OTC-31189-MS

Surface Treatment Strategies for Mitigating Gas Hydrate & Asphaltene Formation, Growth, and Deposition in Flowloops

Marshall A Pickarts and Jose Delgado-Linares, Center for Hydrate Research, Colorado School of Mines; Erika Brown and Vinod Veedu, Oceanit Laboratories; Carolyn A. Koh, Center for Hydrate Research, Colorado School of Mines

This paper was prepared for presentation at the Offshore Technology Conference held in Houston, TX, USA, 16 - 19 August 2021.

Abstract

Numerous solids including gas hydrates, waxes, and asphaltenes have the potential to form in the production lines of gas and oil fields. This creates a highly non-ideal scenario as the accumulation of said species leads to flow assurance issues, especially with long-term processes like deposition. Since an ever-increasing amount of material is deposited in place at the pipe surface, production stoppage or active mitigation efforts become inevitable. The latter production issues result in increased safety risks and operational expenditures. Therefore, a cost-effective, passive deposition mitigation technology, such as a pipeline coating or surface treatment is especially appealing. The ability to address multiple pipeline flow assurance issues simultaneously without actively disrupting production would represent a dramatic step forward in this area.

This study is part of a long-term ongoing effort that evaluates the performance and application of an omniphobic surface treatment for solids deposition prevention in industrially relevant systems. In particular, this specific work concentrates on the efficacy and robustness of the treatment under fully flowing conditions. The apparatuses utilized for this include two flowloops: a lab-scale, high-pressure flowloop for gas hydrate and surface treatment durability studies, and a bench-scale, atmospheric pressure loop for crude oil and asphaltene experiments.

Film growth in high-pressure flowloop tests corroborated previous reports of delayed gas hydrate nucleation observed in rocking cells. Without the aid of the memory effect, treated oil-dominated experiments never experienced hydrate formation, spending upwards of a week in the hydrate stability zone (at the subcooled/fluid test conditions). Subsequent tests which utilized the memory effect then revealed that the hydrate formation rate reduced in the presence of the surface treatment compared to a bare stainless-steel surface. This testing was part of a larger set of trials conducted in the flowloop, which lasted about one year. The surface treatment durability under flowing conditions was evaluated during this time. Even after experiencing ~4000 operating hours and 2 full pressure cycles, no evidence of delamination or damage was detected. Finally, as part of an extension to previous work, corroded surface asphaltene deposition experiments were performed in a bench-top flowloop. Treated experiments displayed an order of magnitude reduction in both total oil (all fractions of crude oil) and asphaltene fraction deposited.

Introduction

For oil and gas systems, flow assurance has become a necessary discipline of study to ensure the safe and timely production of materials. Various pipeline solids including gas hydrates, asphaltenes, and waxes often appear during production and threaten the integrity of flow. Significant time and effort, therefore, is devoted by industry and academia towards the investigation of prevention and mitigation strategies of such issues (Misra et al., 1995; Mullins, 2011; Sloan et al., 2010).

One particular occurrence of research interest that is shared by the aforementioned pipeline solids is deposition, i.e. the accumulation of materials on the surface of the pipe (Lachance et al., 2012; Singh et al., 2000; Vargas, F. M., Tavakkoli, 2018). This behavior is analogous to the buildup of plaque on arterial walls in the human body as it leads to a stenosis type effect in the pipeline. The localization of materials caused when certain areas are prone to deposition - for example, low shear zones – coupled with the cumulative nature of such a process renders this phenomenon particularly dangerous, especially over extended time periods. Consequently, investigative efforts seek to determine the efficacy of potential cost-effective, deployable deposition mitigation strategies.

Coatings and surface treatments are examples of passive deposition mitigation technologies that have generated interest from researchers. Several reports have been published, illustrating the positive impact of coatings for the deposition remediation of scale (Bethke et al., 2018; Heydrich et al., 2019), gas hydrates (Brown et al., 2017; Pickarts et al., 2019; Pickarts, et al., 2020), asphaltenes (Bethke et al., 2018; Pickarts, et al., 2020), and waxes (Bai et al., 2019; Bethke et al., 2018; Rashidi et al., 2016), albeit singular in focus. Though promising, real world conditions generally encounter multiple species simultaneously, necessitating that a coating be tailored to handle each adequately. This presents a particularly difficult challenge given that the common pipeline solids possess vastly different physical and chemical properties. At the minimum, a coating designed for one concern should not display antagonistic effects towards the others, while the acme of this technology effectively aids in all aspects.

To date, reports of formulations successfully passing a comprehensive study of several major flow assurance solids have been limited outside this work. This ongoing work continues to present positive results for the major flow assurance solids issues of gas hydrates, asphaltenes, and waxes with a single surface treatment. Efforts have ranged from initial bench-scale "proof-of-concept" experiments to more representative lab-scale fully flowing trials as the surface treatment transitions from controlled testing to industrial application.

Methods and Materials

Omniphobic Surface Treatment

The material presented here is part of an ongoing study regarding the mitigation of solids deposition in pipelines. Consequently, the surface treatment (similar to a coating) employed in this work was again identical to that utilized in previous studies. Further details regarding the description, application methods, chemical behavior, and chemical/physical durability of the treatment can be found in Pickarts et al., 2019. One important aspect of the surface treatment to highlight is that this has been developed for in-situ application to existing, corroded pipelines.

Hydrate Deposition Flowloop

A lab-scale flowloop specifically designed to investigate hydrate deposition processes was used in this study to probe the effect of the surface treatment on hydrate nucleation. A full description of this flowloop may be found in previous work (Pickarts et al., 2020), which covered transient style hydrate tests. The conditions for the current experiments were similar to the oil-dominated tests described in that work. Namely, 25 vol. % deionized (DI) water content in a model oil phase was circulated at ~500 kg/hr to give a liquid loading of about 50 vol.%. A structure II gas hydrate former comprising a methane/ethane mixture (74.7/25.3 mole%) at 535 psia was used for the gas phase. Unlike the previous experiments outlined in the transient work, efforts in this paper focused on single-pass, continuous flow style tests. As a result, temperatures held throughout the loop were slightly altered. Only one section, either untreated (Viewing Section) or treated (Deposit Leg #2), was cooled inside the hydrate region to 3°C. The remaining portions of the loop were held near the experimentally determined hydrate equilibrium temperature of 11°C. With this setup, the bulk temperature of the fluid remained too high for hydrate formation (due to no/minimal subcooling), while the surface temperature of the untreated/treated section provided a gradient for film growth. The occurrence of hydrate formation was consequently controlled at the wall, allowing the effects of the surface treatment on hydrate nucleation and growth to be distinguished from other processes. All hydrate formed as a deposit on the wall (i.e. formed hydrate and deposited hydrate amounts are the same).

Bench-Scale Asphaltene Deposition Loop

Asphaltene deposition was investigated with a bench-top flowloop apparatus. In the past, this apparatus was used to study crude oil and precipitated asphaltene particle deposition on pristine surfaces. At a high level, the atmospheric pressure loop consisted of a fluid reservoir for the mixing of precipitated asphaltene particles and a carbon steel testing section for the deposition of these particles. Fluids and particles were circulated as a multi-pass setup for a set period of time and the deposited material was chemically extracted to quantify the total material (all fractions of crude oil) and the asphaltene fraction alone. A detailed description of the device, experimental procedures, and analysis methods are provided in Pickarts et al., 2019. For this set of experiments, the pristine surfaces were replaced with corroded ones. Tests consisted of heptane precipitated asphaltenes from a crude oil (3.4 mL/g heptane/oil, 20 API, 2.53% asphaltenes).

Results and Discussion

Gas Hydrate Nucleation & Growth Prevention

As described in the Methods section, hydrate tests focused on film growth style experiments (hydrates did not form in the bulk fluid). In total, 7 experiments were performed for oil-dominated systems. To start, it was important to identify the mechanism that led to hydrate film growth for the chosen experimental parameters. This was done by performing a trial in the Viewing Section of the loop, where visual observations could be made with the windows. Since a significant free gas layer existed, it appeared that hydrate films formed at the top of the line from condensation processes. As seen during the probing run, water droplets first formed and coalesced on the pipe surface in the gas layer before hydrate nucleation (Figure 1a). These subsequently converted to a hydrate film after nucleation occurred and grew down toward the liquid phase. All results for hydrate nucleation and growth as well as surface treatment performance presented hereafter were therefore related to this water condensation process.

Figure 1—Condensation of water droplets in gas phase (a, left) that resulted in hydrate film upon nucleation (b, right).

The first set of experiments probed hydrate induction times in a similar fashion to what had been done earlier in the rocking cells. This previous rocking cell work demonstrated that about 1/3 of hydrate tests displayed significant delays in and for some cases complete avoidance of hydrate formation (Pickarts, et al., 2020). However, the irregular shape of the rocking cell coupon contributed to difficulty with reproducibility in some cases, leading to the low percentage of highly positive results. The treatment of an inner section of the flowloop, on the other hand, was much more straightforward since no short or sharp edges existed in the inner part of the tube. Thus, observations were much more definitive. These clearer results are presented in Table 1.

Table 1—Hydrate induction times for untreated/treated sections of the flowloop. Untreated sections formed hydrates much more rapidly than treated counterparts.

	Trial 1 Induction Time (hours)	Trial 2 Induction Time (hours)
Untreated	10.1	24.1
Treated	>236.1*	>110.4*

*Hydrates Never Formed

In this table, two trials for both untreated and treated surfaces were performed at about 9°C subcooling. What can be seen is that hydrate began to form in the untreated section within a day for both trials. Yet, when identical tests were performed with the treatment, the system operated for extended periods of time without experiencing hydrate formation, spending upwards of 10 days in the hydrate stability zone. Both treated trials were manually discontinued before hydrate nucleation. In essence, hydrates were never able to form from condensation processes on the surface treatment without the assistance from the memory effect. Along with the rocking cell tests, these results further support the idea that the treatment was affecting hydrate nucleation.

Next, hydrate growth rates from film growth experiments were evaluated. In order to investigate these growth rates on treated surfaces, the memory effect was required to ensure timely hydrate nucleation. The length of experiments was quite long in each case, therefore, only 1 trial was executed for untreated and treated surfaces. These results are shown in Figure 2.

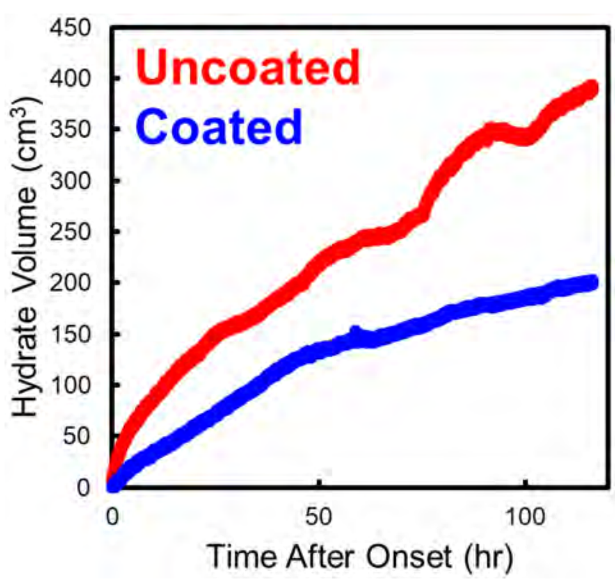

Figure 2—Hydrate volume calculations for untreated and treated film growth experiments (using the memory effect). Results show that untreated surfaces formed hydrate at an overall rate that was #50% greater than the treated surface.

What can be first noticed from a high level is that in this case the red line (untreated trial) is greater than the blue line (treated trial) for the duration of the experiment, revealing that the growth rate is greater throughout. Digging deeper into the details, it was found that the untreated trial for film growth in the deposition loop showed a growth rate 1.5 times that of the treated experiments.

This analysis reveals yet another positive aspect of the surface treatment in regard to hydrate deposition mitigation. While the original idea was to utilize treatments for reduced adhesion of deposits, it appears several ancillary benefits of delayed nucleation and hindered growth can exist, augmenting the efficacy of the surface treatment for hydrate deposition prevention. Moving forward, further testing is being conducted to pinpoint the detailed mechanisms behind these two identified benefits.

Precipitated Asphaltene Particle Deposition on Corroded Surfaces

In the past, crude oil and asphaltene tests were performed for pristine untreated/treated carbon steel surfaces. Overall results were partially inconclusive. A dramatic reduction was observed for crude oil deposition, while a slight, yet statistically insignificant decrease was seen in the asphaltene fraction alone (Pickarts, et al., 2020). Corroded pipe surface experiments were proposed as a means to differentiate results further and ascertain the true surface treatment performance.

This work presents the results of that proposal. The effect of the surface treatment for crude oil and asphaltene deposition is shown in Figure 3. The left section of this figure groups the results obtained for a pristine pipe and the right section corresponds to the results of a corroded pipe. These two sets of results are overlaid together for ease of comparison.

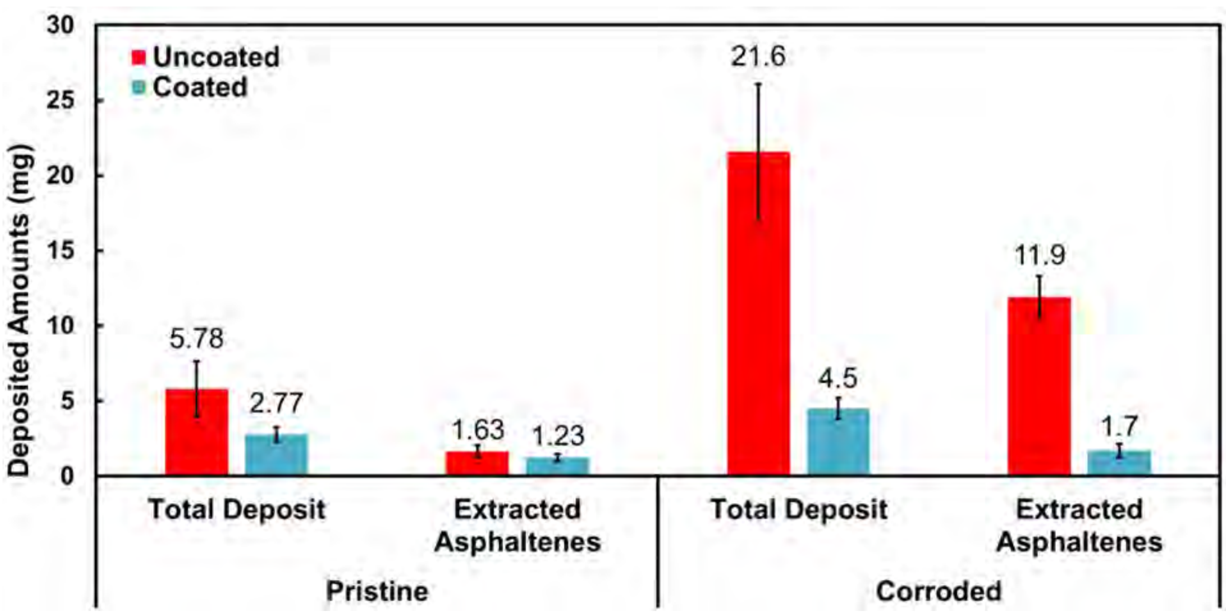

Figure 3—Comparison of the mass of total solids and extracted asphaltenes deposited in the deposition loop in a pristine and a corroded section. Crude oil C. