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AGGLOMERATION OF GAS HYDRATE IN A WATER-IN-OIL EMULSION: EXPERIMENTAL AND MODELING STUDIES

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ABSTRACT

The formation of gas hydrates in water-in-oil emulsion is investigated at the laboratory pilot scale on a flow loop. The Archimede flow loop (30 m long, and 1 cm diameter) has been built to reproduce the thermodynamic conditions encountered in deep-sea pipelines with a maximum flow rate equal to $3x10^{-5}$ $m^3.s^{-1}$ [1].

Recently, a Moineau pump has been added in order to maintain the flow at a constant rate, especially after the beginning of crystallization and independently of the rheological characteristics (the flow rate can be varied in the range $2x10^{-5}$ $m^3.s^{-1}$ to $14x10^{-5}$ $m^3.s^{-1}$).

This work presents some preliminary experiments to characterize the flow properties. Also some crystallization experiments were realized in order to understand the coupling between crystallization and rheology by following the size of the agglomerates and the water conversion.

When water droplets crystallize to form hydrate particles, an agglomeration phenomenon is evidenced by pressure drop measurements. The agglomeration phenomenon is also detected by a Focused Beam Reflectance Measurements (FBRM) probe and is highlighted by a sharp change in the mean chord length and a spread of the Chord Length Distribution (CLD) to larger chord length.

Keywords: gas hydrates, flow loop, rheology, chord length distribution, modeling

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NOMENCLATURE

D	diameter of the pipe [m]
D_f	fractal dimension [-]
f	friction factor [-]
m	mass [g]
m_t	
M_w	molar mass of water [$g.mol^{-1}$]
$n_{CH4cons}$	consumed mole of methane [mole]
n_0	initial mole of methane [mole]
n_{crw}	mole of crystallized water [mole]
n_{iwater}	initial mole of water [mole]
P_0	initial pressure [bar]
P_t	pressure at time t [bar]
P_{eq}	equilibrium system pressure [bar]
T_0	initial system temperature [°C]
T_t	temperature at time t [°C]
T_f	final temperature [°C]
V_0	gas volume [m^3]
Z_0	initial compressibility factor
Z_t	compressibility factor at time t
r	radius of the pipe [m]
R	gas constant [$J.mol^{-1}.K^{-1}$]
Re	Reynolds number [-]
N_p	particle number [-]
$t_{ini\ cr}$	nucleation time [min]
v	velocity of the fluid [$m.s^{-1}$]
$\Delta p/L$	pressure loss [$Pa.m^{-1}$]
ρ	density [$kg.m^{-3}$]
η	conversion

INTRODUCTION

The crystallization of gas hydrates in pipelines is a flow assurance problem that affects the petroleum industry in respect to the increase of the operative pressure and increase of the water cut. The main reason is that the remained off-shore petroleum resources are deeper and also because longer pipelines are needed.

To prevent the formation of gas hydrates three solutions are envisaged: using additives to prevent the formation, heating the pipeline and isolating it. Because the two last are very expensive in energy and capital, adding additives is the most used solution. These additives can be of three different types: thermodynamic, kinetic or anti-agglomerant types [2,8].

In previous works, we modeled the agglomeration and it effect on the viscosity of the suspension in a batch reactor [3]. In a way to better understand the coupling between formation and flowing, a flow loop has been constructed at Ecole des Mines de Saint-Etienne. The first work showed that water droplets start to crystallize and then agglomerate in a fractal-like structure which can be postulated and evidenced from pressure drop measurements [4].

In 2005, a Focused Beam Reflectance Measurements (FBRM) probe was added to the flow loop in order to detect agglomeration phenomenon. It was concluded that agglomeration was highlighted by a sharp change in the mean chord length and a spread of the Chord Length Distribution (CLD) to larger chord length. In order to interpret the CLD measurements, a model has been developed [1] based on literature survey [6,7].

This model [1, 10] allows comparing the size of aggregates from viscosity measurements and from CLD. The model allows determining the fractal dimension of aggregates and their number of constituting particles. Results obtained from the model of Leba [1, 10] were compared to those given by viscosity measurements in order to better understand the rheological properties of emulsions.

Using the flow loop with the recent configuration, the effect of emulsifier on the water-in-oil emulsions can be studied. This model can be used to understand the agglomeration degree of emulsion during crystallization by varying operating parameters: water cut, concentration of additives, concentration of salt in water…

The new configuration of the Archimede flow loop allows the study of the transport of slurries with high concentration of crystals.

