Enabling Gas Hydrate Slurry Transportability with Anti-Agglomerant in Condensate Systems

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Abstract

Gas hydrates management is a critical part in the flow assurance of oil/gas production. Preventing their formation can be expensive and inefficient, while allowing them to form ensuring transportability may be less costly but comes with risks of plugging. Gas hydrate slurry transportability is defined by the absence of agglomeration, wall deposition, bedding, and low pressure drop. To account for each piece, one requires: i) understanding of the multiscale multiphase flow problem, ii) testing ability to assess each component defining transportability, and iii) a multi-dimensional approach to map transportability. Slurry transportability and stability are investigated in gas-condensate-water systems with the application of AA for a range of water cuts (up to 70%) and subcoolings (8 to 16 °C). Slurries appear as a milky solution of finely dispersed suspension of solids, and remain stable: for a prolonged time, during shut-in and restart, when changing the temperature/pressure, and when changing shear. In systems with high water cut, a soft deformable suspension is seen. Water conversion is shown to be a poor metric to evaluate the risk. A hydrate slurry phase map is presented combining the critical measures defining transportability, allowing for a simple way to assess conditions with low and high risk.

Keywords

gas hydrates; slurry transportability; anti-agglomerants

Introduction

One of the significant challenges in flow assurance is the management of solid precipitation (gas hydrates, wax, asphaltenes, scale), which can disrupt and impede flow, leading to costly operational issues and loss of revenue [1]. Among the solids, gas hydrates is the most severe and a constant concern because of their propensity to form in subsea flowlines causing unexpected and sudden blockage of the flowline [2].

Management of gas hydrates in flow assurance based on the concept of slurry transportability has received significant attention over the years, including the cold-flow approach [3]. The appeal of reducing the costly application of THIs through alternative approaches to control gas hydrates in multiphase flow production systems warrants a full understanding of the conditions for which any given hydrocarbon system would allow for safe/low-risk transportability of gas hydrates, that is, enable deployment of cold-flow technology [3]. While much data have been generated toward the goal, there has not been a well-defined set of criteria and testing procedure to translate the knowledge gained to a robust methodology that truly quantifies the risk (safe vs. unsafe) for hydrate slurry transportability. One of the major deficiencies in the current approaches is the one-dimensional criteria (water conversion or hydrate fraction or relative viscosity) used to estimate transportability, whereas, it is understandable and even natural that transportability is a multidimensional problem with many inputs determining the outcomes of many processes involved during transportability.

Here we present what is our definition based on decades of our experience working with gas hydrates. There are four components that must be each identified and together assessed that define gas hydrate slurry transportability: agglomeration, wall deposition, bedding, and relative viscosity. The absence of the first three components and a low relative viscosity are the required conditions for transportability with no/low-risk (safe) for accumulation/plugging. Any positive manifestation of agglomeration, wall deposition, bedding can lead to a high-risk (unsafe) condition, which would immediately translate into undefined relative viscosity, whereas increased viscosity may happen

in dispersed systems with high solid fraction. As such, it is essential and critical that one is able to quantify the dispersion of hydrates in the liquid carrying (continuous) phase, the absence of wall deposition, the absence of accumulation of solid under sheared conditions, and the relative viscosity of the slurry.

Methodology

Materials
Deionized water and kerosene (ICP Solvent, Sigma-Aldrich) were the liquid fluids used. Kerosene was selected as a simple model gas condensate fluid with density of 820 kg/m^3, kinematic viscosity of 3 mm^2/s at 40 ^{o}C, and flash point of 70 ^{o}C. A commercial anti-agglomerant (AA) was used in all tests at the concentration of 3 vol% (water basis). The aqueous solution also included 0.5 wt% NaCl (Sigma-Aldrich). Two different gas mixtures were used: i) methane-ethane at 75/25 mol% (C1C2) and ii) 10-component mixture (NG10). The gas mixtures were sourced from General Air.

Experimental Setup
All the tests performed in this work to assess hydrate transportability used a rock-flow cell (RFC). The RFC is a semi-batch system based on the principle of selecting rocking conditions (angle and rate) and liquid loading to achieve multiphase flow conditions closely matching those in an actual flowline under controlled temperature and at either constant volume or constant pressure. Temperature is controlled by an external chiller circulating coolant through an insulated jacket around the cell. The pressure is controlled by the amount of gas injected into the system. One of the key features of our RFCs is the visual capabilities, via an internal borescope and light, that allow the direct assessment of flow, phase changes, and distribution of the phases. The RFC specific to this study has dimensions of 50.8 mm inner diameter and 1000 mm in length and it is made of stainless steel.

