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Trung-Kien Pham, Ana Alexandra Cameirao, Jean-Michel Herri, Philippe Glenat. Experimental Study on Methane Hydrate Formation and Transport from Emulsions in a “Gas Lift” Riser in a Flowloop. 9th International Conference on Gas Hydrates - ICGH9, Center for Hydrate Research; Colorado School of Mines, Jun 2017, Denver, United States. pp.01C005\_2149\_Pham\_sec. hal-01569712

**HAL Id: hal-01569712**

**<https://hal.science/hal-01569712>**

Submitted on 27 Jul 2017

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# Experimental Study on Methane Hydrate Formation and Transport from Emulsions in a “Gas Lift” Riser in a Flowloop

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## Abstract

Production of crude oil with natural gas and water at low temperature and high pressure favours conditions for gas hydrate formation which can cause many troubles, up to blockage of pipelines. This work deals with hydrate kinetics of crystallization and agglomeration together with slurry transport and deposition under flowing conditions. Effects of various parameters are studied including: commercial anti-agglomerant low dosage hydrate inhibitor (AA-LDHI), water volume fraction, and water salinity in a mixture of Kerdane<sup>®</sup> and water. Experiments were made in the “Archimede” 80 bar flowloop equipped with a FBRM (Focused Beam Reflectance Measurement) and a PVM (Particle Video Microscope) probe and temperature, pressure drop, flow rate and density measurements. The hydrate conversion and volume fraction are calculated from the experimental results. The flow was induced through a “gas lift” system without volumetric pump. The methane is injected at the bottom of the riser at very high flow rate, which enhanced the gas transfer from the bubbles into the liquid phase. The experimental results at high water cut systems revealed a high rate of methane hydrate formation and quick plugging by using our “gas-lift” system (bubble riser). On the contrary, at low water cut systems with the bubble riser, shorter induction time but longer flowing time after gas hydrate formation were observed thanks to salt or AA-LDHI. Some details are given on the mechanism of crystallization, agglomeration and deposition with our “gas lift” system with and without AA-LDHI.

**Keywords:** *Emulsion, Gas bubble, Hydrate formation, Agglomeration, Deposition, Anti-agglomerants, Hydrate slurry transport, Flow assurance, and Multiphase flow.*

## 1. Introduction

Gas hydrates (or clathrate hydrates) are ice-like crystalline structures composed of molecular water cages stabilized by light hydrocarbon gases (methane, ethane, propane, etc) at low temperature and high pressure conditions (Sloan and Koh, 2008). Gas hydrate is a great concern in flow assurance, which may become a potential hazard (plug) to oil and natural gas transportation once they form in production flowlines. There are several chemical strategies to manage this hydrate plug risk including addition of thermodynamic inhibitors (THI), or low dosage hydrate inhibitors (LDHI) as kinetic hydrate inhibitors (KHI) or anti-agglomerants (AA). The most traditional method to prevent gas hydrates is thermodynamic inhibition (e.g. using methanol or glycols) which shifts the hydrate equilibrium conditions to higher pressure and lower temperature. However, the severe conditions (higher pressures, lower temperatures, higher acid gas contents and higher water cuts) in oil and gas transportation make thermodynamic mitigation less acceptable because of high amount of THIs used. To reduce the cost, LDHIs are used at a very small amount compared to THIs. In fact, KHIs can delay the nucleation or growth of hydrate formation while AAs allow the hydrate formation but help maintaining hydrate particles finely dispersed in production fluids.

Low water cut emulsion systems have been studied previously. Camargo and Palermo et al., (2002) developed a rheological model for suspension and agglomeration of hydrate particles in an asphaltenic crude oil based on the data obtained from laboratory and flow loop scales. In their work, water in oil emulsion was prepared at low water cut (15-50%) and without anti-agglomerants. Turner et al., (2005) also studied gas hydrate formation in emulsion, both autoclave and flowloop, and water cut from 5% to 35% and without anti-agglomerants. Numerous works (Fidel-Dufour et al.,(2006); Colombel et al., (2008); Lachance et al., (2008); Didier et al., (2009); Leba et al., (2010); Bo-Hui Shi et al., (2011); Bao-Zi Peng et al., (2012); Liang Mu et al., 2013; Ke-Le Yan et al., (2013); Lin Ding et al.,(2016)) concern the understanding of kinetics and mechanisms of methane gas hydrate

