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# Dynamics of hydrate transportability in multiphase flow systems with crude oil and high salinity brine

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## Abstract
This study investigates hydrate formation in oil and gas production operations, a serious threat given its potential to block pipelines, thus causing economic losses and safety hazards. Hydrate formation in systems with and without inhibitors are herein charaterized, and the deposition on pipe walls and flowability in high salinity brines are examined. The impact of several factors such as water cuts, liquid loading, subcooling, temperature, pressure, and salt concentrations (up to 16 wt%) on hydrate formation was analyzed. The outcomes highlight the significance of the hydrodynamics before hydrate formation, and how it affects transportability. The presence of free water is crucial to the consolidation of hydrate wall deposits under flow. In uninhibited systems, in scenarios with high water cuts, bedding deposition was favored, while lower cuts lead to dispersions or wall deposition. Formation temperature directly influences viscosity, depending on pressure and subcooling. Higher salt concentrations can favor the dispersion of hydrates. This study highlights the complex interplay of factors influencing hydrate formation in oil and gas pipelines, and that are pivotal for better production operations, their safety and efficiency.

## Keywords
Hydrate formation mechanism; Deposition, Salt, Transportability; Slurry

## Introduction
The risk of hydrate formation must be evaluated by studying several variables and their cross-influence on each other. Factors such as subcooling, presence of inhibitors, water cut, gas/oil ratio, etc., uniquely impact the hydrate formation and its morphology.
After their formation and, possibly, their agglomeration, a new non-flowing solid phase is formed. In the oil and gas industry these solids can block pipelines, either partially or completely, causing damage and production impairment. Thus, the characterization of the hydrate formation and transportability is of significant importance.

## Methodology
A rock-flow cell (Figure 1) was used to observe the flow development and the hydrate formation. Internally, the cell has a cylindrical shape, a total volume of 1 L, and was designed to operate up to 100 bar.

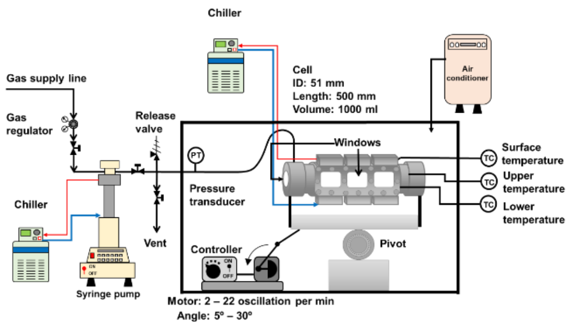


Figure 1. Schematic of the rock-flow cell setup.

The experimental setup used an oscillating rock-flow cell to generate specific flow patterns. Specific parameters included inclinations up to 20º and oscillation rates of 5 to 30 rpm. Its transparent windows allowed observation and illumination, and its pressure and temperature were continuously monitored. Precise temperature control was guaranteed through separate cooling chambers.
Experiments investigated the influence of different parameters such as the liquid loading, water cut, subcooling, formation temperature and salt concentration on flow patterns and hydrate formation. A mineral oil (Sigma-Aldrich), a synthetic gaseous mixture of methane + ethane

(75:25 mol%) and distilled water were used to investigate the hydrate formation mechanism. To evaluate the effect of the salt on hydrate formation, experiments used a crude oil, distilled water (with brine compositions based on mixtures of NaCl and $CaCl_2$), and a synthetic natural gas whose composition is listed in Table 1 below.

Table 1 - Synthetic natural gas composition

| | Synthetic Natural Gas (SNG) |
|---|---|
| $CH_4$ | 82 mol% |
| $C_2H_6$ | 10.5 mol% |
| $C_3H_8$ | 6.3 mol% |
| $IC_4$ | 1.2 mol% |

After the hydrates formed, the system was assessed using a metric for solid transportability (Figure 2), which consists of feeding an index based on weights attributed to the respective morphologies of the formed hydrates. These weights are based on the possibilities of formation and how threatening these profiles are, and their combinations for hydrate[1].

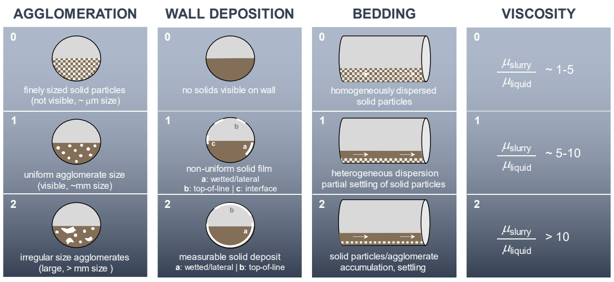


Figure 2. Metric for solid transportability

## Results and Discussion

The dynamic of hydrate formation and accumulation in fresh water, mineral oil and gas systems without the addition of inhibitors was assessed by investigating the influence of the water cut, the liquid loading, the subcooling and the temperature gradient inside the pipeline under different flow rate conditions. The predominant flow pattern in the experiments before the onset of hydrate formation was stratified wavy flow (SW). The system hydrodynamics demonstrated to be necessary for understanding the system morphology in the presence of gas hydrates [2]. It affects the dispersion of the liquid phases, thus 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 hydrate accumulation in multiphase flow.

