

A model for estimating flow assurance of hydrate slurry in pipelines

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Abstract

The problem of hydrate blockage of pipelines in offshore production is becoming ever-increasing severe because oil fields in ever-increasing unusual environments have been brought in production. HCFC-141b and THF were selected as the substitutes to study the flow assurance of the hydrates in pipelines. There are critical hydrate volume concentrations for these two slurries. Hydrate slurries behave like Bingham fluids and have high agglomerating tendency when the hydrate volume concentrations are larger than the critical ones. Based on rheological behaviors of these two hydrates, a non-dimensional parameter is proposed through studying the driving forces of agglomeration among hydrate particles, which shows the agglomerating probability of hydrate particles in pipeline and can be used to judge the safety of the pipeline. Moreover, a safe model to judge the safely flow hydrate slurries was presented and verified with the experimental data, which demonstrates that the model is effective to judge whether the pipeline can be run safely or not.

Key words

hydrate slurry; flow assurance; rheological behavior; safe model

1. Introduction

Over the past decade, hydrates have become the number one issue in flow assurance, especial in offshore condensate pipeline running at high pressure and relative low temperature [1,2]. However, the limitation of traditional methods by preventing the formation of hydrates is obviously ever-increasing in costs [3,4]. So there is an interest in developing technology that hydrates can be transported as a slurry, while avoiding plugs [5–7].

Understanding the formation and flow characters of hydrates in pipeline is necessary to prevent the formation of plugs and let pipeline systems work safely [8]. Unfortunately, little is known about the phenomena involved in the hydrate plug formation [9]. While many works were devoted to the study of hydrate structures as well as rheological behaviors of some kinds of slurries in pipeline and several authors have studied the formation of pipeline hydrates and hydrates plugs with low-pressure flow system, such as CH₃CCl₂F (HCFC-141b) hydrate, tetrahydrofuran (THF) hydrate, TBAB hydrate as well as R11 hydrate, there are short of systematic researches on hydrates morphology and blockage in pipeline [10–13].

In this paper, HCFC-141b and THF were chosen as the substitutes, since HCFC-141b can not unite with water while THF can mix with water very well, to study the flow assurance of hydrate slurry on the flow loop. And both of them can form hydrate of structure II at atmosphere pressure. The detailed flow behaviors of HCFC-141b and THF were reported in Refs. [14,15], respectively. In this work the flow assurance was presented in detail and a model to judge the flow assurance based on the flow behaviors of hydrate slurries was deduced.

2. Experimental

Experiments on flow characters of hydrate slurry were performed on the flow loop in Guangzhou Institute of Energy Conversion (Giec, China). This flow loop (Figure 1), which is a two pass loop consisting of a 42.0 mm diameter pipe, 30.0 m long, was specially built to perform experiments on hydrate slurry in low pressure (no more than 1.5 MPa). The flow loop is enclosed in a temperature chamber (4.83×3.30×2.55 m), which can keep a stable and constant temperature environment with a temperature ranging from –40 °C to 80 °C. More details about the flow loop can be found in Ref. [14].

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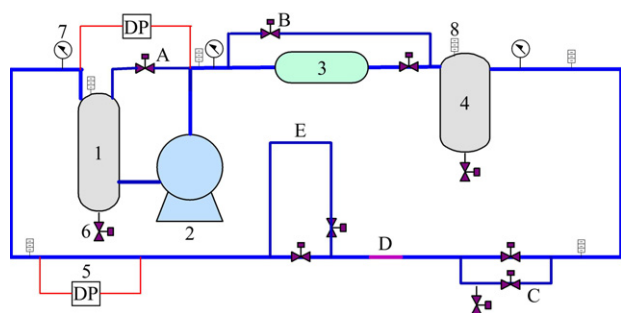


Figure 1. Schematic of the flow loop. 1—Tank; 2—Magnetic centrifugal pump; 3—Flowmeter; 4—Buffer tank; 5—Difference pressure sensor; 6—Drain valve; 7— Pressure sensor; 8— Temperature sensor; A— Sideline, B— Sideline for flowmeter, C— Dip part, D— View port, E— Vertical part

Commercial THF with a certified purity of 99.9wt% and HCFC-141b of 99.5 wt% certified purity (Zhejiang Sunhuan Chemical Co., Zhejiang, China) were used in these experiments. More details about the experimental protocols of these two materials can be found in Refs. [14,15].

3. Results and discussions

3.1. Flow behaviors of hydrate slurries in pipeline

HCFC-141b are unsolvable with water what at the bottom of the pipeline for its higher density when they are flowing in pipeline while THF solves with water very well. However changes of the morphologies of the two refrigerants hydrate slurries are similar. And the other common phenomenon of the two hydrate slurries is that there is a critical hydrate volume concentration zone, which depends on the velocity of the hydrate slurries in pipeline. Pressure drops begin to increase substantially when the solid volume concentrations are larger than the critical ones while pressure drops are almost independent of the solid volume concentration when they are less than the critical ones especially for turbulent flow. The critical hydrate volume concentrations for HCFC-141b hydrate slurry and THF hydrate slurry are 28.5%~37.5% and 39.4%~50.4%, respectively, with a mean velocity from 0.5 m/s to 3.5 m/s in pipeline. More details about the flow behaviors on these two materials can be found in Refs. [14,15].

The relation of pressure drop versus solid volume concentration also has been reported by many researchers. In the experiments of oil-based and water-based hydrate slurries reported in Ref. [12,17], it was seen that even at the high concentration (33%), the frictional pressure drop of the slurry was equal to that of the pure carrying fluids, provided the flow was turbulent. This implied that no additional pressure drop could be initiated when hydrate slurries were transported in pipelines, as compared to pipe transport of pure oil or water. However, the critical solid volume concentration was not found in these experiments due to the limitation of their mass flow meter used in the experiments being limited by the larger hydrate concentration. While in the flow experiments of THF hydrate/Conroe oil slurries in [12,17], the pressure

began to increase substantially at 10% when the motor is at 240 rpm and the pressure drop rise began at 18% hydrates at 520 rpm. Moreover, the trend of increasing flow loop pressure drop with hydrate volume fraction is qualitatively similar to the increase in viscosity observed in the laboratory rheological studies [12].

All these above mentioned facts suggest that agglomeration may be the cause of the suddenly and/or steadily increase at the critical volume concentration zone of hydrate. Hydrate particles begin to agglomerate and slush-like hydrates are formed when the solid volume concentration reaches the critical volume concentration, which may be responsible for the blockage of pipelines in offshore production.

3.2. Rheological behaviors of hydrate slurries in pipeline

In order to understand the agglomerating characters of hydrate particles when the hydrate volume concentrations are larger than the critical ones, rheological behaviors of these two kinds of hydrates were analyzed with the assistance of experimental data on their flow behaviors. The following section aims at the correlation of the measured data (Q , ΔP) with the classical rheological parameters: the shear rate ($\dot{\gamma}$) and the shear stress (τ). In the case of a horizontal cylindrical pipe, the integration of this equation gives a simple relation between the linear pressure drop $\Delta P/L$ and the shear stress: $\tau = (D_{\text{int}}\Delta P/4L)(r/R) = \tau_w(r/R)$, where $\tau_w = (D_{\text{int}}\Delta P/4L)$ is the wall shear stress. The shear rate is the opposite of the local gradient of velocity, $\dot{\gamma} = -du_z/dr$ in our case. It is related to the volume flow rate by the Rabinovith Eq. (1). Its τ_w derivatve gives the expression of the wall shear rate Eq. (2) [11]:

$$\frac{Q}{\pi R^3} = \frac{1}{\tau_w^3} \int_0^{\tau_w} \tau^2 \dot{\gamma} d\tau \quad (1)$$

$$\dot{\gamma} = 32Q(3n+1)/4n\pi D_{\text{int}}^3 \text{ with}$$

$$n = \frac{d \ln \left(\frac{D_{\text{int}} \Delta P}{4L} \right)}{d \ln \left(\frac{8w}{D_{\text{int}}} \right)} = \frac{d \ln(\tau_w)}{\ln \left(\frac{8w}{D_{\text{int}}} \right)} \quad (2)$$

Consequently, in the case of a laminar flow in a horizontal cylindrical pipe, the expressions of the shear rate and the shear stress are functions of measured data (Q , ΔP). The curves representing ΔP versus Q are approximately straight lines which, however, do not intercept the origin. Consequently, it seems that these two kinds of hydrate slurries induce yield pressure drops at the hydrate content higher than the critical ones. This leads us to assume that both HCFC-141b and THF hydrate slurries with hydrate volume concentrations higher than the critical ones behave like Bingham fluids and are characterized by an extrapolated yield shear stress τ_0 and an apparent viscosity μ_0 . This assumption of Bingham behavior is validated when we plot the curve of $\ln[(D_{\text{int}}\Delta P/4L)-(4/3)\tau_0] = f[\ln(8w/D_{\text{int}})]$ as we obtain straight lines with slopes very close to 1. That implies that

plotting $\tau_w = (D_{int}\Delta P/4L)$ versus $\gamma = (8w/D_{int})$ is sufficient to derive the apparent viscosity and the yield shear stress, respectively, from the slope and the intercept point if straight lines are obtained [11]. This is done and the results are listed

in Table 1. The data presented in Table 1 are the yield stresses of HCFC-141b and THF hydrate slurries with their hydrate volume concentrations larger than the critical ones.

Table 1. Yield stresses of HCFC-141b and THF hydrate slurries

HCFC-141b		THF	
Hydrate volume concentration (%)	Yield stresses (Pa)	Hydrate volume concentration (%)	Yield stresses (Pa)
37.5	2.81	39.4	0.80
41.6	4.44	44.5	1.99
47.9	8.96	50.6	2.71
53.2	10.56	55.8	12.04
62.1	15.34	61.3	18.92
68.0	18.56	65.2	30.20

By now there are no well approbated models to calculate the yield stress of Bingham fluid [13], so here polynomial equations were regressed with experimental data for the two hydrate slurries with hydrate volume concentrations larger than the critical ones. The results calculated by Eq.(3) are for HCFC-141b hydrate slurries and those by Eq.(4) are for THF hydrate slurries, respectively. Both the experimental data and the calculated curves are shown in Figure 2. It is clearly illustrated that the two equations can be well used to calculate the yield stresses of the two slurries.

$$\tau_B = -24.31 + 9.92\Phi_h - 26.03\Phi_h^2 \quad 37.5\% < \Phi_h < 68\% \quad (3)$$

$$\tau_B = 92.91 - 444.85\Phi_h + 536.39\Phi_h^2 \quad 39.4\% < \Phi_h < 52\% \quad (4)$$

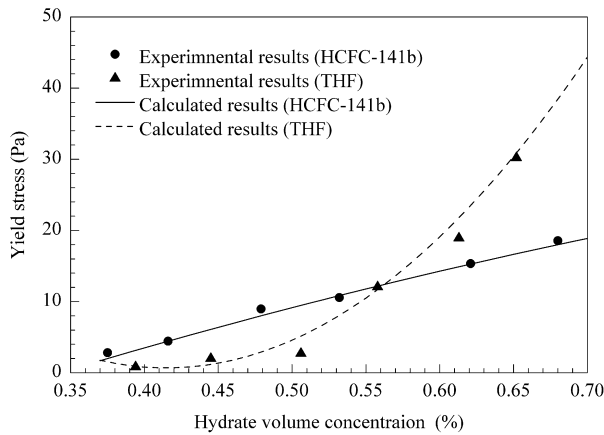


Figure 2. Yield stresses of HCFC-141b and THF hydrate slurries with solid volume concentrations larger than the critical ones