formation and agglomeration as well as flow characteristics and rheological properties of natural gas hydrate slurry, in low water fraction, with and/or without anti-agglomerants. In high water cut systems, insights into gas hydrate formation and dissociation in emulsion were developed by Greaves et al., (2008). This contribution mainly focused on the effects of hydrate formation and dissociation on the stability of high water content emulsions. Afterwards, the hydrate formation and agglomeration, deposition/plugging and rheology of hydrate slurry were investigated in high water fraction with and/or without anti-agglomerants (Gao et al., (2009); Shiva Talatori et al., (2011); Hossein Moradpour et al., (2011); Prasad et al., (2011); Joshi et al., (2013); Jun Chen et al., (2014, 2015); Prithvi Vijayamohan et al., (2015); Grasso, Giovanni A, (2015); Mendes-Melchuna et al., (2016); Huangjing Zhao et al., (2016); Erlend O. Straume et al., (2016); Guang Chun Song et al., (2017)). In addition, gas hydrate formation on surface of gas bubbles was investigated at high rate of hydrate formation and agglomeration (Hideo Tajima et al., (2009); Y.-T.Luo et al., (2006)).

Besides this works, at high water cut, the gas hydrate formation, agglomeration and deposition/plugging mechanisms in the presence of AA-LDHI and salt in flowlines remain poorly understood. The aim of this work is to deeper understand hydrate crystallization and transportability in pipelines at high water cut which is compared to low water cut and the effects of salt and AA-LDHIs in the flowloop with the gas bubble riser and without volumetric pump.

## 2. Experimental Methodology

### 2.1. Flow loop apparatus

The experiments were performed in the Archimede flow loop (Fig.1) at Ecole des Mines de Saint Etienne. The flow loop operates at maximum pressure of 80 bar, temperature between 0°C and ambient temperature and flowrate between 0 and 500 L/h. The flow loop is designed with 30 m of horizontal pipe with 1 cm of diameter, a riser and a descending pipe (both of them have a height of 12 m and a diameter of 1.5 cm), a gas injection system, and one sapphire window. At the top of flow loop riser, there is a separator, which separates gas and liquid ensuring no gas phase in the horizontal pipeline. The total liquid volume is 11.5 L.

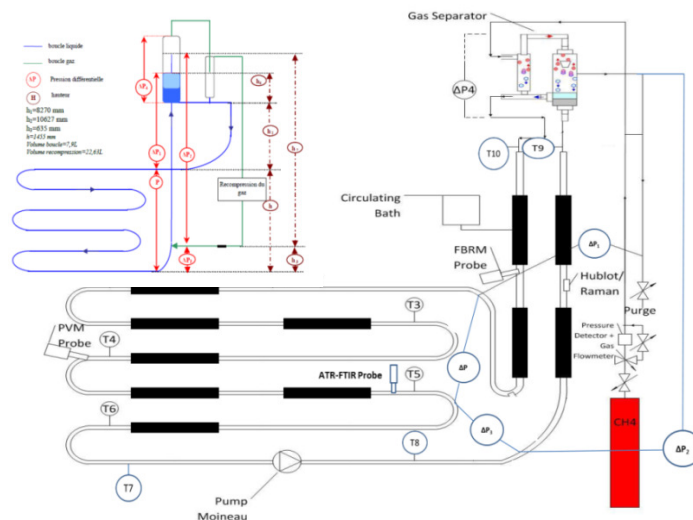


Figure 1: Schematic of the Archimede flow loop: simplified with “gas lift” system and with pump Moineau

This experimental apparatus is equipped with temperature (thermocouples), pressure and pressure drop (differential pressure transducer) probes for the determination of the beginning of the crystallization. Afterward the viscosity is evaluated and the plugging troubles are identified. The Focused Beam Reflectance Measurement (FBRM) probe allow to measure the particle size distribution of droplets and hydrates (via the chord lengths); the Particle Video Microscope (PVM) probe to observe the liquid-liquid dispersion, the gas hydrate formation and agglomeration phenomena. Also, a mass flow meter is installed to measure the flowrate and density. A pump Moineau and/or a gas-lift system can be used to circulate the fluids in the flow loop. In this experimental work, the gas-lift was used which is described in detail in Fidel-Dufour et al., (2006), implying that the flowrate depends on the viscosity of the mixture. A gas compensation system (or pressure controller) can be used to keep the total pressure at a constant value (75bar).

## 2.2. Materials and experimental procedure

Liquid-liquid dispersions are formed by mixing water (ultrapure water, provided from Millipore filter) and oil (Kerdane<sup>®</sup>, provided by TOTAL FLUIDES) with 30 % and 90% water cut. For some experiments NaCl (provided by Chimie – Plus Laboratoires, 99.8% NaCl) was added into the water phase with a concentration of 3%wt. A commercial anti-agglomerant (provided by TOTAL) was added to the water for some experiments with a concentration of 0.01%wt. The mixture was injected into the flow loop and to induce dispersion circulated at the flow rate of 150L/h. It is important to note that, because of high viscosity at low water cut with salt and/or AA-LDHI, the flowrate for emulsification and crystallization is always in the range of 30-60L/h. This circulation in the loop is carried out by a “gas lift” system injecting compressed air (at 4-5°C and atmospheric pressure) at the bottom of the riser.

Once flowrate in the flow loop was stable, the system was cooled down to 4-5°C. Then it was pressurized up to 75 bar by injection of methane (99.99 % purity supplied by AIR LIQUID) and ballast system was started (flowrate of approximately 100-150L/h for high water cut and 30-60L/h for low water cut with salt and/or AA-LDHI). Then, we performed a second injection up to 75 bar, and gas was consumed again by solubilization into liquids but in smaller quantity. Then, pressure is stabilized and we waited for the gas hydrate formation (and agglomeration) which will again consume gas. During the crystallization, we monitored the gas consumption rate, the pressure drop in the horizontal section and in the separator, the temperature, the FBRM and the PVM signals. At the end of experiment (when crystallization is finished or/and pipe is plugged), the flow loop was depressurized until the ambient pressure and the cooling system was stopped.

## 3. Results and discussion

The beginning of gas hydrate formation can be identified by an increase of temperature (crystallization is exothermic), an increase of pressure drop in the horizontal pipeline and in the separator and also from the pattern of the PVM images and chord length measurements (A.Melchuna et al., (2016)). These results will be presented by experiments at 30% and 90% water cut (WC) with NaCl and with/without AA-LDHI.

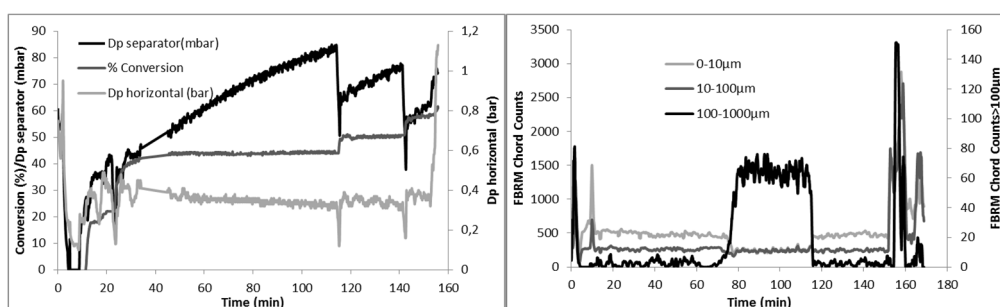


Figure 2: Pressure drop (Dp), conversion and chord length results of 30%WC+NaCl (3%wt) without AA-LDHI

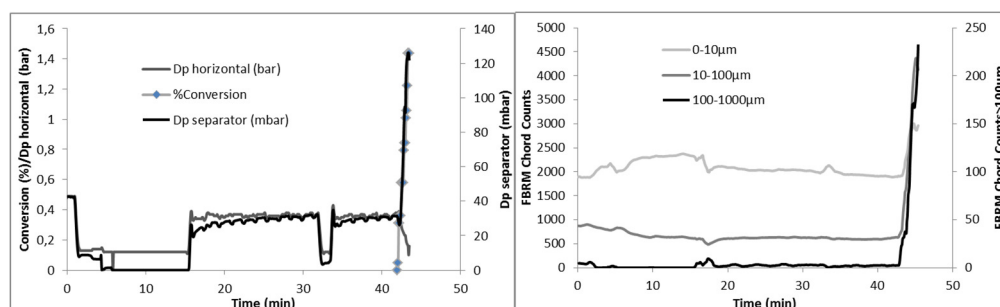


Figure 3: Pressure drop (Dp), conversion and chord length results of 90%WC+NaCl (3%wt) without AA-LDHI

Fig.2 and 3 showed the experimental results of mixtures with 30%WC+NaCl and 90%WC+NaCl (3%wt) respectively, without AA-LDHI. At high water cut, the tests showed a quick increase of pressure drop in the separator once hydrate formation starts followed by a quick plug. On the other hand, at low water cut, plugging time is slower, we did not observe quick plug after gas hydrate formation but shorter induction time.

