Investigation of Methane Hydrate Formation in a Recirculating Flow Loop: Modeling of the Kinetics and Tests of Efficiency of Chemical Additives on Hydrate Inhibition

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Résumé — **Étude de la formation de l'hydrate de méthane dans une conduite de recirculation : modélisation de la cinétique et tests d'efficacité d'additifs chimiques inhibiteurs d'hydrates de gaz** — Les hydrates de gaz des composés légers du gaz naturel se forment lorsque ceux-ci entrent en contact avec l'eau dans certaines conditions de température et de pression. Ces composés solides sont nuisibles pour les industries gazière et pétrolière car des bouchons solides peuvent obstruer les lignes de transport et les installations de traitement d'effluents pétroliers. Pour contrôler ces dépôts d'hydrates, on utilise fréquemment, comme inhibiteurs, le méthanol ou les glycols.

Aujourd'hui, les équilibres thermodynamiques des hydrates de gaz sont bien connus ; par contre, les cinétiques de formation et de croissance doivent être étudiées afin de mettre en évidence de nouveaux moyens de contrôle grâce à l'étude des mécanismes de formation des hydrates hors équilibre.

Le présent travail propose une étude de la cinétique de formation de l'hydrate de méthane dans une boucle de recirculation de laboratoire dans laquelle le mélange liquide, saturé de méthane, circule à une pression maximum de 75 bar. La pression constante au cours des expériences est maintenue par ajout de gaz frais.

Dans un premier temps, nous avons étudié les effets de la pression (35-75 bar), de la vitesse d'écoulement du liquide (0,5-3 m/s), de la rampe de refroidissement (2-15 °C/h) et de la quantité d'hydrocarbure présent dans la charge (0-96 %) sur les cinétiques de formation de l'hydrate.

Nous proposons ensuite une nouvelle méthode de prédiction, en premier lieu, des conditions thermodynamiques (pression et température) correspondant aux valeurs de vitesse de croissance maximum de l'hydrate, puis de ces vitesses de croissance maximum.

Nous avons obtenu un bon accord entre valeurs expérimentales et calculées. Enfin, nous avons évalué, en utilisant la procédure expérimentale décrite précédemment, l'efficacité de quelques inhibiteurs cinétiques et tensioactifs mis au point pour éviter, soit la nucléation, soit la croissance des cristaux et l'agglomératon de particules d'hydrates de méthane.

Mots-clés : hydrate de méthane, inhibiteur cinétique, additif, hydrate de gaz, conduite de transport.

Abstract — Investigation of Methane Hydrate Formation in a Recirculating Flow Loop: Modeling of the Kinetics and Tests of Efficiency of Chemical Additives on Hydrate Inhibition — *Gas hydrates can be formed when light gases, such as the components of natural gas, come into contact with water under particular conditions of temperature and pressure. These solid compounds give rise to problems in natural gas and oil industry because they can plug pipelines and process equipment. To prevent hydrate formation methanol and glycols are commonly and extensively used as inhibitors.*

Today, the thermodynamic equilibria of hydrate formation are well known, but the kinetics of gas hydrate formation and growth has to be studied in order to find means of controlling these processes and to explore the mechanisms for hydrate formation that follows non equilibrium laws.

The present work deals with the kinetics of methane hydrate formation studied in a laboratory loop where the liquid blend saturated with methane is circulated up to a pressure of 75 bar. Pressure is maintained at a constant value during experimental runs by means of methane gas make-up.

First the effects of pressure (35-75 bar), liquid velocity (0.5-3 m/s), liquid cooling temperature ramp (2-15°C/h), and liquid hydrocarbon amount (0-96%), on hydrate formation kinetics are investigated.

Then a new method is proposed to predict firstly the thermodynamic conditions (pressure and temperature) at the maximum values of the growth rate of methane hydrate and secondly the methane hydrate growth rate.

A good agreement is found between calculated and experimental data. Finally the evaluation of the efficiency of some kinetic additives and some surfactants developed to avoid either nucleation or crystal growth and agglomeration of methane hydrates is tested based on the proposed experimental procedure.

Keywords: methane hydrate, gas hydrate, kinetic inhibitor, additives, transportation lines.

NOTATION

a, b	constants in Equation (6)
c	constant in Equation (7)
$F(t_k)$	volumetric consumption rate at the *kth* data acquisition (normal conditions) (m^3/s)
f_{eq}	three phase equilibrium fugacity at the experimental pressure (bar)
K, K'	constants in Equations (6) and (7) respectively
$N_G(t_i)$	number of moles of methane consumed (mol)
P	experimental pressure (bar)
$n_{H_2O}(t_k)$	water conversion rate (%)
R	universal gas constant (8.31 J/mol)
r	maximum growth rate formation (mol/s)
T	experimental temperature at which the hydrate growth is maximum (K)
T_{eq}	hydrate formation equilibrium temperature at the experimental pressure (K)
t_k	time at the *kth* acquisition (s)
$V_{H_2O}(t_k)$	free water volume in the loop at the *kth* acquisition (m^3)
u	liquid circulating flow (m/s).

Subscripts

i, k	*ith* or *kth* acquisition
0	normal conditions.