3.3. Safe model of hydrate slurries in pipeline

Based on the results of THF and HCFC-141b hydrates as well as the results reported by other researchers, it is obvious that hydrates are inclined to agglomerate with a large driving force induced from themselves. On the other hand, there are little difference between the densities of these kinds

of hydrates and the correspond liquids, which means that the gravity should not be the main driving force to initiate the agglomeration of hydrate particles. The energy to separate the hydrate particles in the zone defined by the two dashed lines with a length of L in Figure 3 can be described as follows [18]:

$$E = SD\tau_y \quad (5)$$

in which, E is the energy, S is the wetted perimeter of the pipeline, D is the diameter of the pipeline, and τ_y is the sum of agglomerating forces among hydrate particles.

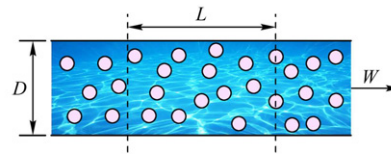


Figure 3. Schematic diagram of hydrate particles in pipeline

If the superficial surface and the volume of the particles are described as S_p and V_p respectively, the energy to separate the hydrate particles into a unit volume can be deduced from Eq. (5) as follows:

$$E_h = D\Phi_h\tau_y(S_p/V_p) \quad (6)$$

in which E_h is the energy to separate the hydrate particles in a unit volume.

In the deduction, the hydrate particles are supposed as spheres with a same diameter of d_p . Now a new non-dimensional parameter of C_h was defined as the ratio of kinetic energy and separating energy of the hydrate particles into a unit volume, which is shown as follows:

$$C_h = \frac{\rho_m w^2/2}{6D\Phi_h\tau_y/d_p} \quad (7)$$

where ρ_m is the density of the mixture of hydrates and water in pipeline, which depends on the volume concentration of hydrate slurries. Since the densities of HCFC-141b and THF hydrates are very close to water density, ρ_m is replaced with the density of water ρ_l in this work.

In the Eq. (7), the determination of the sum of agglomerating forces among hydrate particles (τ_y) is very difficult because there are more than one kind of force among the hydrate

particles, including the force from the liquid bridge among hydrate particles, attractive force among hydrate particles and so on. By far there are short of systemic related research on the forces among hydrate particles. Fortunately both the two kinds of hydrates slurries are Bingham fluids based on the analysis of the experiments, and the yield stress of the Bingham fluid, which is determined by the characteristic parameters of Φ_h , d_p , should be considered as the least force among the particles [11,19,20]. So the yield stresses (τ_B) of the two hydrates slurries are used to replace the sum of agglomerating forces among hydrate particles (τ_y). And the Eq. (7) can be transformed as follows:

$$C_h = \frac{\rho_l w^2 / 2}{6D\Phi_h\tau_B/d_p} \quad (8)$$

As shown in Eq. (8), if C_h has a value larger than 1.0, which means the force to separate the particles is larger than the force to agglomerate the particles, the hydrate particles will not be agglomerated. On the contrary, if C_h has a value larger than 1.0, hydrate particles will be agglomerated and the pipeline can not be run safely. So the non-dimensional parameter of C_h can be used to judge whether the pipeline runs safely or not.

3.4. Validation on the model of hydrate slurries in pipeline

In order to judge the applicability of the non-dimensional parameter of C_h , a test with the data from the experiments was carried into execution. The basic parameters of the two kinds of hydrates are listed in Table 2, in which the diameters of the hydrate particles are the average values measured in the experiments.

Table 2. Basic parameters of the two kinds of hydrates

Parameter	HCFC-141b	THF
Diameter (mm)	42	42
Diameter of hydrate particles (mm)	0.3	0.45
Liquid density ($\text{kg}\cdot\text{m}^{-3}$)	998.5	998.5

The critical lines calculated by supposing the value of C_h equal to 1.0 with the yield stresses calculated with Eq. (3) for HCFC-141b hydrate and those with Eq. (4) for THF hydrate respectively, are shown in Figure 4. Figure 4 presents the corresponding critical hydrate volume concentrations for every flow velocity of hydrate in pipeline. Meanwhile both the experimental critical points obtained by calculating the increase of pressure drop and the observing ones through the view point on the experimental flow loop are also shown in Figure 4.