In the absence of a free water phase on 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 onset of the hydrate formation, hydrate particles flowed in the bulk. Because of the dynamic flow conditions, hydrate particles can collide at some point. The hydrophilic and porous nature of hydrate particles makes the external surface of the hydrate particle to be covered with water, as it is not a dry particle (the subcooling is insufficient to convert all the water trapped inside the porous particle[3], forming capillary bridges, which hold the solid particles together after hydrate particle-particle collision. Depending on the contact time, cohesion force and flow conditions, the capillary bridge may crystallize, consolidating the aggregate and forming an agglomerate. Further aggregation and consolidation could increase the size of the agglomerate. Figure 3 shows some captured images of the process of hydrate agglomeration.

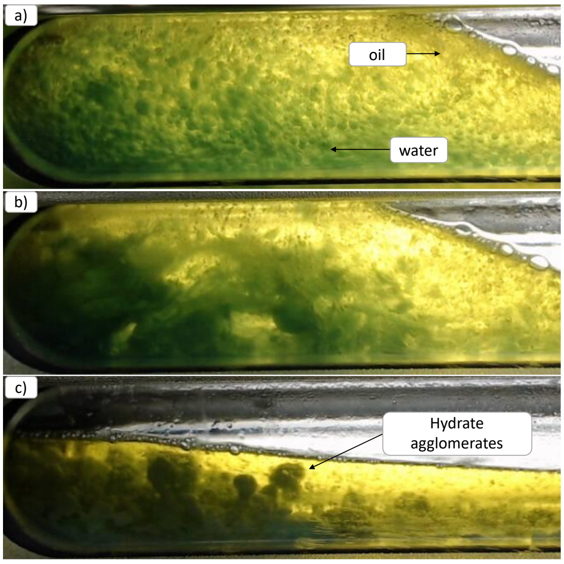


Figure 3. Captured images of the rock-flow experiment showing the agglomeration mechanism: a) flow conditions before the onset of hydrate formation; b) the onset of hydrate formation; c) hydrate agglomerates flowing in the oil phase (five minutes after the onset of hydrate formation).

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 on the gas-hydrate-wall interface[4]The flow pattern makes the hydrate particles to be pushed towards the wall by waves, and the liquid bridges hold them attached to the wall. Figure 4 presents some captured images of the process of hydrate wall deposition.

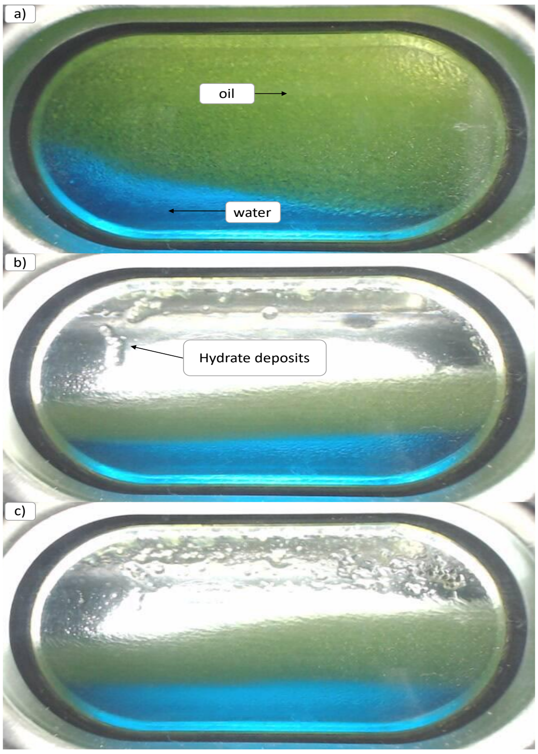

Figure 4. Captured images of the rock-flow experiment showing the hydrate deposit mechanism: a) flow conditions before the onset of hydrate formation; b) the onset of hydrate formation with some hydrate wall deposits; c) increase in the thickness of the hydrate wall deposit (two minutes after the beginning of hydrate formation).

