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# Formation and Transportation of Methane Hydrate Slurries in a Flow Loop reactor : Influence of a Dispersant

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In this paper, we present the experimental results obtained from a new flow loop reactor in which methane hydrate particles are crystallized in water droplets transported in a oil flow. The final goal of this apparatus is to couple the rheology with the Particle Size Distribution of water droplets and gas hydrate during crystallization and to observe the influence of dispersants and/or kinetics additives (PVP). In this paper, we describe the flow loop plant and we show preliminary results of the rheology of the emulsion before crystallization and suspension after methane hydrate appearance. The influence of a dispersant additive is observed at a water content of 9 % vol.

## 1. Introduction

Gas hydrate particles are crystals which can form from cold liquid water and hydrocarbon gas under pressure. These conditions are commonly met during the transportation of the hydrocarbon fluid in the submarine pipelines between the well-head and the production platform. Such a crystallization must be absolutely prevented because of the risk to plug the pipelines. For this, a first method consist in insulating the pipelines in order to maintain the temperature of the fluid at a value superior to the thermodynamic temperature of formation of the hydrate phase. This method is the most expensive but the more efficient too. Another method consists in using thermodynamic additives such as glycol, which are injected at the level of the well-head. In this method, the quantities of glycol to be used can be very large (50% of the water phase) and the cost of the post-treatment becomes too high. A new way of research which is now developed is the use low dosage inhibitors (Bloys et al., 1995 ; Lederhos et al, 1996 ; Urdahl et al., 1995 ; Lund et al., 1996 ; Larsen et al., 1998, Kelland et al, 2000, Palermo and Goodwin, 2000, Palermo et al, 2000). The first ones are anti-agglomerants, *i.e.* surfactant compounds, which emulsify water and allow a thin hydrate crystals suspension to be transported. The second ones consist of kinetic inhibitors, which may prevent crystals nucleation or growth during a sufficient delay compared to the residence time in the pipeline.

The advantage of this approach is the poor quantity of additive which is necessary : 1% of the water phase. The efficiency of some of these additives has now been clearly proved. However, the nature of the additive effect is rarely well understood, mostly because of the lack of experimental results concerning the nucleation-growth of the hydrate phase. Kinetic inhibitors can have an influence at different steps of the crystallization. They can act on the nucleation step by

lengthening the induction period and reducing the number of nuclei, thus the number of hydrate crystals. They can also slow down or even block the crystal growth and lastly prevent the crystals from agglomerating.

The aim of this work is to extend previous results obtained on methane hydrate crystallization in water in a batch reactor (Herri et al, 1999a) that have explained the influence of a reference additive : the PolyVinylPyrrolidone (PVP). For this, we firstly developed a complete model of crystallization in pure water (Herri et al, 1999b) that has been adapted to the quantification of the influence of kinetic inhibitors in pure water (Pic et al, 2000, 2001).

In this work, we present preliminary results on the up-scaling of the previous results to the methane hydrate crystallization in a water in dodecane emulsion in a flow loop plant which has been specially designed for this application.

The paper is organized as follow :

- presentation of the new flow loop reactor which present the main originality to generate the flowing without any pump or mechanical machine,
- experimental results concerning the quantification of the rheology of water in oil emulsion prior to the crystallization and effect of a dispersant additive on the hydrate slurry behaviour after crystallization.

## 2. Apparatus description

The flow loop reactor is a large streamer of 30 m long, ½inch diameter and constant slope of 4° in which the pipes wind round inside a scaffold of 9 meters long and 3 meters wide. The streamer is connected to two vertical pipes of 10 meters high and ¾inch diameter (the rising and descending pipes) which ensure the