INTRODUCTION

Gas hydrates are clathrate crystalline compounds looking like ice or snow that may form when light gases, such as the components of natural gas, come into contact with water under particular conditions of pressure and temperature.

In 1934, Hammerschmidt determined that the plugging of natural gas pipelines was not due to ice formation but to formation of clathrate hydrates of natural gas. This discovery was the determining factor in causing a more pragmatic interest from oil and gas companies

A good deal of work has been devoted to the thermo-dynamics of clathrate hydrates of natural gases, in order to find prevention methods (Van Der Waals and Platteuw, 1959; Munck *et al.,* 1988; Sloan, 1998; Bishnoi and Dholabhai, 1993; Chen and Guo, 1996). Industry has developed several techniques to prevent the formation of gas hydrates. Natural gas can be dried; gas can be heated to a temperature above the equilibrium hydrate formation temperature at a given pressure; the pressure of the gas can be reduced to a pressure below the equilibrium hydrate formation pressure at a given temperature and the partial phase diagram of the gas-water system in the hydrating region can be altered by injecting the so-called thermo-dynamic inhibitors such as methanol, glycols, or electrolytes (Englezos, 1993). Electrolyte injection is not a preferred option because aqueous salt solutions are corrosive. Methanol and glycol injection are used extensively to act as antifreeze-like agents, but the high cost of these conventional

inhibitors in offshore development and the onshore processing facilities stimulate development of new methods for hydrate control (Béhar *et al.*, 1994; Corrigan *et al.*, 1995; Argo *et al.*, 1997). This is the reason why the kinetics of gas hydrate formation and growth are now studied in order to find means of controlling these processes. Major research contributions in this field have been published in the two last symposia on natural gas hydrates (Sloan *et al.,* 1994 and Progep and Monfort, 1996).

The kinetics of hydrate growth has been modeled by numerous authors who have measured gas consumption rate during hydrate formation in batch agitated reactors. This rate has been related to the main crystallization parameters (subcooling, pressure and liquid/gas interfacial area: Pangborn and Bardhun (1970), Smirnov (1987), Vysniauskas and Bishnoi (1983, 1985), Monfort and Nzihou (1994) have proposed empirical or semi-empirical models.

Very little experimental work has been performed by oil and gas research companies on the evaluation of gas hydrate formation in flow conditions in a long pipe line. What has been done is to try to simulate these conditions in a laboratory loop and study the hydrate formation conditions (Dholabhai *et al.*, 1991 and 1992; Urdahl *et al.,* 1995; Gaillard, 1996) or in a rotating autoclave (Lippmann *et al.*, 1996).

In this article, a short description of the experimental apparatus and procedure is given in a first step. It is followed by a presentation of a complete experimental and theoritical study of methane hydrate kinetics on macroscale viewpoint. The necessity of a new model for hydrate formation taking into account the quantification of nucleation, growth and agglomeration rates of the hydrate formation is then recommended. The evaluation of the efficiency of some kinetic additives and some surfactants patented to avoid either nucleation or crystal growth and agglomeration of methane hydrate particles is finally proposed.

1 EXPERIMENT

1.1 Apparatus

A simplified flowsheet of the hydrate loop is given in Figure 1. The equipment is essentially composed of a pipe and a pump. The pipe has an inner diameter of 1 inch ($2.54 \cdot 10^{-2}$ m) and a length of 22 m. The pump is of the Moineau type. Ethanol is used as a refrigeration fluid in the external jacket of the pipe; it is cooled with liquid nitrogen in a heat exchanger. The adequate amounts of liquid hydrocarbons and distilled water are stored in a 90 l tank. Temperatures of hydrate fluid and ethanol are measured with platinum resistance thermometers, pressure with transducers. The latter is maintained at a constant value during experimental runs by means of regulator and gas make-up. There is also a differential pressure transmitter between the inlet and the outlet of the Moineau pump. During the whole period of an experiment, mass-flowrate is controlled by means of a Coriolis type flow meter. All parameters and data are controlled and collected via a computer system every 12 s. The accuracy of the pressure and temperature measurements is estimated to be +/– 0.05 bar and +/– 0.5 K respectively.
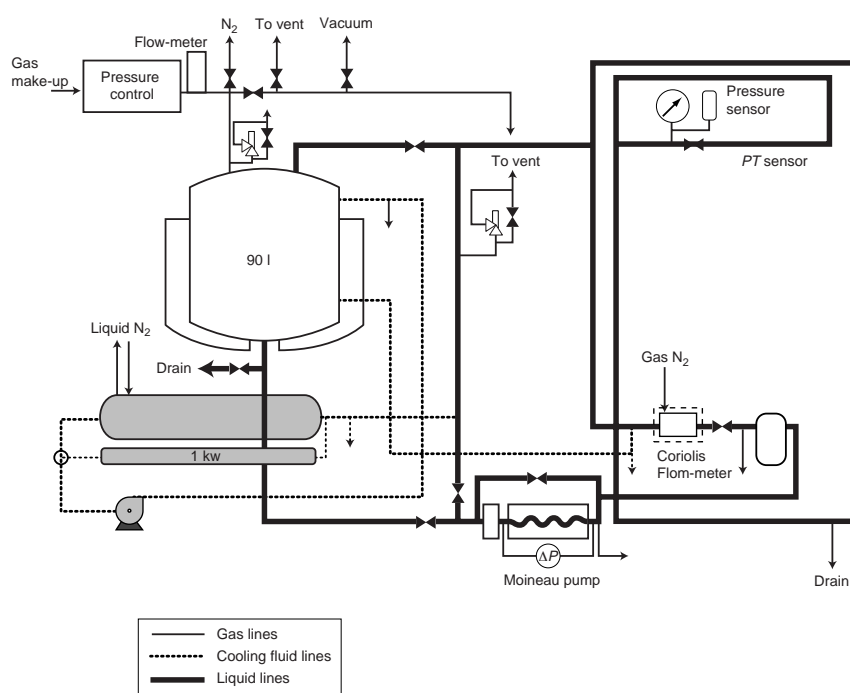