This behavior can be explained by the presence of numerous gas bubbles in the riser. For water continuous phase, hydrates formed on the surface of gas bubbles and deposited inside the separator. In oil continuous phase, the role of gas bubbles is to enhance the gas transfer into the liquid phase which increases the hydrate formation on the surface of water droplets.

At high water cut, deposition in the separator is observed because the hydrate particles have higher adherence onto the pipe surface. This is different from the oil continuous phase. [G.Aspenes et al., \(2009\)](#) considered that the adhesion force of hydrate particles and pipe surface with water droplets is much higher than hydrate-hydrate adhesion force or hydrate-pipe wall interaction without water layer.

The low flowrate and the small diameter of pipe may also contribute to the gas hydrate deposition. Moreover, from the average chord length results, using “gas lift” system, mean droplet size of emulsion is quite small (~10 $\mu$ m) compared to that of previous work, [Mendes-Menchuna et al., \(2016\)](#), using protocol with pump Moineau. It is perhaps another reason which causes higher gas hydrate formation due to larger contact surface between oil and water.

At high water cut, despite the small hydrate volume in the flowloop for each test, the plug happened very quickly (several minutes) after the beginning of gas hydrate formation. In opposite view, at low water cut (30%), gas hydrate formed at beginning of experiment and it takes longer time to plug except experiment of 30%WC without AA-LDHI.

Plug time defined in this work is when the flow rate falls to zero. At the same time, a dysfunction of the gas-lift system is observed. When hydrates form, they may agglomerate and it is evidenced by an increase of pressure drop, and the increase of the average chord length. The increases of both parameters were reported by [Leba et al., \(2010\)](#); [Jun Chen et al., \(2014\)](#). In all tests, there is a slight increase of pressure drop in horizontal sections once hydrate is formed. Also, from previous work, [Young hoon Sohn et al., \(2015\)](#) and [Joshi et al., \(2013\)](#) showed that agglomeration may not produce sharp increase in pressure drop. High-pressure drops were observed only once hydrates deposited on the pipe wall.

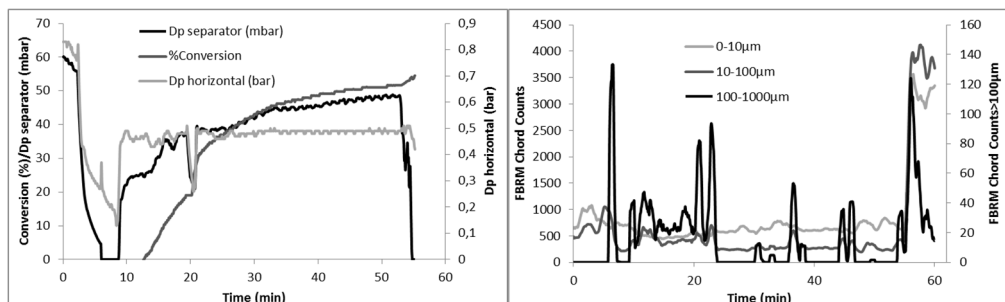


Figure 4: Pressure drop (Dp), conversion and chord length results of 30%WC+NaCl (3%wt) with 0.01%AA-LDHI

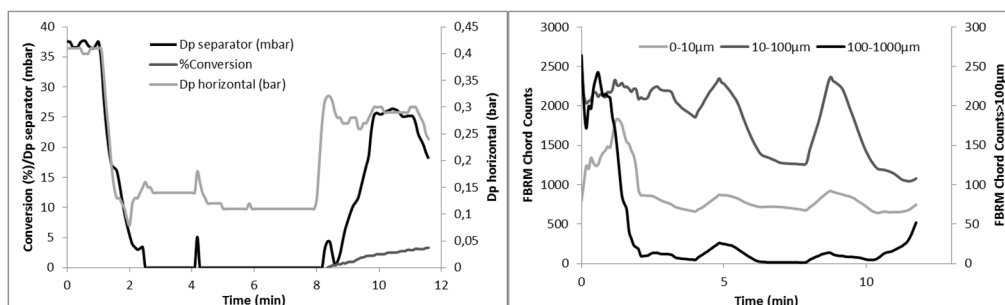


Figure 5: Pressure drop (Dp), conversion and chord length results of 90%WC+NaCl (3%wt) with 0.01%AA-LDHI

At high water cut, the results of mixture with AA-LDHI ([Fig.4 and 5](#)) compared to mixtures without AA-LDHI, at the same water cut, demonstrated that the addition of low quantity of AA-LDHI (0.01%AA) is not sufficient to prevent plugging. The addition of AA-LDHI also seemed to inhibit hydrate nucleation in the experiments at 90%. In addition, salt inhibits hydrate formation for experiments at 90% WC. The mixture with

both salt and AA-LDHI at low water cut shows a lesser ability to prevent blockage up to 0.1%AA-LDHI. We can suppose that there is an effect of salt on the performance of AA-LDHI.

All experiments at high water cut systems showed higher rate of hydrate growth, and faster agglomeration and plug events, compared to previous studies, [Fidel-Dufour et al.,\(2006\)](#); [Leba et al., \(2010\)](#); [Mendes-Melchuna et al., \(2016\)](#). These experiments differ due to the presence of a “gas lift” section in water continuous phase. It can be hypothesized that gas hydrate is formed in the riser at a higher rate due to the high gas diffusion and then particles accumulate in the separator (once a significant surge in the pressure drop of the separator was observed).

PVM results ([Fig.6](#)), show clearly hydrate particles with hydrate film covering droplets, in some cases, together with agglomerates. In the experiments with AA-LDHI, PVM images had a bad quality and therefore, it was impossible to follow the morphology of hydrate particles during crystallization.

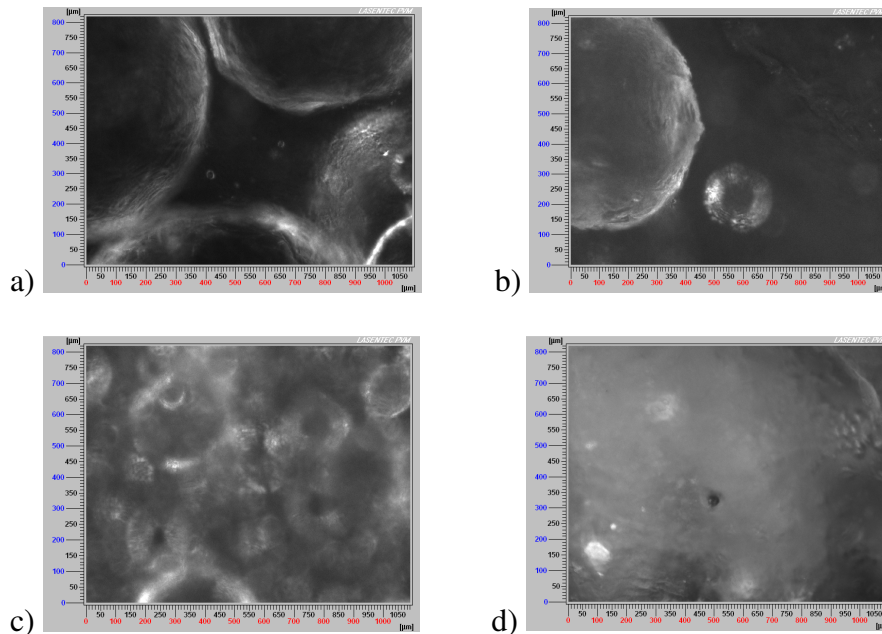


Figure 6: PVM images of gas hydrate formation for different mixtures: (a) 90%WC without AA-LDHI; (b) 90%WC+NaCl without AA-LDHI; (c) 90%WC with 0.01% AA-LDHI; (d) 30%WC+NaCl with 0.01% AA-LDHI

#### 4. Conclusions

In high water cut systems using “gas-lift” system, the risk of hydrate blockage is high because of high rate of hydrate formation (high gas water interface due to bubbles) and high risk of quick plug formation. Low dosage of AA-LDHI (0.01%) is not sufficient to prevent their agglomeration, and plugging occurs rapidly. The presence of a gas phase in the riser induces quick plugging in high water cut systems due to the formation of huge amounts of hydrate that cumulated in the separator.

In low water cut systems or oil continuous phase using gas-lift riser, gas hydrates form sooner but an amount of 0.01%AA-LDHI was sufficient to prevent plug without salt. Because hydrates form and disperse in the oil continuous phase (with AA), plug is avoided if the dosage of AA is sufficient.

Salts and AA seem to affect nucleation and growth of gas hydrate formation (inhibition). In case of experiments at high water cut using AA and salt simultaneously, gas hydrate formed sooner and caused flowrate increase after crystallization.

#### Acknowledgements

The authors are grateful to TOTAL E&P for the financial support in the Archimede-3 project and their approval for publishing this paper. We also would like to acknowledge the contribution on technical support and reviewing this manuscript from the members of TOTAL and the Gas Hydrate Dynamics Centre team at Ecole des Mine de Saint Etienne, France.



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