Experimental Conditions
The purpose of this study was to map a range of relevant conditions to evaluate the transportability of gas hydrate slurries for the specified fluids and additives. As such, we considered water cut from 10 to 70% (by volume) in increments of 20, and initial subcoolings of 8, 12, and 16 ^{o}C based on a fixed set temperature of 4 ^{o}C (pressure was adjusted to achieve the desired subcooling). All tests were done at constant volume, that is, the final subcooling was slightly lower due to the pressure drop associated with hydrate formation. At the proposed conditions, both gases formed sII hydrates. All tests were done with 15% liquid loading (by volume) in the RFC with the rocking angle set to 8$\circ$ and rate to 10 rpm, resulting in flow conditions where the aqueous phase was fully dispersed in kerosene.

Apparent Viscosity Calibration
We have developed a methodology to determine the apparent viscosity based on image analysis correlated to the flow in the cell for fluids with known viscosity. A calibration curve was constructed using water + glycerol mixtures, for which the viscosities are well defined.19 The calibration is used to extract the apparent viscosity of the liquid dispersion before the onset of hydrates formation (μ_{on}) and after hydrate formation of the slurry at steady-state (μ_{ss}). The relative viscosity (μ_{ss} / μ_{on}) is calculated from the apparent viscosity values.

Transportability Assessment
To assess hydrate slurry transportability, one must consider a quantification in terms of hydrate agglomeration, wall deposition, bedding, and relative viscosity. In our definition, a true hydrate slurry is one that looks and flow similarly to a milky solution, that is, it constitutes of a homogeneous finely dispersed suspensions of solids such that: i) hydrate particles are less than ~100 µm in size (not visible to the naked-eye) and do not agglomerate, ii) there is no or only scatter films of hydrate on the wall, iii) hydrate particles remains uniformly suspended under shear, and iv) hydrate suspension has nearly unchanged apparent viscosity compared to the fluid system. Any deviation from this definition would result in a high-risk scenario for transportability. A simple way to classify the described criteria is by using an updated version from the original Hydrate Flow Risk Index (HFRI) [4], which excluded the relative viscosity. The advantage of the proposed methodology to quantify transportability is that it encompasses the key criteria necessary to assess conditions of low/high-risk for transportability.

Results and Discussion
It has become clear from our data and results that it is insufficient to make any kind of assessment on transportability by using a one-dimensional approach. One is able to assign the risk for each of the tests performed to generate a version of the Hydrate Slurry Phase Map [5], as shown in Fig (1). Compared to the original, this version considers a simplified mapping along a fixed mixture velocity and interfacial tension. The phase map plots the subcooling as a function of the water cut and for each combination, there is a classification of the transportability into no/low-risk (green) and high-risk (red) conditions, which is determined by evaluating the type of slurry in terms of agglomeration (A), wall deposition (D), bedding (B), and relative viscosity (V). For completeness, each box also includes the water conversion, even though, as we will discuss next, the water conversion is not a meaningful parameter in the assessment.

a)

Legend:
LOW RISK / HIGH RISK
0|0|0|0 ← A|D|B|V
zz% ← water conversion
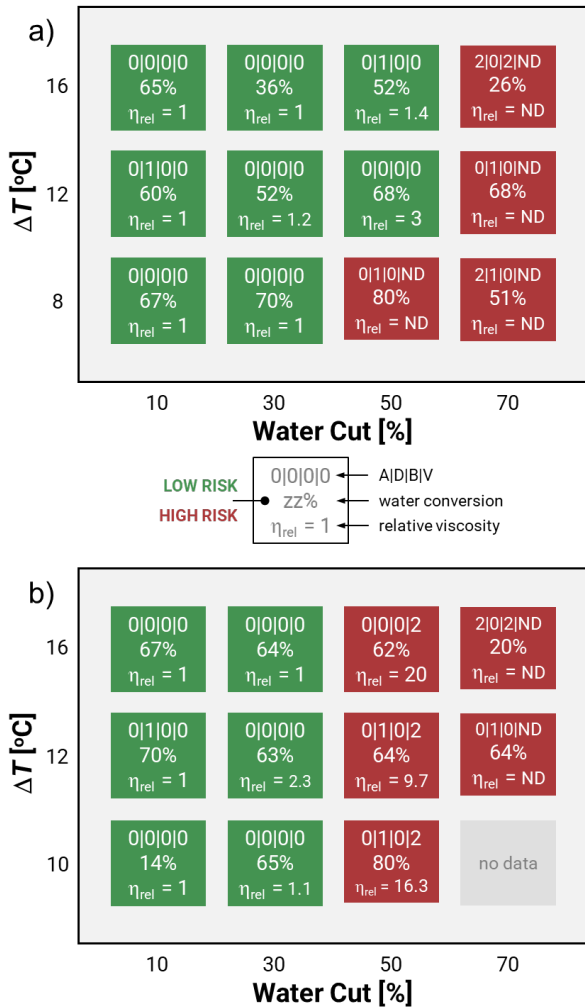η_{rel} = 1 ← relative viscosity

