



Rheological Properties of Hydrate Slurry in a Brine Suspension

Guilherme Mühlstedt¹, Diogo E. V. Andrade², Cezar O. R. Negrão^{1*}

¹Academic Department of Mechanics – DAMEC, Postgraduate Program in Mechanical and Materials Engineering – PPGEM, Research Center for Rheology and Non-Newtonian Fluids – CERNN, Federal University of Technology – Paraná – UTFPR, Brazil, *Corresponding Author: negrao@utfpr.edu.br

²Department of Mechanical Engineering – DEMEC, Rheology and Non-Newtonian Fluid Flow Laboratory – ReoSul, Federal University of Rio Grande do Sul – UFRGS, Brazil

Abstract

Hydrate formation is one of the main challenges of the oil and gas industry. Hydrates are crystalline structures resembling ice that are formed by small molecules, such as light hydrocarbons, occluded in cage-like structures composed of water molecules. The investigation of hydrate formation processes in pipelines is critical for the oil and gas sector since these structures can halt production and represent safety and economical issue owing to pressure buildup in the pipelines. Understanding the rheological properties of the system is crucial for maintaining oil transportability or an eventual breakage of agglomerates jammed along the process. In this work, the rheological influence of the hydrate formation in a brine suspension was investigated under static and dynamic conditions. The tetrahydrofuran (THF) was used as a guest fluid. To ensure that the sample behaves as a liquid suspension, the guest fluid cut was set to produce hydrate structures not exceeding 40% in volume. Rheometric tests revealed that the slurry formed by the suspension of hydrate crystalline structures was a time-dependent elasto-viscoplastic material in which the microstructure is irreversibly affected by the imposed shear.

Keywords

rheology; hydrate slurry; THF hydrate

Introduction

Flow assurance was identified as the main technical difficulty of offshore production by 110 energy corporations around the turn of the century [1]. There are several definitions of flow assurance, such as: Flow assurance is the examination of thermal, hydraulic, and fluid-related hazards to flow and product quality and their mitigation utilizing equipment, chemicals, and procedures [2]. The main problems related to flow assurance are hydrate formation, paraffin wax, asphaltenes, scale and sand. Despite several works being conducted to investigate the processes of hydrate formation and dissociation in water-oil systems, the phenomena are still not completely understood, and one of the key reasons is the complexity of the crude oil composition [3].

Waxes and asphaltenes are two of the most abundant components in crude oil and, after hydrates, are considered the two most critical flow assurance concerns for subsea pipelines [4]. Waxes and asphaltenes can complicate liquid flow and affect the interfacial characteristics of water-oil emulsions, thereby influencing hydrate behavior [5]. Some researchers reported that waxes significantly retarded hydrate nucleation and increased the induction time in waxy emulsions,

but studies evaluating the effects of waxes still in the initial stages [5].

Considering the complexity of waxy oil emulsions, this work presents a discussion about the rheological properties of hydrate slurries formed in a brine fluid, both in the solid and liquid-like regime. We consider this as a first step to understand the rheological changes in a mineral oil-wax-hydrate slurry. The shear influence in the hydrate formation, the system brittleness in the solid-like regime and the irreversible shear degradation of the hydrate microstructure were examined.

Methodology

Tetrahydrofuran (THF) was employed as a guest fluid to avoid the high pressure required to form gas hydrates in oil and gas lines due to its unique properties of being liquid at atmospheric pressure, infinitely soluble in liquid water, and forming a hydrate under atmospheric pressure. Unlike hydrophobic hydrate compounds, THF-water solution allows hydrate crystals to form and grow anywhere [6].

Materials

The THF (from Sigma-Aldrich, 99,9%) was added to a brine sample mainly composed of water (79%) and sodium chloride (14%). Other components are

thickening agents, emulsifiers and stabilizers. In a water-THF system, the hydrate forms the sll structure with a molar ratio of 1:17, meaning a mass fraction of about 19.08 wt% [7]. To obtain roughly a 40% volume fraction of the solid hydrate in the system, 6.94 wt% THF at ambient temperature was added to the drilling fluid.

Apparatus

The rheometric tests were performed using a Haake Mars III (Haake Co., Germany) stress-controlled rotational rheometer that can control the shear rate indirectly by a feedback PID controller and can measure a minimum and a maximum torque of, respectively, 1×10^{-8} and 2×10^{-1} Nm. As apparent wall slip is a concern in rheological tests of hydrate slurries [8,9,10], two different sensors were employed in the experiments: a Couette geometry with a serrated surface cup (internal cylinder diameter of 25 mm, length of 40 mm, cup diameter of 26 mm, and 0.5 mm groove depth) and a four-blade Vane geometry (cup diameter of 27.2 mm, vane diameter of 22 mm, and length of 16 mm) with a piece of waterproof sandpaper glued on the cup wall to prevent wall slip, as proposed by Ahuja *et al.* [9]. The sandpaper reduces the effective cup diameter to 25.7 mm which was considered in the data analysis. The system temperature was controlled by a Peltier thermostatic bath system.

Experimental Procedure

Before each experiment, the brine sample was vigorously mixed to homogenize the fluid, then the experimental amount was separated. The THF was added and gently mixed until completely solubilization in the brine and the sample was finally poured into the cup that was already at 5 °C. The rotor was lowered to its measuring position, the sample hood was attached to the system, and the rheometric test was then performed. In all the experiments, the sample was cooled from 5 to -10 °C with a cooling rate of 1.5 °C/min, and the tests were performed at -10 °C.

Results and Discussion

Despite the experimental temperature being below zero degrees Celsius, the high amount of salt in the sample inhibits ice formation, as verified by microcalorimetry tests. Thus, rheological property changes were caused by hydrate formation.

Hydrate Formation During the Flow

The shear influence on the hydrate formation was observed imposing different shear rates using the Couette geometry. Figure 1 shows the shear stress increasing during the cooling for all applied shear rates, meaning a growth of the material's apparent viscosity. After reaching -10 °C, the stress tends to stabilize before undergoing a significant change that is linked to hydrate formation. The greater the shear rate, the shorter the induction period (time required for hydrate formation) and the shorter the

time required for the stress to achieve a steady state.

The effect of the shear history on the material rheology is now discussed. The sample was kept at -10 °C and sheared at 3 s⁻¹ for 60 min. From this point on, the shear rate was stepped-up and maintained for another 60 min and the step-up procedure was repeated every 60 min up to the limit of 100 s⁻¹. A shear step-down course to the limit of 3 s⁻¹ was then initiated. The stresses measured at the end of each shear rate-60 min plateau were plotted as a function of the shear rate in Fig. (2). The filled and the hollow blue diamonds represent the step-up and step-down flow curves, respectively. In addition, the orange diamonds were obtained at the end of stress curves shown in Fig. (1).

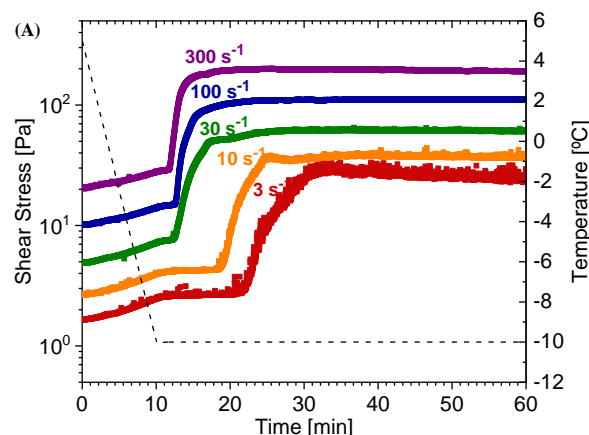


Figure 1. Shear stress as a function of time during the hydrate formation for different imposed shear rates.

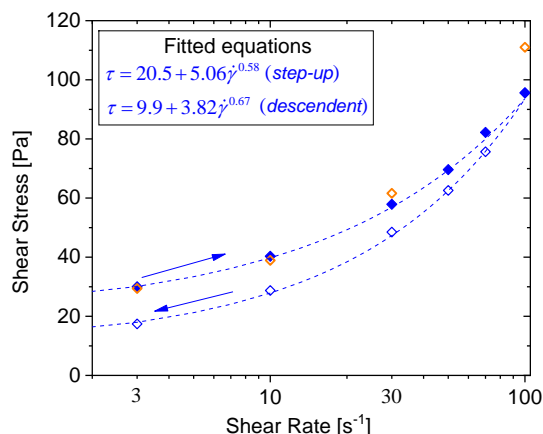


Figure 2. Flow curves for hydrate slurries: (i) in shear rate step-up and step-down (filled and the hollow blue diamonds, respectively); (ii) imposing constant shear rates obtained after 1 h of shearing (orange diamonds).

The dashed lines in Fig. (2) are fitted curves for step-up and step-down curves (in blue). The Herschel-Bulkley equations in the figure demonstrate that the parameters fitted to both curves are strongly influenced by the sample's maximum shear rate. The dynamic yield stress, for example, declined from 20.5 to 9.9 Pa. In practice,

hydrate slurries that have previously been sheared at high shear rates require lower pumping pressures than those that have only been mildly sheared.

Hydrate Formation During Stoppage and the Flow Startup

In addition to the viscosity, the flow startup of the hydrate slurry after a shutdown is also investigated. Stress-controlled creep tests were firstly used to evaluate the flow startup. The hydrate was formed by imposing a shear rate of 100 s^{-1} for 1 h and then left aging for 10 min. After aging, the sample was submitted to a constant shear stress. Figure 3 shows the measured strain as a function of time for each creep test. While the stress was equal to or less than 10 Pa, the strain increased to a certain amount and then remained nearly constant, suggesting a solid-like material behavior. When the strain reached 13 Pa or above, it increased dramatically with time, indicating material breakage. As noted, the higher the stress, the faster the material breaks down. The material static yield stress for this 10 min aging experiment was between 10 and 13 Pa, which was higher than the dynamic yield stress determined from the material flow curve with the same maximum shear rate applied to the sample (as expected for time-dependent materials).

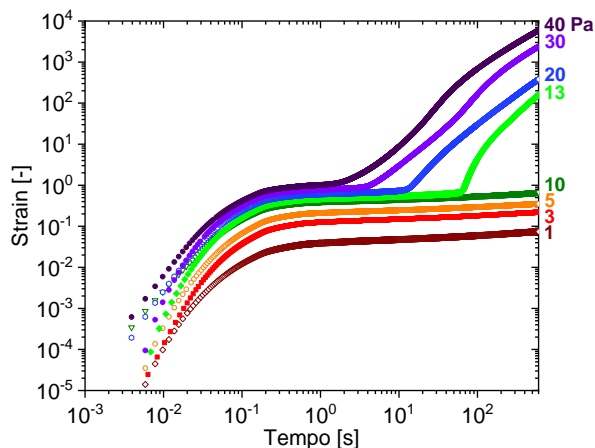


Figure 3. Shear strain as a function of time for creep tests at different stress levels (indicated in Pascal next to each curve).

Another method for determining static yield stress is the ramp test which consists of a steady increase in stress and strain measurement. It is worth mentioning that in the solid-to-liquid phase, low deformation levels are measured, whereas rapid strain changes are observed as the material yields. This procedure was also used by Qin *et al.* [11] to determine the yield stress of gas hydrate-in-oil slurries.

The Fig. (4) shows the stress ramp results for the f hydrate slurries dynamically formed (blue curves) and statically formed (black curve). The hydrates were formed as described for creep tests and were submitted to three different aging times (10, 60 and 120 min). The hydrate slurry formed statically

(black curve) was obtained with no shear imposed during the hydrate formation (for this test, a vane geometry was used).

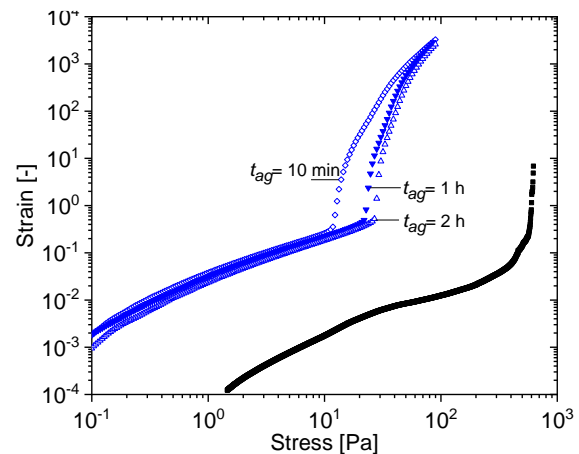


Figure 4. Strain as a function of stress for stress ramp test. (i) the hydrate slurry after shearing at 100 s^{-1} for 10 min and aging time of 10 min (blue diamonds), 1 h (blue down-triangles), and 2 h (blue up-triangles), respectively; and (ii) the hydrate slurry formed statically (black squares).