Figure 1

Experimental setup.

1.2 Experimental Procedure

The kinetics of methane hydrate formation is studied at pressures between 35 and 75 bar. Liquid hydrocarbons, whose properties appear in Table 1 and distilled water were introduced in known amounts into the 90 l tank. Gas-liquid equilibrium and stabilized operating conditions were reached by pumping the liquid blend at the test pressure through both the loop and tank for several hours at a liquid velocity of 3 m/s and at a temperature of 20°C. The tank was then set off-stream and the methane saturated liquid phase was recirculated through the loop only, at the chosen liquid velocity which could vary between 0.5 and 3 m/s. The loop temperature was decreased down to 3°C, at a given cooling rate which could vary between 2°C/h and 15°C/h. This temperature was then kept constant during the whole period of the run.

TABLE 1

Composition and physical properties of hydrocarbon phases

Hydrocarbon phase carbon atoms	Frigg condensate wt%	Froy crude oil mol%
C_1	0.00	0.000
C_2	0.04	0.107
C_3	0.02	0.682
C_4	0.06	1.551
C_5	0.05	3.012
C_6	0.72	8.505
C_7	1.72	11.698
C_8	2.87	9.770
C_9	5.70	7.223
C_{10}	12.42	4.291
C_{11}	14.37	$C_{11}+$ 53.161
C_{12}	15.80	
C_{13}	13.10	
C_{14}	11.07	
C_{15}	8.76	
C_{16}	5.55	
C_{17}	3.28	
C_{18}	2.38	
C_{19}	1.27	
$C_{20}+$	0.82	

Properties	Frigg condensate	Froy oil	Vic Bilh crude oil
Volumic mass$_{15°C}$, kg/m³	820	836	890
Normal HC $C_{10}+$, wt%		12	5
Resin, wt%		15	20
Asphaltenes (insoluble C_5)		0.5	5

At the end of each experiment, the loop was heated up to 25°C and maintained at this temperature for several hours to ensure total hydrate dissociation.

2 EXPERIMENTAL RESULTS AND DISCUSSION

2.1 Kinetics Parameters

2.1.1 Methane Consumption

Make-up gas is added to the loop in order to keep the pressure constant when temperature decreases and hydrate forms. So consumption rates of methane are measured all along the experiment, and the number of moles of methane consumed at the *ith* data acquisition is calculated with the following equation:

$$N_G(t_i) = \frac{P_0}{RT_0} \sum_{k=1,i} \frac{\left[F(t_k) + F(t_{k-1}) \right] (t_k - t_{k-1})}{2} \quad (1)$$

where:

P_0 and T_0 are the normal pressure and temperature;

R is the universal gas constant;

t_k is the time at the *kth* acquisition; t_0 is the beginning of the experiment;

$F(t_k)$ is the volumetric consumption rate of methane at the *kth* data acquisition at the normal pressure and temperature conditions.

By using gas consumption data corresponding to temperature higher than the equilibrium temperature, the saturation of the liquid can be evaluated. Then the circulating fluid is cooled and the gas consumption due only to the formation and growth of methane hydrate is measured until the preset final temperature has been reached.

2.1.2 Thermodynamic Conditions at which Methane Hydrate Growth Rate is Maximum

When dealing with hydrate kinetics, it is common to use the similarity with the crystallization process by splitting the hydrate formation process in two separate steps. The first involves the formation of hydrate nuclei where the gas consumption is not very important. The second step is the actual growth, including eventually agglomeration of hydrate particles, which begins after stable nuclei have been formed. The rate is expressed through the rate with which the amount of methane is converted to hydrate; in this case, the gas consumption increases very strongly. There are two ways to describe the thermodynamic conditions at this particular point, either by the subcooling ΔT or by the driving force Δf defined respectively as:

$$\Delta T = T_{eq} - T \quad (2)$$

where:

T_{eq} is the hydrate formation equilibrium temperature at the experimental pressure;

T is the temperature at which methane hydrate growth rate is maximum;

and:
$$\Delta f = f_{eq} - f \quad (3)$$

where:

f_{eq} is the three-phase equilibrium fugacity at the experimental pressure;

f is the methane fugacity at the experimental pressure and at the temperature at which methane hydrate growth rate is maximum.

Methane fugacities are calculated with the Peng-Robinson Equation of State (Peng-Robinson, 1976).

2.1.3 Maximum Growth Rate

The maximum growth rate corresponds to the maximum slope of the gas consumption curve and is only due to hydrate formation and is obtained from the avancement curve.

2.1.4 Water Consumption or Water Conversion Rate

The stoichiometric equation of methane hydrate formation is assumed to be:

$$CH_4 + 5.75 \ H_2O \rightarrow CH_4, 5.75 \ H_2O \qquad (4)$$
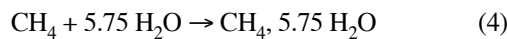
The water conversion rate is obtained with:

$$n_{H_2O}(t_k) = \frac{V_{H_2O}(t_0) - V_{H_2O}(t_k)}{V_{H_2O}(t_0)} \cdot 100 \qquad (5)$$

t_k is the time at the *kth* acquisition;

t_0 is the beginning of the experiment;

$V_{H_2O}(t_k)$ is the free water volume in the loop at the *kth* acquisition.

2.2 Modeling of the Hydrate Kinetics

Results from a preliminary study of the influence of the operating conditions such as pressure, liquid flow velocity, cooling temperature ramping and liquid hydrocarbon composition are shown in Table 2. The following trends have been observed:

– Gas hydrates can form in saturated liquid without any free gas. So, plugging can occur in natural gas pipelines, but also in liquid hydrocarbon pipelines where there is always a variable amount of dissolved gas which can form hydrate.

This effect is still not well estimated in industry but this is the reason why separating liquid hydrocarbon phase and gas phase is not sufficient to prevent hydrate formation.

– Mass transport of the dissolved methane molecules from the hydrocarbon phase to the water phase is the rate determining step in the overall hydrate formation process as Skovborg and Rasmussen (1994), and Herri (1996) thought. Indeed, as soon as a variation of the dissolved methane in contact with water droplets is present, either by a pressure effect that modifies the amount of dissolved gas or by mixing effects that change the interfacial area of water droplets we observe a direct consequence on the values of the subcooling to which the growth rate is "explosive" and of the observed maximum growth rate.

TABLE 2

Influence of the experimental parameters

Experimental parameters	Kinetic parameters			
	ΔT or Δf Maximum growth rate	Dissolved gas volume	Maximum growth rate	Water conversion rate
$P \uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
$u \uparrow$	$\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$
$\Delta T/\Delta t$	$\rightarrow$	$\rightarrow$	$\rightarrow$	$\rightarrow$
Liquid hydrocarbon amount	$\uparrow$	$\rightarrow$	$\uparrow$	$\uparrow$

No change $\rightarrow$ Increase $\uparrow$ Decrease $\downarrow$

The semi-batch empirical models mentioned above are not well adapted to the specific flowing conditions in a hydrate loop (Gaillard, 1996), a new semi-empirical model is proposed as follows.

2.2.1 The Subcooling at Maximum Growth Rate

Makogon (1978) has reported that the methane hydrate nuclei rate of formation increases with the subcooling ΔT and it presents a maximum value at a $\Delta T = 2$ K. We have also

TABLE 3

Parameters for the subcooling at maximum growth rate

Parameter	Pure water	Water and Frigg condensate	Water and Froy crude oil at constant P	Water, Frigg condensate and crude oil from Vic Bilh at constant P
K	0.32	0.14		
KP^b			3.06	4.22
a	–0.25	–0.045	–0.11	–0.35
b	0.31	0.54	—	—
*R^2	0.9272	0.9287	0.9813	0.8924

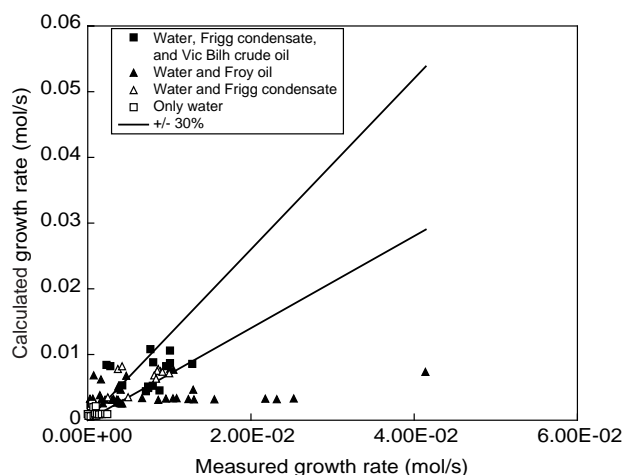* R^2 is the non-linear regression coefficient.

Figure 2

Comparaison between calculated and experimental subcooling ΔT for various water-hydrocarbons-gas systems.
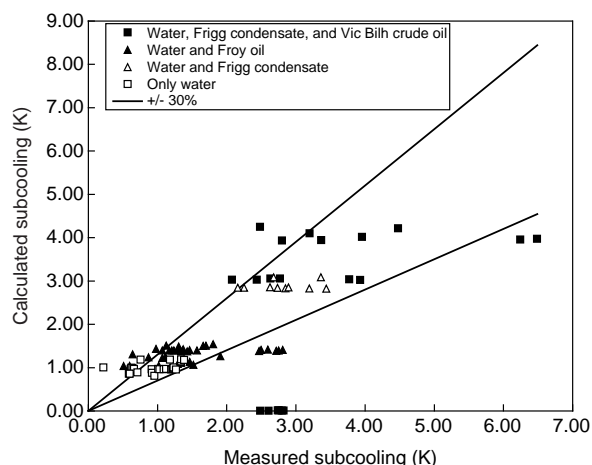

Figure 3

Comparaison between calculated and experimental maximum growth rate for various water-hydrocarbons-gas systems.

observed that the methane hydrate growth presents a maximum value that depends on the following parameters: the nature of the liquid phase, either pure water or water/hydrocarbon condensate mixtures, on the liquid circulating flow and pressure. Therefore from this experimental information we represent the particular subcooling ΔT at the maximum methane hydrate growth value with the equation:

$$\Delta T = K\, u^a\, P^b \qquad (6)$$

where the constants a, b and K appear in Table 3.

To test this model experimental ΔT are compared with predictions of Equation (6) as shown in Figure 2. For the systems studied it appears that the proposed equation reflects fairly well the influence of the operating parameters.

2.2.2 The Maximum Growth Rate

Considering the observed effects of both flow velocity in the loop and the strongly correlated temperature-pressure-subcooling variables on the hydrate formation, the proposed equation is:

$$r = K'\, u^c \exp(-\Delta E_A/RT) \qquad (7)$$

we have used the following equation:

$$\ln r = \frac{12774.8}{T} + \ln K' + c \ln u \qquad (8)$$

where the fitted constants K' and c appear in Table 4, ΔE_A the apparent energy of formation is taken from Vysniauskas *et al.* (1983) and $T = T_{eq} - \Delta T$ (at maximum consumption rate).

The comparison between calculated and experimental growth rates is shown in Figure 3 where it appears that, apart from the particular case of the water/Froy oil, this new equation model can represent the growth rate of the methane hydrate formation in a loop with good agreement within the maximum limits –30/+30% of absolute deviation. The discrepancy observed in the particular case of the mixture water/Froy oil can be explained by the presence of natural dispersant agents in specific oils or crudes. These additives may have a natural effect on the growing and agglomeration of hydrate crystals (Fadnes, 1996).

We postulate that it is possible to predict the maximum growing rates of the methane hydrate for a specific water/oil system once the fitted parameter K, a and b have been determined.

TABLE 4

Parameters for the maximum growth rate model

Parameter	Pure water	Water and Frigg condensate	Water and Froy crude oil at constant P	Water, Frigg condensate and crude oil from Vic Bilh at constant P
K'	$1.35 \cdot 10^{-23}$	$6.15 \cdot 10^{-23}$	$8.08 \cdot 10^{-23}$	$8.98 \cdot 10^{-23}$
c	0.45	0.16	0.95	0.86
*R^2	0.9998	0.9952	0.9999	0.9998

* R^2 is the non-linear regression coefficient.

3 INHIBITION STUDY WITH CHEMICAL ADDITIVES

The pilot validation of new chemical agents especially in field flow conditions (Argo *et al.,* 1997; Palermo *et al.,* 1997) can be performed in a test loop especially designed to reproduce the various operation modes of multiphase flow. The experimental set-up we have described in this paper features such possibilities as we can see in the next section.

In order to test the efficiency of various additive compounds we have selected additional criteria related to the pressure drop between inlet and outlet of the Moineau pump, and pressure safety limit of the equipment. We will qualify an additive compound as being inefficient if one of these operating incidents occurs:

– The pressure drop between inlet and outlet of the Moineau pump increases up to the safety threshold value of 5 bar within 24 h, this means that hydrates are blocking the recirculating tubings.

– The total pressure in the loop approaches the safety threshold value of 80 bar within 24 h, this reveals that heat exchange between the recirculating fluid and the cooling jacket is slowing down due to hydrate deposit on the walls of the tubing. This means inefficient transport of particles.

– The pressure drop between inlet and outlet of the Moineau pump decreases abruptly during hydrate growing: this phenomenon is probably due to the grinding of too large hydrate particles (diameter's ≈ 8 mm) inside the pump.

The chemical additives properties with experimental results categorised in terms of the crystallisation steps and anomalies of operating conditions are given in Table 5.

3.1 Effects of High Molecular Weight Chemicals: Kinetic Inhibitors

These chemicals delay hydrate nucleation or crystal growth (Englezos, 1996), they are presented today as future low-dosage and environment-friendly hydrate inhibitors.

3.1.1 Poly(N-Vinylpyrrolidone) (PVP)

One typical test result from the data acquisition system is shown in Figure 4. Peculiarities for this concentration test are as follows:

– Increase of subcooling corresponding to the consumption peak, in some cases it does not appear thus inducing a low and constant growing rate.

– Constant dissolved volume of methane per unit liquid volume and °C.

– Decrease of formation rate either with or without consumption peak, this rate is always smaller when PVP is present in the liquid phase.

– Decrease of water conversion rate.

The two operating incidents that are observed show a tendency to hydrate clogging of the circulating pump.