b)

Figure 1. Hydrate Slurry Phase Map for the test conditions considered for kerosene with a) C1C2 and b) NG10 gas. ND stands for not defined relative viscosity. Maps are valid at the tested liquid loading (15%), AA type and concentration (3%), and shear (well-dispersed).

The Hydrate Slurry Phase Map clearly identifies the ranges in water cut and subcooling for low/high-risk transportability as defined by the outcome in terms of agglomeration, wall deposition, bedding, and relative viscosity. This map represents an evolution into how one can easily and confidently assess and transfer knowledge from the lab to the field, as the metrics used for the classification in the map are the resulting phenomena that would be manifested in real conditions. In particular, the phase map defines the safe (low-risk) conditions to deploy cold-flow technology. For both gas mixtures, no transportable slurry is possible with 70% water cut, irrespective of the subcooling. This is due to the large effective volume fraction of solids and not enough oil to disperse the hydrates. At 50% water cut, the transportability depends on the gas mixture and subcooling. For the NG10 gas, there is high-risk for any subcooling, whereas for the C1C2 gas, there is low-risk for subcooling equal or greater than 12 °C. This is consistent with our mechanistic model in that at high subcooling, the rate of hydrate formation is higher, ensuring fast

trapping of the unconverted water. For 10% and 30% water cut, any subcooling will result in safe conditions for hydrate slurry transportability.

Water Conversion and Risk
Water conversion is often used to quantify hydrate transportability, with lower rates considered safer and more favorable conditions for transportability. Our data very much disclaims this evaluation based on water conversion alone, and much less on hydrate fraction, which is often based on a non-porous solid. Our results instead show that hydrate slurry transportability is uncorrelated to water conversion. Based on our determination of low/high-risk conditions for transportability, Figure 2) shows a plot of the water conversion for the tests performed, with the points colored for the assigned low-risk (green) and high-risk (red). As it is clear from the data, there is no correlation between water conversion and risk. Moreover, it is often the case that low (< ~20%) water conversion has the worst results in terms of transportability. The formation of the hydrate porous structure depends on the formation conditions (temperature, pressure, subcooling, flow regime) and the amount of water converted and unconverted to hydrates just depends on how quickly the unconverted water is sealed.
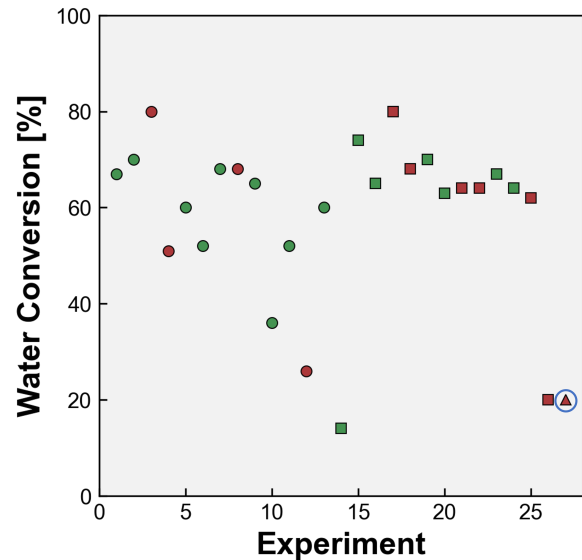

Figure 2. Steady-state water conversion in systems with low (green) and high-risk (red) for all the systems tested with C1C2 (circle) and NG10 (square). A test without AA is shown as triangle.