As noted in Fig. (4), the stress that abruptly increased the strain for an aging time of 10 min was approximately 10 Pa, which was roughly the same value obtained from creep test shown in Fig. (3). As a time-dependent material, the higher the aging time, the larger is the static yield stress, as observed in the comparison to the blue color curves of Fig. (4). However, the higher the aging time, the smaller the rate of increase in the yield stress. Furthermore, once the static yield stress reached 550 Pa, the black-squared curve reveals that the material structure is substantially stronger in comparison to dynamically formed hydrate slurries. Even though yield stress increases with aging time, yield stress measured after a dynamic hydrate formation cannot reach the counterpart obtained after a static formation.

Conclusions

The main conclusions can be summarized as follows:

- The higher the imposed shear rate during cooling period, the shorter is the induction time and the faster the material reached the steady state;
- The apparent viscosity of hydrate slurry is at least 1 order of magnitude larger than the brine fluid apparent viscosity;
- The THF-hydrate slurry in brine fluid can be described as an elasto-viscoplastic, irreversible time-dependent material, as the material yield stress and elasticity at low deformations degrade irreversibly with shear;
- The statically formed hydrate is much more resistant than that dynamically built. The material brittleness is also reflected on the material yield point.

These findings may bring new perspectives for the flow startup, especially, the material brittleness, the shear influence on the hydrate formation, and the shear degradation of the microstructure. The next steps will be taken with methane in to compare the behavior of THF hydrate and gas hydrate in operational conditions.

Acknowledgments

The authors acknowledge the financial support of PETROBRAS S/A (TC 0050.0070318.11.9), CNPq (process: 487091/2013-2), CAPES, FINEP, PRH, and PFRH/PETROBRAS (6000.0067933.11.4 and 6000.0082166.13.4). The authors also thank the Multilab LabReo-CERNN/UTFPR for providing the rheometers used in the current work.

Responsibility Notice

The authors are the only responsible for the paper content.

References

- [1] Sloan, E. D. *Fluid Phase Equilibria*, 228, 67-74, 2005.
- [2] Makogon, T. Y. *Handbook of Multiphase Flow Assurance*. Gulf Professional Publishing, 2019.
- [3] Daraboina, N., Pachitsas, S., & von Solms, N. *Fuel*, 148, 186-190, 2015.
- [4] Li, R., Huang, Q., Zhang, D., Zhu, X., Shan, J., & Wang, J. *AIChE Journal*, 66(4), e16892, 2020.
- [5] Zhang, D., Huang, Q., Li, R., Wang, W., Zhu, X., Li, H., & Wang, Y. *Chemical Engineering Science*, 244, 116831, 2021.
- [6] Iida, T., Mori, H., Mochizuki, T., & Mori, Y. H. *Chemical engineering science*, 56(16), 4747-4758, 2001.
- [7] Larsen, R. *Degree thesis unpublished*. NTNU. Trondheim, 1997.
- [8] de Lima Silva, P. H., Naccache, M. F., de Souza Mendes, P. R., Campos, F. B., Teixeira, A., & Sum, A. K. *Energy & Fuels*, 31(12), 14385-14392, 2017.
- [9] Ahuja, A., Zyliftari, G., & Morris, J. F. *Journal of Non-Newtonian Fluid Mechanics*, 220, 116-125, 2015.
- [10] Peixinho, J., Karanjkar, P. U., Lee, J. W., & Morris, J. F. *Langmuir*, 26(14), 11699-11704, 2010.
- [11] Qin, Y., Aman, Z. M., Pickering, P. F., Johns, M. L., & May, E. F. *Journal of Non-Newtonian Fluid Mechanics*, 248, 40-49, 2017.