The activity of this kinetic inhibitor is demonstrated: both nucleation and growing steps are strongly prevented but, as soon as this prevention is lost, the hydrate agglomeration rate
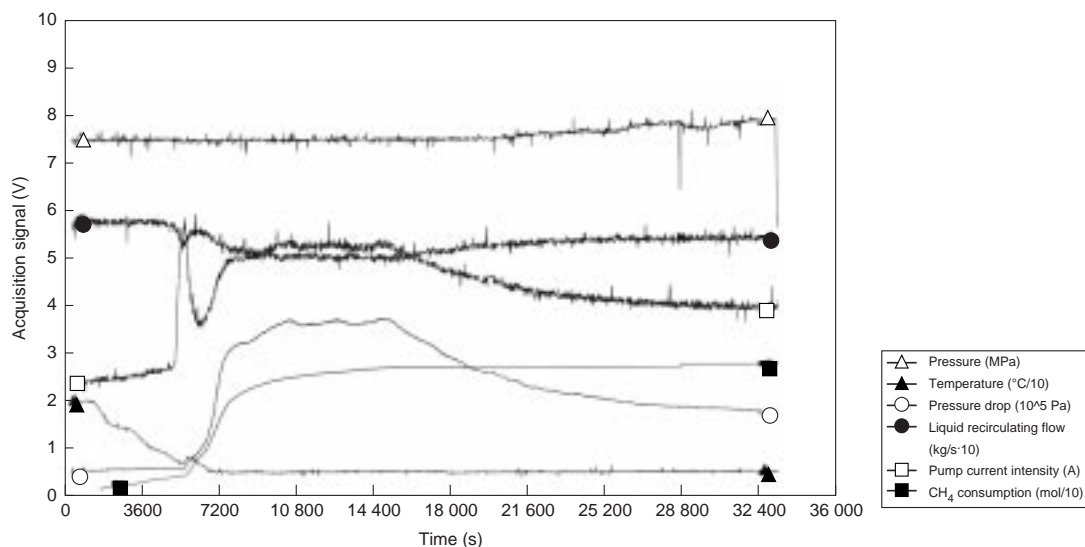

Figure 4

On line experimental results for a water-Frigg oil-gas mixture. water content 20/80 V/V, PVP concentration 0.5 w%, *u* = 1.22 m/s, temperature ramp cooling: 10°C/h.

TABLE 5

Effects of kinetic additives on the crystallization steps, $P = 76$ bar, $U = 2$ m/s, cooling temperature ramp: 10°C/hr

Tested compounds	Liquid phases	Water content V/V	Kinetic effects				Additional effects
			Methane solubilization	Nucleation	Growth	Agglomeration	
PVP	Water/Frigg condensate	20/80	No effect	Inhibition	Inhibition	↑	Pressure ↑ up to Threshold limit
Compound A	Water/Frigg condensate	20/80 10/90 05/95	↓	Inhibition	Inhibition	↑	I_{pump} ↑, μ ↑
Berol 26	Water/Frigg condensate	20/80	No effect	Inhibition	Uncertain	Uncertain	No incident 9-10 h
Natural active agent	Water/Froy oil	10/90 20/80 30/70	↑	Inhibition	Inhibition	Inhibition	I_{pump} ↑ Transportability 4 h

Increase ↑; Decrease ↓

is strongly increased; this would readily result in the blockage of a real transportation pipe. In some early agitated reactor experiments Herri (1996) has observed similar activity of the PVP: decrease of the secondary nucleation rate and agglomeration effect that increased with the polymer concentration.

Similar results are obtained with a commercial patented inhibitor (compound A) which is a blend of several copolymers, better performances are observed with higher subcooling or slower growing rates. However as soon as hydrates are formed the viscosity of the recirculating liquid is abruptly modified. The use of these additives in commercial deployment could be limited to a narrow security domain that corresponds to nuclei whose size is lower than the critical one. Obviously this condition is highly unlikely in a pipe line where the solid impurities can affect nucleation behavior very drastically.

3.2 Surface Active Agents or Anti-Agglomerators

These chemicals modify the hydrate crystals (Kalogerakis *et al.*, 1996) and prevent their agglomeration.

3.2.1 Berol 26

A non ionic surfactant, Berol 26 (nonylphenolEO) that has anti-agglomeration properties (Urdhahl *et al.*, 1995) has been tested in similar experimental conditions. Test results are shown in Table 5. We could conclude that nucleation is delayed, depending on the additive concentration, but no trend can be drawn about growth and agglomeration rates. We could observe that it was possible to recirculate the hydrate-liquid mixture up to 10 h before attaining the threshold safety pressure limit. Thus, such additive with a

minimum 1% weight concentration shows potential capability to allow a safe tranport of hydrates without plugging.

3.2.2 Natural Active Agents

Oil producers have observed that specific oils could be easily transported in presence of hydrate crystals without blocking or lowering production in transport facilities. It has been hypothesized that natural anti-agglomeration agents are present in the oil, such as resins or asphaltenes, that could have inhibiting properties (Fadnes, 1996). Such a behaviour has been encountered on the oil from the Froy field in North Sea. A test result appear in Figure 5 and experimental observations are shown in Table 5. It seems therefore that this oil contains natural inhibiting agents of nucleation and crystal growth. But in counter part, the dissolution of methane is increased and apparently an anti-agglomeration effect exists that causes the formation of a larger quantity of hydrate particles.

3.3 Discussion

The case study on two kinetic inhibitors has shown the dual behavior of these chemicals that can favourably inhibit nucleation and enhance agglomeration of particles. As a consequence, the number of hydrate particles decrease and they form a deposit that will necessarily lead to a plugging of a real transportation line. A quick variation of the viscosity of the aqueous phase has also been observed which could lead to a slowing down of the facilities' production. The use of such compounds must therefore be limited to a domain where nuclei sizes are smaller than the critical size from which they grow.
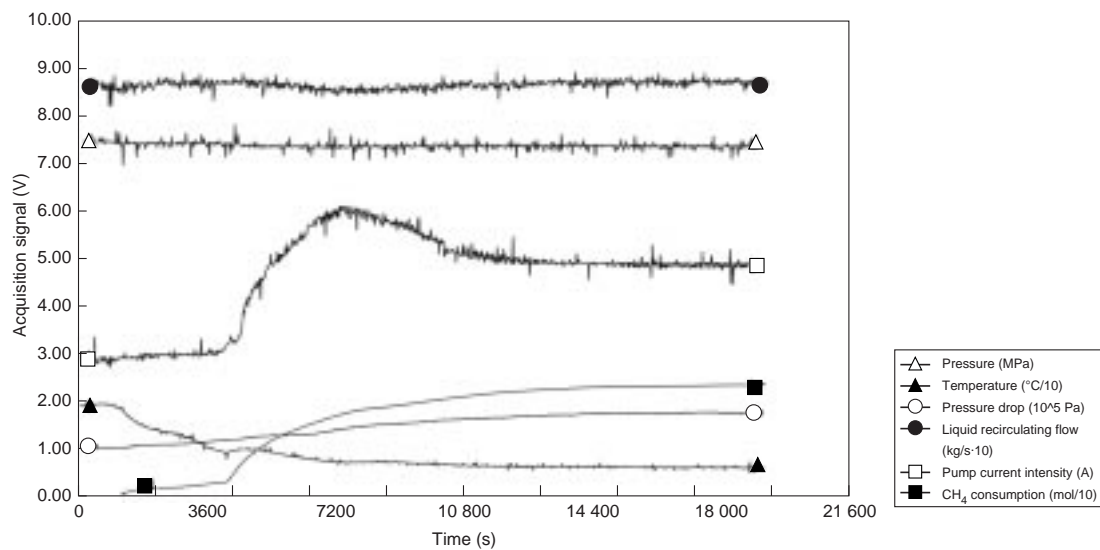
Figure 5

On line experimental results for a water-Froy oil-gas mixture, water content 20/80 V/V, u = 2.03 m/s, temperature ramp cooling: 10°C/h.

On the other hand, surface active additives that have been studied prevent agglomeration whereas they lead to a greater quantity of hydrates. Most of the time they have no effect on the solubilization of methane: thus it is supposed that they have no effect on the diffusion of methane towards the fine water droplets in suspension.

We have been able to observe that some of these agents could allow the transportation of hydrate particles during several hours without hydrate deposits. Nethertheless, the main problem would be to find an economical downstream process for both hydrate dissociation and emulsion breaking.

The observation made with Froy oil and other similar fluids showed potential interest of the positive effect of the natural surfactants on the transportation of solid hydrates without plugging. It is certainly worth studying, in greater depth, their behavior in order to take advantage of it in view of minimizing the cost of chemical injection.

CONCLUSION

We have therefore developed a new correlation, that once kinetic parameters for a fixed composition of the hydrocarbon phase known, enables firstly, to evaluate the temperature for which the growth rate of hydrate is maximum and secondly, to estimate the growth rate. The particular conditions of applicability of these equations are as follows:

– Pressure varies from 35 to 75 bar.

– Liquid recirculating rates vary from 0.5 to 3 m/s, the corresponding Reynolds numbers are between 1100 and 9700, which correspond respectively to laminar and turbulent flow in the loop, respectively.

– The liquid cooling temperature ramp varies from 2 to 15°C/h.

– The hydrocarbon content in the liquid phase varies from 0 to 96% in volume.

This mathematical tool could be useful for testing the efficiency of additives for maximum growth rate inhibition, it is inoperative for estimating the rate profile of the hydrating reaction when numerous microscopic crystallization phenomena take place. In the latter it is necessary to use a crystallization approach based on the measurement of crystal size distribution and resolution of population balance equations (Gaillard *et al.,* 1996).

This study has shown that the tested kinetic inhibitors and dispersant agents could be effective for the transport of multiphase streams during a short period without plugging. Nethertheless, work must be done on their formulation: analytical identification of their molecular activity as the study of their working mechanisms along the dowstream process are our present research goals.

ACKNOWLEDGMENTS

REFERENCES

Argo, C.B., Blain, R.A., Osborne, C.G. and Priestley, I.D. (1997) Commercial Deployment of Low Dosage Hydrate Inhibitors in a Southern North Sea 69 Kilometer Wet-Gas Subsea Pipeline. *SPE Paper* No. 37255, Houston, Texas.

Béhar, E., Delion, A.S., Herri, J.M., Sugier, A. and Thomas, M. (1994) Le problème des hydrates dans le contexte de la production et du transport polyphasiques des pétroles bruts et des gaz naturels. Première partie : Physico-chimie de la formation et de la dissociation des hydrates. *Revue de l'Institut français du pétrole,* **49,** 3, 247-263.