Hydrate Slurry Stability
One of the purposes of performing long tests, greater than 30 hours after hydrate formation, was to verify the stability of the hydrate slurry over long distances flowlines, that is, verify the reliable, low-risk transportability of hydrates slurry state. Our results confirm that once a transportable hydrate slurry is formed, it will remain unchanged irrespective of time (distance), changing shear, changing temperature/pressure, changing cooling

rate, and mode (shut-in/restart). Without exception, for all tests performed in which a low-risk transportable hydrate slurry was formed (green boxes in Fig. (1)), upon reaching steady-state, no further changes were observed in the state of the system for the duration of the test (30+ hours, equivalent to 200+ kms).

Different tests with 30% water cut at 4 °C were subject to changing shear (by adjusting rocking from 10 to 13 then 5 rpm), temperature (from 4 to 22 °C in increments of 2 °C) and driving force (adjusting the pressure to increase from 8 °C to 12 then 16, then decreasing to 12 and 8 °C again). No changes were seen in any of the tests, including no change in water conversion and no visual change in the suspension state of the system.

Regardless of the changes in temperature or pressure, once a low-risk hydrate slurry is formed, it remains as such. The key mechanism is the sealing of the unconverted water in the hydrate particles (sponges), as changes in shear, temperature, and pressure are unable to "unplug" the surface pores, preventing the water to permeate to the surface, and thus agglomeration.

Hydrate Slurry Rheology
For all tests, the apparent viscosity was evaluated for the liquid dispersion before the onset of hydrate formation and at steady-state (no changes in water conversion and A, D, B) after hydrate formed based on the correlation of the images. A summary of the apparent viscosity measured is shown in Figure 14. For some cases, the apparent viscosity was some undefined high value, and these are shown to go beyond the plot scale (high and undefined).
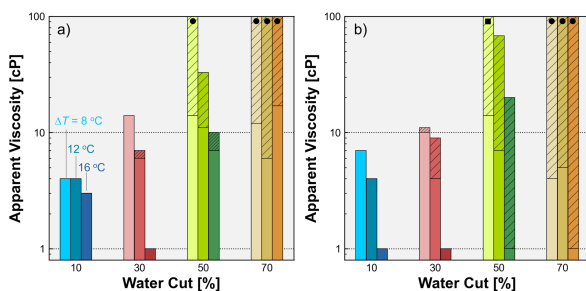

Figure 3. Apparent viscosity measured for the dispersion before the onset of hydrate formation (solid bar) and hydrate slurry at steady-state (hatch bar) for a) C1C2 gas and b) NG10 gas systems. Bars without hatch have unchanged apparent viscosity at steady-state. Solid circle: undefined apparent viscosity at steady-state; solid square: defined but beyond the limit of the plot.

Conclusions
The low-risk cases are defined for a limited set of conditions for the four defined criteria, which are obtained directly from the rock-flow cell (based on visual assessment), resulting in a multi-variate based risk for each subcooling and water cut considered. The hydrate slurry phase map clearly shows that a low-risk transportable hydrate slurry is obtained for the cases with 10 and 30% water cut at all subcoolings, and for 50% water cut for the high subcooling (12 and 16 °C) with the C1C2 gas. All cases with 70% water cut had a high-risk, non-transportable slurry.

When a low-risk slurry is formed, it remained unchanged for a long time, irrespective of changes in shear, temperature, pressure, or mode of operation. The stability of the hydrate slurry is explained by the mechanistic understanding of the hydrate particles being like sponges that soak and trap unconverted water, which are sealed in the particles by plugging the surface pores with the oil, made possible by the AA, which main function is to lower the interfacial tension between oil and water so that the oil can seal the porous hydrate medium. Our results also show that water conversion, and much less hydrate fraction, is a poor metric for hydrate slurry transportability, as it is uncorrelated to the outcome in terms of low/high-risk. As such, it would be prudent to move away from water conversion as a measure for transportability.

Adoption of the approach presented here, which may also be applicable for crude oil systems, will result in better decisions and more confidence on translating lab testing to field applications. Lastly, the results and methodology presented are a pathway to enable the cold-flow technology by defining the safe (low-risk) conditions of operation.

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Responsibility Notice
The authors are the only responsible for the paper content.

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