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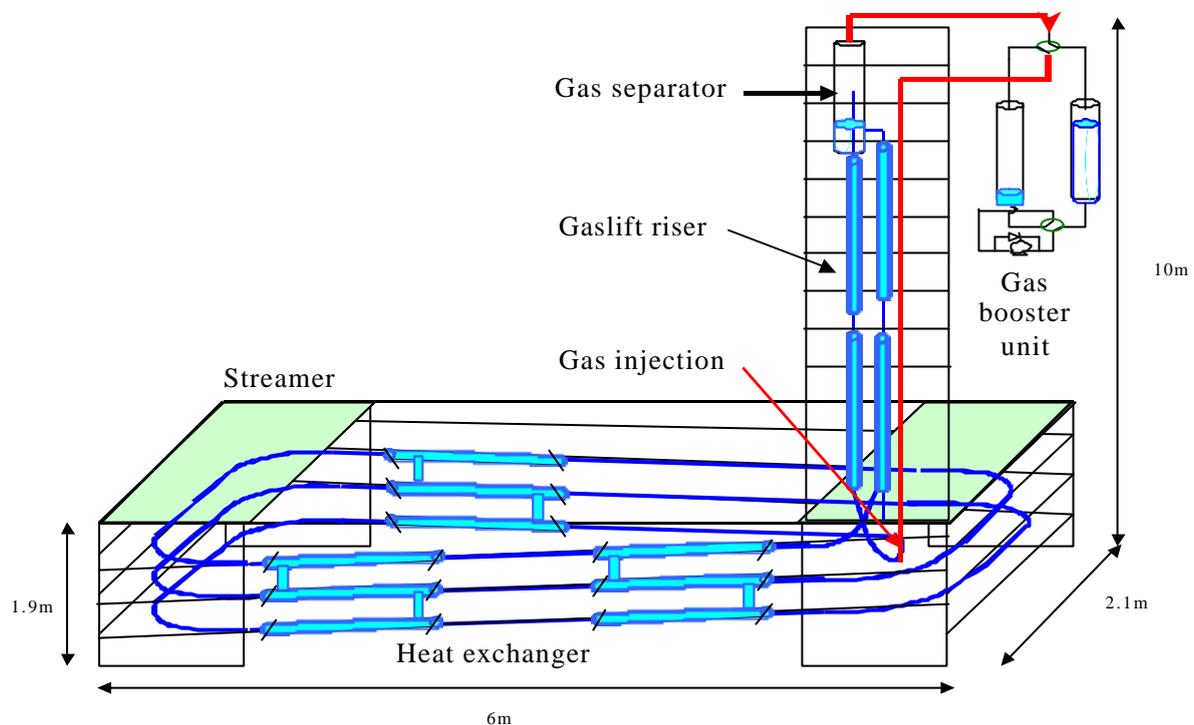


Figure 1  
Principle of the flow loop pilot plant

flowing driving force by the means of a gas-lift. At the total, the flow loop is 50 m long. The streamer is divided into three successive levels, each of them consisting of two straight sections of 5.5 meters, two straight sections of 0.5 meters and four quarter circles of 1 meter diameter.

The pipes are maintained at constant temperature by means of external cooling jackets. It was built up on the 1shell-and-1tube principle. The water suspension or the hydrate slurry is on the pipe side and the glycol/water cooling media on the shell side. The shell is an pipe of 2 inch diameter connected to cryothermostats.

Each level of the streamer loop is equipped with three heat exchanger of 1.5 meters long and the rising and descending pipe are equipped respectively with 3 and 2 cooling jackets of 2 meters long. As a result, 40% of the flow loop reactor is equipped with heat exchanger. The total cooling power is 3 kW.

The flow rate is measured by a Coriolis flowmeter [0-500l/h]. Pressure drop is measured by the way of a differential pressure transducer [0-500 mbar].

The two main originalities of this new flow loop reactor are :

- the first one consists to use our self-made methods of particle sizing from turbidimetric measurement for low particle concentration (Eliçabe et al, 1987, Crawley et al, 1997, Herri et

al, 1999a) or backscattering for high particle concentration (Tontrup and Gruy, 2000) or methods developed in association with T.U. Dresde (Dynamic back scattering) in order to study the behaviour of a suspension of water droplets into oil phase and to couple the hydrodynamics to the Particle Size Distribution, firstly P.S.D. of water droplets, and secondly PSD of gas hydrates particles after their appearance. These techniques will be operational during the years 2002-2003 and experimental results will not be presented in this paper.