Bishnoi, P. and Dholabhai, P.D. (1993) Experimental Study on Propane Hydrate Equilibrium Conditions in Aqueous Electrolytes Solutions. *Fluid Phase Equilibria,* 83, 455-462.

Chen, G.J. and Guo, T.M. (1996) Thermodynamic Modeling of Natural Gas Hydrates Based on New Formation Mechanism. *Proceedings, 2nd International Conference on Natural Gas Hydrates,* Toulouse, 33-42.

Corrigan, A., Duncum, S.N., Edwards, A.R. and Osborne, C.G. (1995) Trials of Threshold Hydrate Inhibitors in the Ravenspurn to Cleeton Line. *SPE Paper* No. 30696.

Dholabhai, P.D., Kalogerakis, N. and Bisnoi, P.R. (1991) *SPE Paper* No. 22829 presented at SPE 66th Annual Technical Conference, Dallas, United States, 6-9 October.

Dholabhai, P.D., Kalogerakis, N. and Bisnoi, P.R. (1992) *CIM Paper* No. 92-83 presented at the CIM, Calgary, June 7-10.

Englezos, P. (1993) Reviews, Clathrate Hydrates. *Industrial Engineering Chemistry Research,* 32, 1251-1274.

Fadnes, F.H. (1996) Natural Hydrate Inhibiting Components in Crude Oils. *Fluid Phase Equilibria,* 117, 186-192.

Gaillard, C. (1996) Cinétique de formation de l'hydrate de méthane dans une boucle de laboratoire. *Thesis,* Institut national polytechnique de Toulouse, France.

Gaillard, C., Monfort, J.P. and Peytavy, J.L. (1996) Formation and Growth Kinetic of Natural Gas Hydrate. *Proceedings, 2nd International Conference on Natural Gas Hydrates,* Toulouse, France, 183-190.

Kalogerakis, N., Jamaluddin, A.K.M., Dholabhai, P.D. and Bishnoi, P.R. (1993) Effects of Surfactants on Hydrate Formation Kinetics. *SPE Paper* No. 25188, New Orleans, LA, United States, March 2-5.

Hammerschmidt, E.G. (1934) Formation of Gas Hydrates in Natural Gas Transmission Lines. *Industrial Engineering Chemistry,* **26**, 8, 851-855.

Herri, J.M. (1996) Étude de la formation de l'hydrate de méthane par turbidimétrie *in situ. Thesis,* Université Pierre et Marie Curie, Paris VI, France,

Lippmann, D., Kessel, D. and Rahimian, T. (1995) Gas Hydrate Nucleation and Growth Kinetics in Multiphase Transportation Systems. *Proceedings, 5th International Offshore and Polar Engineering Conference,* The Hague, The Netherlands, June 11-16.

Makogon, Y.F. (1981) *Hydrates of Natural Gas,* Penn Well Book, Tulsa, United States.

Monfort, J.P. and Nzihou, A. (1994) Cyclopropane Hydrate Growth Kinetic Measurements in a Semi Batch Reactor. *Proceedings, 44th Canadian Chemical Engineering Conference Chimique,* Calgary, Canada, 2-6 October, 603-604.

Munck, J., Skjold-Jorgensen and S., Rasmussen, P. (1988) Computation of the Formation of Gas Hydrates. *Chemical Engineering Science,* **43**, 10, 2661-2674.

Palermo, T., Sinquin, A., Dhulesia, H. and Fourest, J.M. (1997) Pilot Loop Tests of New Additives Preventing Hydrate Plugs Formation. *BHR Group 1997, Multiphase'97,* Cannes, France, June 1997.

Pangorn, J.B. and Bardhun, A.J. (1970) The Kinetics of Methylbromide Hydrate Formation. *Desalination,* 8, 35-68.

Progep and Monfort, J.P. (1996) *Proceedings of the 2nd International Conference on Natural Gas Hydrates,* Toulouse, France.

Skovborg, P. and Rasmussen, P. (1994) A Mass Transport Limited Model for the Growth of Methane and Ethane Gas Hydrates. *Chemical Engineering Science,* **49**, 8, 1131-1143.

Sloan, E.D. (1998) *Clathrate Hydrates of Natural Gases,* Marcel Dekker, New York.

Sloan, E.D., Happel, J. and Hnatow, M.A., Eds (1994) (First) International Conference on Natural gas Hydrate. *Annals of New York Academy of Sciences,* 715.

Smirnov, L.F. (1987) Kinetics of Gas Hydrate Formation. *Theoritical Foundation of Chemical Engineering,* Plenum Publishing Company, 465-474.

Urdhal, O., Lund, A., Mok, P. and Nilsen, T.W. (1995) Inhibition of Gas Hydrate: Formation by Means of Chemical Additives, Part 1. *Chemical Engineering Science,* **50**, 5, 863-870.

Van der Waals, J.H. and Platteeuw, J.C. (1959) Clathrates Solutions. *Advanced Chemical Physics,* 2, 1-57.

Vysniauskas, A. and Bishnoi, P.R. (1983) Kinetic Study of Methane Hydrate Formation. *Chemical Engineering Science,* **38**, 7, 1061-1072.

Vysniauskas, A. and Bishnoi, P.R. (1985) A Kinetic of Ethane Hydrate Formation. *Chemical Engineering Science,* **40**, 2, 299-303.