The experimental results obtained in this work can permit a better understanding of crystallization under flow and contribute to a further work on modeling this type of crystallization by population balances as it was done before [4].

EXPERIMENTAL APPARATUS AND PROCEDURE

Crystallization of water-in-oil emulsions of hydrate slurries under shear stress was studied in the Archimede loop. Details on the apparatus and results are given in [4]. The crystallization of gas hydrates is studied from the rheological properties deduced from pressure drop measurements, and from the size and shape of crystal deduced from the signal provided by the FBRM probe.
The Lasentec D600L FBRM probe was used in this study to measure the chords length distributions during the crystallization process. The FBRM (Focused Beam Reflectance Measurement) probe is an *in-situ* particle size analyzer equipped with a rotating low intensity LASER beam which is reflected when it intercepts an object, see more details on [9].
For appropriate sampling of the particles, the probe is placed at the centre of a vertical section so that all categories of particles are expected to circulate in front of the probe window. It is also necessary to avoid forming a “dead zone” in front of the measurement window.

The ARCHIMEDE flow loop reproduces the thermodynamic conditions of the deep-sea pipelines with working pressures up to 100 bar. Temperature is controlled within the range 0 ºC to 14ºC. The flow loop is equipped with a FBRM probe but also with several temperature probes, differential pressure probes and a Coriolis flow-meter. Figure 1 represents the flow loop composed by a horizontal section of 30 meters and a riser of 12 m ending in a gas-liquid separator. The Moineau pump maintains the flow rate at a constant value between $2x10^{-5}$ $m^3.s^{-1}$and $14x10^{-5}$ $m^3.s^{-1}$.

A water in kerdane emulsion stabilized with an emulsifier is circulated in the flow loop. The organic phase is a C10-C13 distillation cut which is delivered by TOTAL Fluids under the commercial denomination of Kerdane. The additive is a specific surface-active solution, IPE202, patented by IFP. The NaCl is from Sigma Aldrich.

The formation of the emulsion (total volume of 11,5L) is generated by using an Ultrat Turrax impeller at 8800 rpm during 3 min. Then, the emulsion is introduced in the flow loop and circulated until the operative temperature of 4ºC is reached. The loop is then pressured up to 80 bar and Moineau pump (non-shearing progressive capacity pump from PCM) is run. Methane dissolves in the emulsion. The loop is then pressured again to 80 bars so that final pressure after solubilization is in the range 70-75 bar.

As the nucleation is observed, the pressure becomes de decrease again because of the gas consumption due to hydrate formation. The slurry is circulated in the flow loop until the end of crystallization and agglomeration.

At the end of the experiment, once the crystallization is considered as accomplished (pressure and temperature remains constants during hours), the slurry can be studied. A rheological characterization is done by varying the flow rate and measuring the pressure loss in the horizontal pipe.

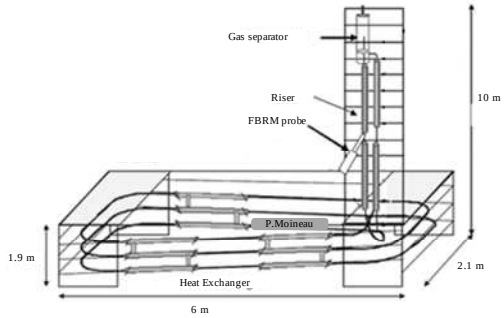
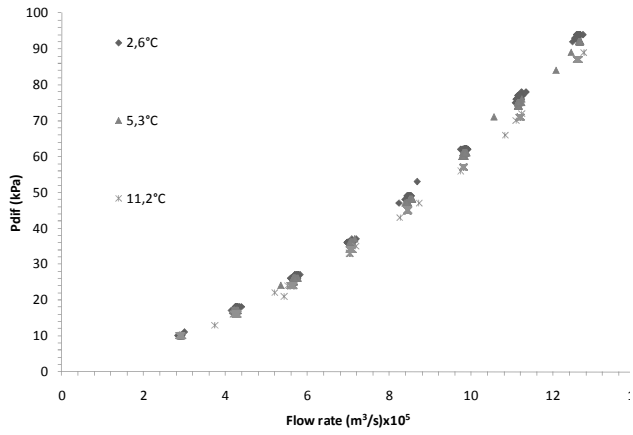


Figure 1. Archimède flow loop.