- the second one is the system which induces the flowing by the way of a gas lift riser. Indeed, we want to preserve the suspension from the high shear stress generated by a pump, and so we have developed a method to create a differential pressure by the way of a gas lift riser. The principle is to dispose of two identical vertical columns filled with fluids with different densities : the rising and descending pipes. Initially, the flow loop reactor is entirely filled with the fluid (water + oil). Then the riser column is made lighter by the way of gas methane injection at the bottom. Gas bubbles go up to the gas separator located at the top of the riser and are separated from the fluid. Then the remaining fluid goes back in the descending pipe. As a result, the density of the fluid column is lower in the rising

pipe than is the descending pipe due to the gaslift effect. At the base of the two vertical pipes, this generates a differential pressure proportional to the height of the pipes and dependent on the volume of gas injected at the base of the riser. So, we impose the differential pressure and observe the flowing rate whereas it is the contrary in other where the flow is forced using mechanical pumps, for example centrifugonal Pump (Anderson and Gudmusson, 2000), Leistriz twin helical screw pump (Matthew et al, 2000), Volumetric Pump (Moineau Type, Palermo and Goodwin, 2000). In our system, the flowing force is due to gravitational force like in the rotational test loop of SINTEFF (Urdahl et al, 1995; Lund et al, 1996)

### 3. Experimental results

#### 3.1 Rheological characterisation

In order to firstly characterize the flow loop rheological properties, we tested the flowing of pure liquids which viscosity are known precisely, *i.e.* water and dodecane at different temperature from 2°C to 34°C.

We used the next relation :

$$\frac{f}{2} = \frac{\Delta P}{L} \frac{D}{4\rho u^2}$$

- $f$  : friction coefficient  
 $\Delta P$  : pressure drop (Pa)  
 $L$  : equivalent flow loop length (38 m)  
 $D$  : inner diameter (1 cm)  
 $\rho$  : fluid density (kg/m<sup>3</sup>)  
 $u$  : flow speed (m/s)

$u$  is back-calculated from the measurement of the volumetric flow rate  $Q$ :

$$Q = u \frac{\pi D^2}{4}$$

The figure 2 shows the variation of the friction coefficient as a function of the Reynold Number :

$$Re = \frac{\rho u D}{m}$$

$m$  : liquid viscosity (Pa.s)

We can observe two zones :

- the laminar zone ( $0 < Re < 2500$ ) in which the Hagen-Poiseuille relation is applicable :

$$Q / \frac{\Delta P}{L} = \frac{\pi D^4}{128m}$$

In such a case, the friction coefficient expression is :

$$f = \frac{8}{Re}$$

The figure 2 shows the good agreement with the experimental results in the laminar zone.

- the intermediate zone ( $2500 < Re < 10^4$ )

The intermediate zone is the zone between the laminar zone ( $Re < 2500$ ) and the turbulent zone ( $Re > 10^5$ ). This is the zone in which the turbulence phenomena appears. The experimental data shows two behaviours :

- in the experiments done with water, the flowing “obeys” to a classical behaviour. That means the friction coefficient firstly increases around  $Re = 2500$  as the flowing changes from laminar to turbulent flowing, and then decreases as  $Re$  increases. From the experimental data, we can retrieve a correlation giving :

$$\frac{f}{2} = 0,00058 + \frac{0,0521}{Re^{0,32}}$$

- Concerning the experiments done with pure dodecane, the flowing shows a chaotic behaviour. During a same experiment, it changes continuously and randomly from a classical behaviour to an unexpected laminar behaviour, and *vice versa*. It is why on the figure 2 we can observe points of the intermediate zone located in the prolongation of the laminar flow.

NB: The figure 2 shows that we never reach the turbulent zone. In fact, we observe here a limit of our apparatus in which the flowing is induced by the way of a pressure difference generated in the gas lift riser. And, this pressure difference is physically limited by the riser height and the maximum bottom gas rate injection.

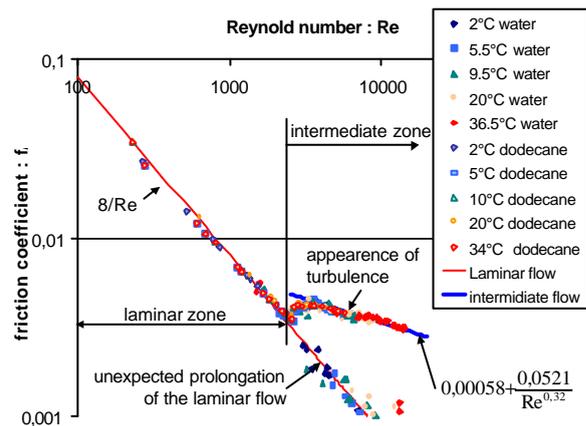


Figure 2

Hedström diagram of the flow loop plant calculated from pure water and pure dodecane flowing

#### 3.2 Influence of a dispersant on the water in oil emulsion

We did previous experiments to test the influence of a dispersant on the flowing of a water in oil emulsion,

here water (9% vol.)-dodecane at atmospheric pressure and temperature of 4°C.

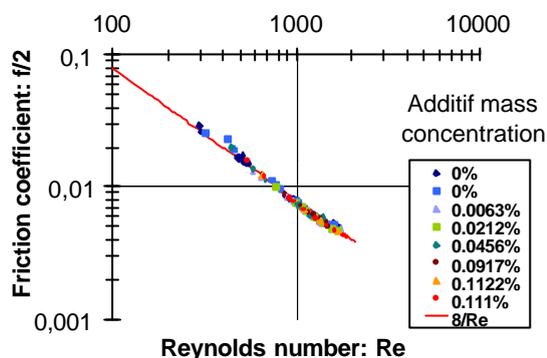


Figure 3

Hedström diagram of the flow loop pilot plant calculated for water (9 % vol.) in dodecane at various additive concentration

We calculate the viscosity of the water in dodecane emulsion from the measurement of the couple ( $Q$ ,  $DP/L$ ) which is connected to viscosity by the Hagen Poiseuille relation in the laminar zone. From viscosity values, it is then possible de calculate the Re number and to plot the corresponding Hedström diagram (figure 3) and to verify that the flow is *a posteriori* laminar.

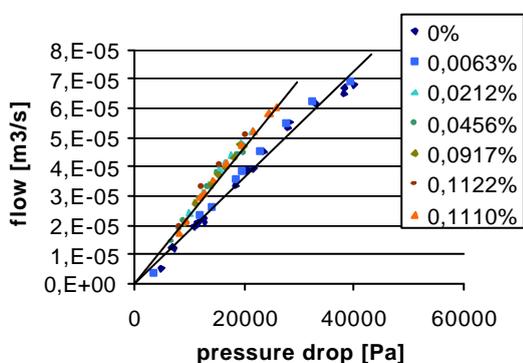


Figure 4

Influence of the additive concentration (% mass) on the fluid flow rate  $Q$  and pressure drop  $DP$

More, on the figure 4, we can observe that the fluid has a Newtonian behaviour, *i.e.* the fluid viscosity doesn't depend on the flowing rate (at least in the laminar zone). In fact,  $DP/L$  is a linear function of  $Q$ .