The impact of high salt concentration on the flowability of the hydrates was evaluated in multiphase systems, using crude oil as oil phase. The water cut of a system is pivotal to a flow assurance study because a greater amount of available water would imply a higher amount of hydrates, when under optimal pressure and temperature conditions. However, a large amount of water not necessarily implies a greater risk, since this will be directly dependent on other variables such as subcooling or salt concentration. Higher water cuts mean a bigger proportion of water relative to the other phases.
The higher the water cut, the more water molecules are available for hydrate formation, resulting in an elevated risk of hydrate blockages or flow assurance issues.
Figure 5 illustrates the impact of a higher water cut on the system involving Bacalhau crude oil, a 16% w/w brine and natural gas. In Figure 5a), hydrates formed dispersedly at a 30% water cut, while at a 50% water cut (Figure 5b) increased aggregation and consequent formation of larger aggregates in the oil phase were observed. This corroborates the assertion that a higher water cut might entail a greater risk.

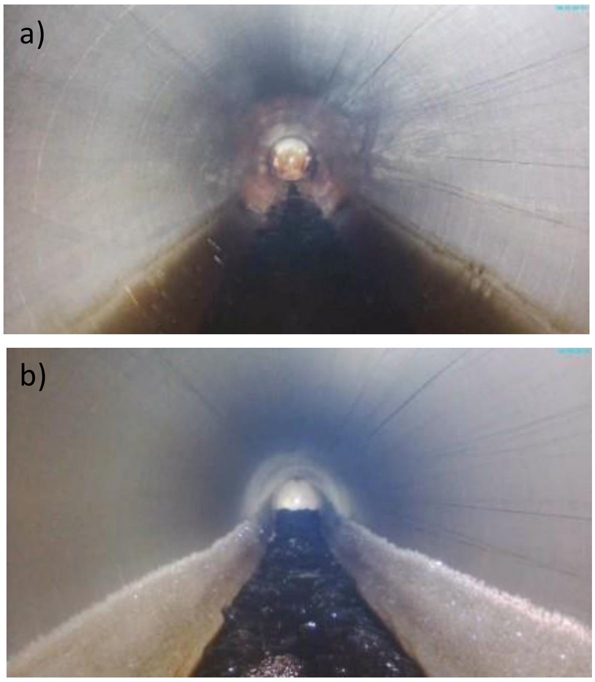

Figure 5. – a) Dispersed gas hydrates in crude oil (30% WC); b) Large gas hydrates aggregates in crude Oil (50% WC).

Figure 6 shows this trend, between NUEM's and P2F's data, where this risk tends to increase as the points stand out in the region with the highest water cut. Notably, this risk tends to increase as the points stand out in the region with the highest water cut evaluated: aggregation, deposition, and bedding. In the upper center region of the square (A|D|B|V), the indexes are represented. In the center, the water conversion (%) can be seen and, at the bottom, the relative viscosity is given (cP). The colors of the squares represent whether the system has a safe or unsafe condition based on the formed morphology. Figure 6 summarizes all this information.

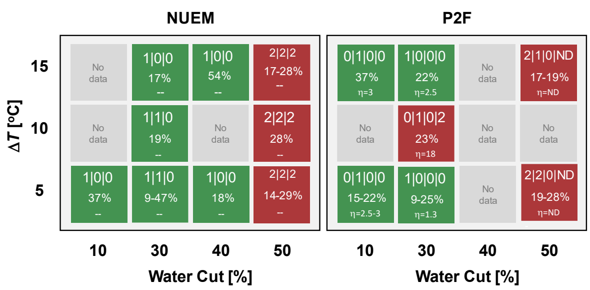

Figure 6. Hydrate slurry phase map – inhibited systems (16% w/w brine salinity (salt mixture - NaCl and $CaCl_2$)

## Conclusions

Proper management and mitigation strategies, considering factors such as subcooling, formation temperature, pressure, water cuts and hydrate inhibitors, are essential for ensuring a safe and efficient operation of oil and gas production systems.

In summary, the following observations were made:

- The hydrodynamics of the system impact on the phase distribution before the hydrate formation onset, which influenced the morphology of the hydrate formed;
- Different phase distributions were obtained depending on the liquid loading and water content in the system. Stratified-wavy flow was identified in all experiments, but the number of phases presented in the system was different;
- Depending on the experimental conditions, different deposition and agglomeration locations were observed. Based on the evidences obtained from the experiments, the liquid loading and water content influenced the phenomena involved in the hydrate deposition and agglomeration;
- The existence of free water after the hydrate formation onset was the most important condition to consolidate the hydrate wall deposit under flow;
- An increase in salt concentration promoted the dispersion of hydrates;
- The morphology and deposition of hydrates are strongly dependent on water cut and formation temperature, favoring agglomeration and deposition;
- The viscosity of the system is an important risk indication when the hydrates are present.

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## Responsibility Notice

The authors are the only responsible for the article and its contents.

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