onset of hydrate formation as a function of the liquid loading and water cut.

The four flow patterns identified before the onset of hydrate formation for the gas-oil-water system are: (region I) a water phase dispersed in the oil-continuous phase; (region II) three liquid phases: a free water phase at the bottom, an intermediate layer of dispersed water and oil and an oil phase at the top; (region III) a dispersed water and oil phase with a thin oil phase above; (region IV) dispersed water and oil phase above of a free water phase.

The system hydrodynamics demonstrated to be necessary for understanding the system's morphology in

the presence of gas hydrates⁸. It affects the dispersion of the liquid phases influencing the gas-oil-water interfacial area and the flow energy, which will provide an important insight into the leading mechanism associated with the process of the hydrate accumulation in multiphase flow.

Figure 3 summarises the macro morphology of the hydrate deposits observed in the rock-flow cell for the gas-oil-water-hydrate system at the end of the experiments. In region I, hydrate agglomeration is the primary mechanism of accumulation. In Region II, the

liquid phase dried up, indicating that part of the fluid was trapped in the lower porous hydrate structure. Region III is dominated by hydrate deposition. Region IV is a hybrid region where hydrate wall deposition and agglomeration followed by settling occurred.



Figure 3. Illustrate the final hydrate morphology as a function of liquid loading and water-cut based on the characteristic gas-oil-water flow map for rock-flow cell experiments.

The water and oil dispersion before the onset of hydrate formation was relevant to this classification as it relates to the different mechanisms involved in the hydrate accumulation and deposition processes. Two main mechanisms were related to hydrate accumulation in multiphase flow, while the others were related to one or both mechanisms.

In the absence of a free water phase at the bottom, the process of hydrate deposition on the wall is driven mainly by the agglomeration of hydrate particles due to the capillary force. At the beginning of hydrate formation, hydrate particles flowed in the bulk. Due to the dynamic flow conditions, hydrate particles can collide at some point. The hydrophilic and porous nature of hydrate particles covers the outside of the hydrate particle with water, as it is not a dry particle (the subcooling is low to convert all the water trapped inside the porous particle)^{9,10}, forming capillary bridges, which hold the solid particles together after hydrate particleparticle collision. Depending on the contact time, cohesion force and flow conditions, the capillary bridge can crystallise, consolidating the aggregate and forming an agglomerate. Further aggregation and consolidation could increase the size of the agglomerate. If the flow energy is not enough to keep the agglomerate suspended in the flow, it settles down, forming a moving bed or deposit at the bottom of the pipeline (immobile). Figure 4 shows some captured images of the process of hydrate agglomeration for the system composed of 40 %vol. LL, 20 %vol. WC, 11.25rpm and wall temperature at 4°C.

In systems where hydrate particles form in the presence of a free water layer, the hydrate wall deposition process is controlled by the *wave effect* due to the liquid bridges formed in the gas-hydrate-wall interface¹⁰. Due to the flow pattern, hydrate particles are driven towards the wall by waves, and the liquid bridges hold them attached to the wall. The waves breaking on the deposit's surface can feed it with new particles, thus increasing the size of the deposit or washing away/detaching particles from the deposit's surface, decreasing its size. The swash and backwash movement of the liquid phase gradually develops into a thick hydrate deposit, which may characterise most of the deposits of hydrates observed in multiphase flow. Figure 5 presents some captured images of the process of hydrate wall deposition for the system composed of 80 %vol. LL, 70 %vol. WC, 11.25rpm and wall temperature at 4°C.



Figure 4. Capture images of the rock-flow experiment showing the agglomeration mechanism: a) flow conditions before the beginning of hydrate formation; b) the beginning of hydrate formation; c) hydrate agglomerates flowing in the oil phase (five minutes after the beginning of hydrate formation).

Estimating the amount of water converted into hydrates is an approximate way to understand the rate of hydrate formation in the experiments performed. The volume of gas consumed to form hydrates causes a pressure drop in the system, which can be related to the water conversion by the hydration number, which depends on the crystalline hydrate structure formed. The water conversion rate depends on the mass and heat transfer in the system. The average amount of water converted into hydrates for the experiments can be split into two main trends: one with a low formation rate ranging from 9% to 16%, and the other with a higher water conversion rate from 50% to 60%. The unconverted water remained trapped inside the porous hydrate deposits or dispersed in the liquid phase.



Figure 5. Capture images of the rock-flow experiment showing the hydrate deposit mechanism: a) flow conditions before the beginning of hydrate formation; b) the beginning of hydrate formation with some hydrate wall deposits; c) increase the thickness of the hydrate wall deposit (two minutes after the beginning of hydrate formation).

Conclusions

This work focused on describing the process of hydrate formation and accumulation in a gas-hydrate-oil-water system. The combination of several factors such as flow conditions after the onset of hydrate formation, flow energy and dispersion of the phases influence the process of hydrate accumulation. Four different hydrate formation processes were identified based on these factors:

1. The formation of a water dispersion in the oil phase and the small amount of water in the system (>20%vol. WC) leads to hydrate agglomeration. If the flow energy is not enough to keep the agglomerates suspended, the agglomerates settle down and deposit at the bottom of the cell, and an oil phase flows along with the rock-flow cell.

2. At the beginning, thicker dispersed water in the oil phase with a thin oil layer above was observed. At the beginning of hydrate formation, the liquid phase in the

system decreases gradually as the water is converted into hydrates, or the oil and water get entrapped inside the hydrate porous structure. A bottom hydrate deposit on the wall is observed at the end, and the liquid phase dries out. The remaining liquid phases (the oil and the unconverted water) are entirely entrapped in the porous hydrate structure.

3. A free water phase and a water-oil dispersed phase flow along with the cell before the beginning of hydrate formation. At the beginning of hydrate formation, the system forms a stabilised dispersed phase (hydrate-oilwater). Hydrate particles collide with the pipe wall and adhere to it because of the liquid bridge formed at the solid-wall and water-wet hydrate particle interface. The motion of the cell causes constant wetting of the hydrate deposit, prompting the deposit growths and the adhesion of new hydrate particles that were flowing. It causes the formation of a thicker hydrate deposit a few minutes after the beginning of hydrate formation (< 30 min approximately).

4. A combination of hydrate agglomeration and hydrate adhesion to the wall was observed. Depending on the size of the agglomerates, the flow energy cannot lift them. The agglomerates settle and later deposit at the bottom of the cell. The thickness of the deposit will depend on the flow energy, which can wash away the hydrate particles adhered to the wall decreasing the thickness of the deposit or feed the surface of the deposit with hydrate-forming compounds (water and gas) and carry new hydrate particles, which were flowing dispersed, to be adhered in the deposit surface increasing its thickness.

These findings may help in the development of production strategies for hydrate management.

Responsibility Notice

The authors are the only ones responsible for the paper content.

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