As a final, we can plot the water (9 % vol.) in dodecane emulsion as a function of the concentration

of additive. The figure 5 shows that the viscosity reaches rapidly a constant value of 0.003 Pa.s which is 50 % higher than the pure dodecane at the same temperature (4°C) : 0.002 Pa.s

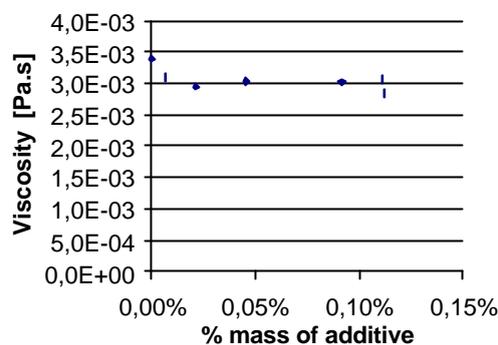


Figure 5

Influence of the additive concentration on viscosity of the water (9 % vol.) in dodecane emulsion

### 3.3 Influence of a dispersant on the hydrate slurry behaviour.

Then, from the emulsions which have been characterized before, we performed a sensitivity study of the effect of the additive concentration on the hydrate crystallisation of a water (9% vol.) in dodecane emulsion at pressure of 7 MPa and temperature of 4°C.

We observed the evolution of the flowing rate, pressure drop, mean temperature, gas consumption (from pressure decrease).

For mass concentration of 0%, 0,0066 % and 0,021% (figure 6), we observed that the crystallization is instantaneous and blocks immediately the flow, *i.e.* the flow rate reaches a zero value in a few second just after the appearance of the temperature drop which is characteristic to the crystallisation beginning.

For concentration of 0,046 %, we observed that the blocking was not immediate, however the flowing reaches finally a zero value.

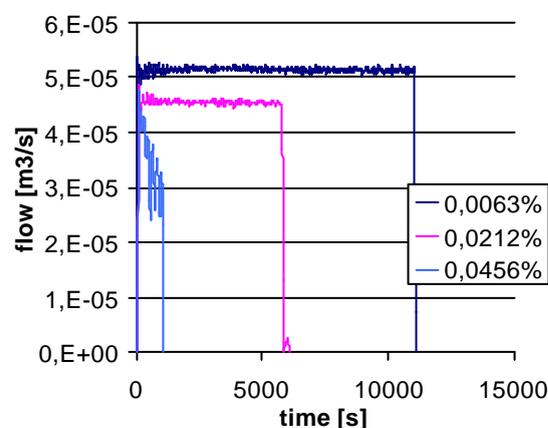


Figure 6

Flow rate as a function of time and additive mass concentration

For concentration of 0,09 % mass and 0,11 % mass, we can observe the efficiency of the additive on figure 7. In fact, the flow rate is not blocked but just decreases due to the increase of the slurry viscosity. The oscillations which appears on the plot are not artefact but are relevant to a physical phenomenon which is not explained at the moment but which disappears with time.

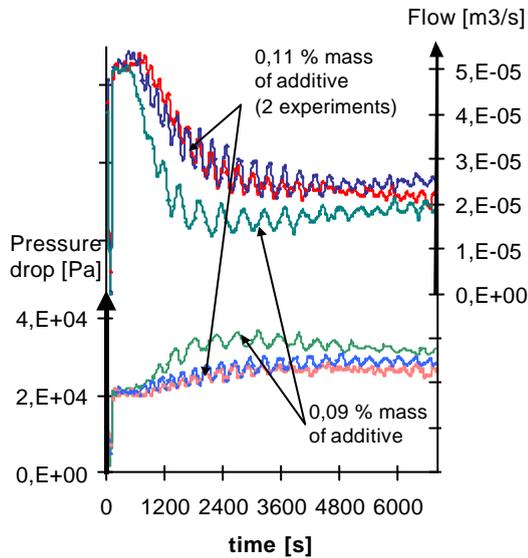


Figure 7

Flow rate  $Q$  and pressure drop  $\mathbf{DP}$  after the appearance of the first crystals at additive concentration of 0,09 % mass (1 experiment) and 0,11 % (2 experiments)