According to Figure 4, the calculated critical line fits well with the experimental critical points especially at the normal flow velocity in pipeline. While the little difference between the calculated values and the experimental ones can be explained as follows: at first, the hydrate particles in the safe model are supposed to have equal diameters instead of actual ones distributed over a relative considerable extent. And

difference among particle diameters can increase the agglomerating force among hydrate particles; secondly, yield stress is just the minimal value of the agglomerating force among hydrate particles. Both the two factors explain the above result that the values of agglomerating force used in calculation was less than the values in experiments, which also can be used to explain that the calculated critical values are a little larger than the experimental critical values.

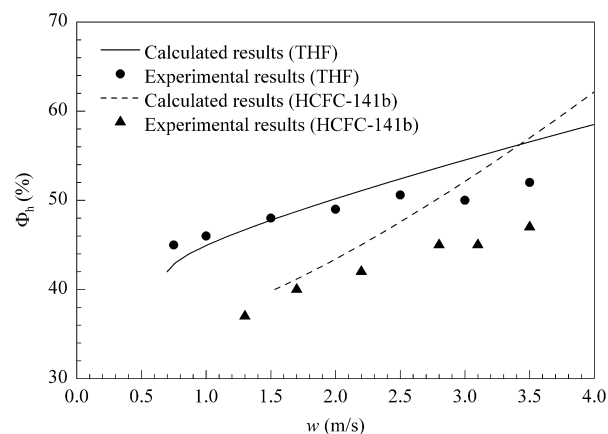


Figure 4. Application of safe model of hydrate slurry in pipeline

Moreover, HCFC-141b hydrate particles have a higher agglomerating tendency than THF hydrate particles in pipeline as shown in Figure 3 since HCFC-141b hydrates have larger critical volume concentrations than THF hydrates with a mean velocities less than 3.5 m/s. The agglomerating tendency also can be seen from the experimental critical hydrate volume concentrations of 28.5%~37.5% and 39.4%~50.4% for HCFC-141b hydrate slurry and THF hydrate slurry, respectively. And the higher agglomerating tendency of HCFC-141b can be explained with its higher yield stress values than THF, as shown in Figure 2.

In a word, the model supposed above can be used to calculate the critical volume concentration of a kind of hydrates flowing in pipeline at a velocity. And when the actual hydrate volume concentration is lower than the calculated one, the pipeline will be free of hydrate blockage; on the contrary, pipeline will be easy to be blocked. The proposed model, of course, should be further improved in order to correctly judge whether the pipeline can be run safely or not with natural gas hydrate slurries.

4. Conclusions

Risk management on hydrates in pipeline has been accepted more and more widely around the world. HCFC-141b and THF were selected as the substitutes to study the flow assurance and the mechanism of the pipeline blockage. Systemic researches of flow assurance of the two hydrate slurries were conducted and some conclusions are as follows:

1) Turbulent flow in pipeline can accelerate the formation of hydrates. Agglomeration of hydrate particles accelerates

quickly when the solid volume concentration is larger than the critical one, which leads the pipeline to a dangerous situation.

2) Hydrate slurries with solid volume concentration larger than the critical ones behave like Bingham fluids and the calculating equations of yield shear stress (τ_0) and apparent viscosity (μ_0) for HCFC-141b and THF hydrate slurries were regressed.

3) A model based on a new and non-dimensional parameter of C_h , which is defined as the ratio of kinetic energy and separating energy of the hydrate particles in pipeline, can be used to calculate the critical volume concentration of a kind of hydrates flowing in pipeline at a velocity. The new model can be used to judge whether the pipeline can be run safely or not and can give some introductions to further study of the flow assurance on natural gas hydrate slurries.

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