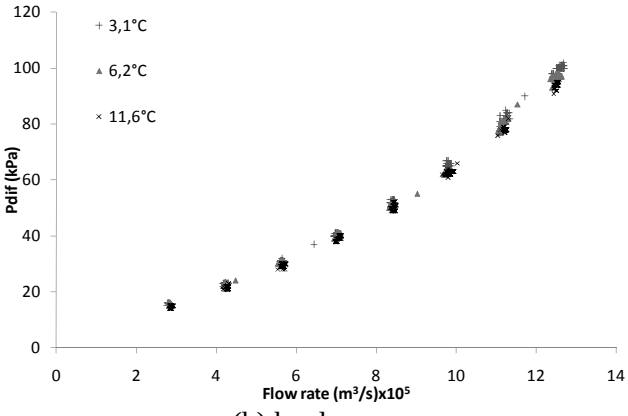
Different parametric studies were done by varying the percentage of water, concentration of IPE, flow rate and NaCl concentration (see Table 1).The main results are presented below.

EXPERIMENTAL RESULTS

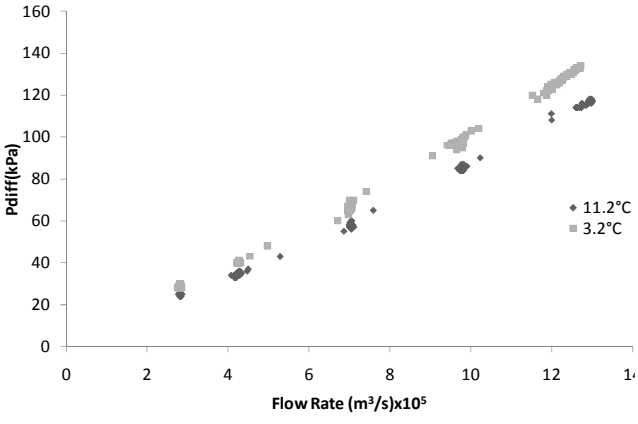
Before studying the crystallization, the rheology of pure water, pure kerdane and emulsion of water in kerdane (30% volume water) have been studied at different temperatures by measuring the pressure loss at different flow rate. Figure 2 shows the results of this study.



(a) water



(b) kerdane



(c) emulsion 30%water

Figure 2. Pressure loss with varying temperature and flow rate.

For each curves two different slopes were detected. This means that there are two different regimes of flow: laminar and turbulent. The transition between both regimes is approximate equal to values between $6x10^{-5}$ and $8x10^{-5}$ $m^3.s^{-1}$.

At low flow rate, the flow can be considered as laminar and pressure loss can be calculated threw the following equations [11]:

$$\frac{\Delta p}{L} = f\frac{\rho v^2}{r} \quad (1)$$

$$Re = \frac{\rho v D}{\mu} \quad (2)$$

$$f = \frac{16}{Re} \quad (3)$$

Dissolution of methane

After the injection of methane, the pressure (in this case the pressure divided by the initial pressure) decreases quickly due to the dissolution of methane in the emulsion. Figure 3 shows the decrease of pressure during the dissolution of 6 experiments at different conditions (see Table 1):

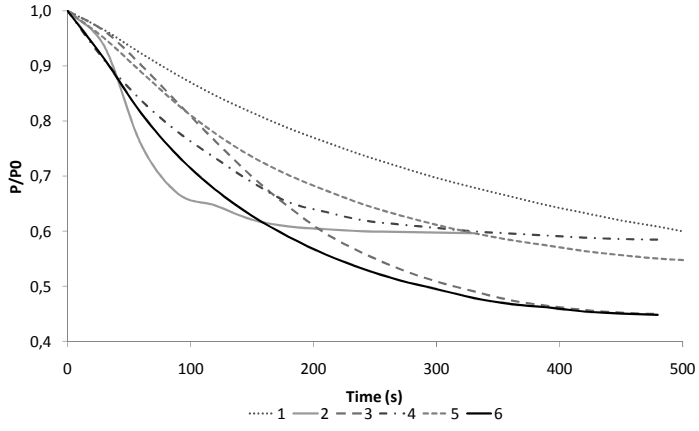


Figure 3. Dissolution of methane in water in kerdane emulsion.

The transfer rate for each experiment is showed in Table 2 in s^{-1}.

1	2	3	4	5	6
0.0034	0.0208	0.0087	0.0106	0.0073	0.0092

Table 2. Transfer rate.

From Table 2, it is observed that experiments with increasing flow rate have increasing dissolution rate. When the percentage of water increases the transfer rate increases and when the percentage of additive increases the transfer rate decreases. Experiments with salted water show that the transfer rate is approximately the same.

Crystallization study

The crystallization experiments were analyzed in terms of conversion and average chord length during the crystallization process.

The conversion is calculated threw the equation $PV=nZRT$ (4) where Z is the compressibility factor of the gas defined in the case of methane by the following equation $Z = -0{,}0196P[MPa]+0{,}994$(5) [4].

The conversion is then calculated assuming that the cavities are filled at 100% with

$$\eta = \frac{n_{crw}}{n_{iwater}} \qquad (4)$$

where the number of mole of water crystallized is equal to : $n_0 = \frac{m}{M_w} = \frac{m_t \times (\%w)}{M_w}$ (5)

The formation of methane hydrates can be described by the following reaction:

$$CH_{4\ (g)} + 5.75\ H_2O_{\ (l)} \rightarrow CH_4\ 5.75\ H_2O_{\ (s)}$$

From this reaction the number of mole of water crystallized is equal to 5.75 mole of the consumed methane.

$$n_{CH4}\big|_{cons} = \frac{P_0V_0}{Z_0RT_0} - \frac{P_tV_0}{Z_tRT_t} \qquad (5)$$

Table 1 show some interesting results about conversion.

Experiments at the same conditions but different flow rate show that when the flow rate increases the conversion increases (experiments 1 and 2) because the transfer rate increases (see Table 2).

For experiments at low water cut (experiment 4 and 2 and experiment 5 and 3) the conversion is complete or higher comparing with experiments with high water percentages in which the total conversion is not attained, probably because there is not enough methane to totally convert the water.

Comparing experiments at different percentages of additive (experiment 2 and 3), when the additive decreases the conversion decreases because the dissolution rate is smaller.

Finally, when the emulsion is done with salted water (experiment 6), the conversion decreases (experiment 3).

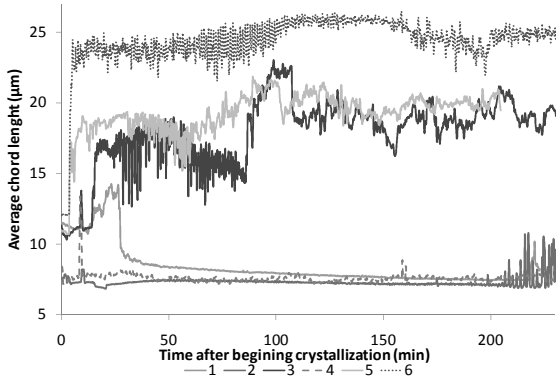


Figure 4. Average chord length during crystallization.

Comparing experiment 1 and 2 agglomeration is more pronounced in 1 at low flow rate than in 2, because the shear rate is lower.

Experiments 4, 2, 5 and 3 have large final agglomerates.

Experiments at different percentages of additive show, has expected, that decreasing the quantity of additive increases the agglomeration.

The use of salted water also seems to increase agglomeration when comparing experiment 3 and experiment 6.

From the work of LE BA [10] by using the model of interpretation of the CLD, we can give an estimation of the number of primary particles (N_p) and fractal dimension of the agglomerates (D_f). the results for each experiment during time are shown in Table 3.

Comparing the first times of crystallization, when the additive percentage increases, the fractal dimension decreases, probably because agglomerates are more compact.

During each crystallization, the fractal dimension and the number of primary particles increases due to agglomeration.

When the percentage of water decreases or when the quantity of emulsifier decreases agglomerates are bigger (N_p is larger) and viscosity higher (table

1) this was already observed in a preceding work [10].

The experiments with salt show large agglomerates as the experiment with low concentration of additive. Nevertheless the viscosity of the suspension with salt is lower at the same conditions of water and additive (3 and 6 in table 1).

Comparing experiments 1 and 2, at high flow rate agglomeration is lower because of the shear rate.

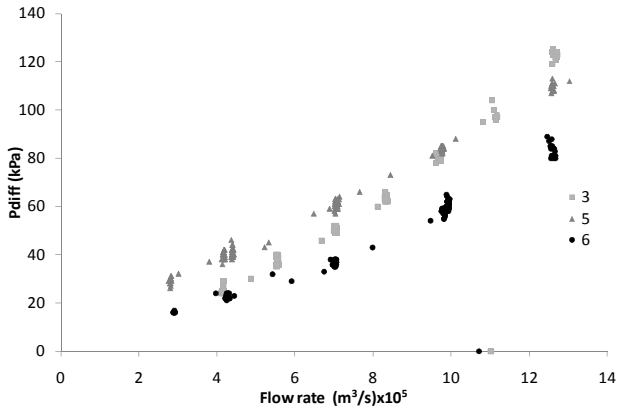
Table 1. Methane hydrate experiments.

Experiment	**Flow rate** $m^3.s^{-1}$	**Volume %water**	**Mass % IPE**	g_{NaCl}/l_{water}	**% conv**	p_{eq} **(bar)**	T_f **°C**	**Final slurry Viscosity (Pa.s)**
1	$7.5x10^{-5}$	30	0.5	-	29	45.2	5	0.0074
2	$13.5x10^{-5}$	30	0.5	-	53	39.1	4.2	-
3		30	0.1	-	39	42.2	4.4	0.0068
4		10	0.5	-	100	57.1	3	0.0052
5		50	0.1	-	32	35.4	3	0.0096
6		30	0.1	35	13	47.7	4.3	0.0059

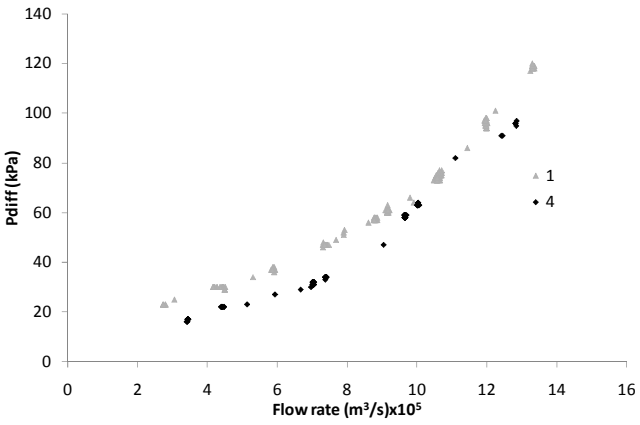
Table 3. Results from the interpretation of CLD during crystallization.

		1	**2**	**3**	**4**	**5**	**6**
$t_{ini\ cr}$	N_p	**176**	**290**	**338**	**979**	**275**	**690**
	D_f	2.0	2.1	2.2	2.1-2.3	2.2	1.8
$t_{ini\ cr}$ + **100min**	N_p	**383**	**385**	**716**	**1004**	**717**	**655**
	D_f	2.3	2.1	2.7	2.5	2.4	2.3
$t_{ini\ cr}$ + **200min**	N_p	**383**	**386**	**1127**	**1004**	**717**	**1124**
	D_f	2.3	2.3	2.3	2.5	2.7	2.5

After the crystallization a rheological study is done. This study helps in understanding the capacity to transport the slurry in a pipeline as a function of the quantity of solids in the slurry.



(a) 0.1%IPE



(b) 0.5%IPE

Figure 5. Pressure loss with varying flow rate.

From Figure 5 experiments were assembled by affinity: experiments at equal percentage of IPE have the same behavior in terms of pressure loss with flowrate.

Experiments at low quantity of emulsifier have the transition between the laminar and the turbulent regime at higher flow rate.

Comparing Figure 5 and viscosity in table 1 experiment 5 has higher viscosity than 3, so the pressure loss with flow rate is more important to 5 than to 3.

CONCLUSIONS

An experimental study has been made in order to understand the crystallization of methane hydrates in a pipeline.

Experiments were made in Archimede flow loop with different flow rates using a Moineau pump, percentage of water in the emulsion, percentage of IPE and with or without NaCl.

For experiments at high percentage of water the conversion is not complete because there is not enough gas in the system to totally convert water and also because gas diffusion is more difficult. At low water percentage, conversion is complete and agglomeration is high.

At high flow rates, the conversion is higher because the methane transfer rate from gas into oil is higher.

Experiments at high water cut and low percentage of IPE show a pronounced agglomeration because the frequency of collision between droplets increases and because there is a lot of water not converted that enhances agglomeration by consolidating aggregates and increases the final viscosity, as observed in preceding works [10, 12].

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