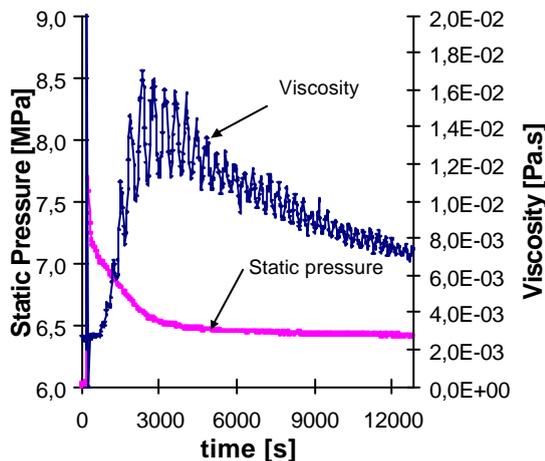


Figure 8

Viscosity and static pressure after the appearance of the first crystals at additive concentration of 0,09 % mass

On figure 7, we can observe that  $Q$  and  $\mathbf{DP}$  are very sensible to the additive concentration. For the higher concentration of 0,11% mass, the decrease of the flow rate is lower than at concentration of 0,09 % mass. The viscosity of the hydrate slurry is lower at additive concentration of 0,11 % than at additive concentration of 0,09 %. This observation is confirmed by the

pressure drop which is lower at concentration of 0,11 % than at additive concentration of 0,09 %.

Another point must be underlined. After the appearance of the first crystals, the flowing rate and pressure drop evolves smoothly, *i.e.* we don't observe a sudden decrease of the flow rate connected to a sudden increase of the pressure drop, but  $Q$  and  $\mathbf{DP}$  evolves during 30 min at additive concentration of 0,09% and 60 minutes at additive concentration of 0,11 %. Then, the flowing rate maintains constant for a while and then becomes to increases and the pressure drop becomes to decrease.

Supposing a Newtonian behaviour, all this variations could be directly connected to the suspension viscosity (which is showed on figure 8 for a additive concentration of 0,09 % and a long time of 3h30. On the same plot is showed the static pressure).

We observe that the viscosity increases during one hours which corresponds to the decrease of static pressure from 73 MPa to 6.5 MPa. After that, the static pressure maintains constant but the viscosity decreases.

The pressure depletion during the first time of the experiments shows that the total volume of solid hydrate increases. This explain qualitatively the increase of the viscosity but we can not point what is the crystallisation process which is at the origin of this evolution. In fact, the viscosity is intimately dependent on the evolution of the water droplets after the appearance of the crystal and how the crystal forms in the droplets. Some authors postulate that the crystals appears at the water/oil interface and rapidly forms a hard shell which growth from the external to the heart of the droplet. In such a case, the individual contribution of a hard sphere to the viscosity remains constant (as long as the external sphere size maintains constant). To explain the global dependence of the viscosity towards the hydrate conversion, we can postulate two hypothesis. The first one considers that the nucleation doesn't start at the same time in all droplets and so the global viscosity depends on the number of water droplets which have been converted in hydrate hard spheres. Secondly, the viscosity increase could be explained by agglomeration or aggregation which increases the mean diameter of the particles.

Concerning the viscosity decrease which takes place as the static pressure becomes constant, we can postulate that this phenomenon is linking to fragmentation which reduces the particle size.

## Conclusions

A fine interpretation of the crystallisation mechanisms at the origin of the evolution of the flow rate and pressure drop during hydrate crystallisation in an water in oil emulsion is not immediate. It needs to postulate more precisely a global crystallisation mechanisms taking into account the nucleation, growth, agglomeration or aggregation and finally

attrition of particles. It will inevitably lead to a complex set of equations with many parameters which could not be calibrated individually, but globally by their effect on the viscosity of the slurry.

We hope in the future to obtain a more precise analysis of the quality of the suspension by the way of a particle size distribution measurement which is under progress currently in our laboratory.

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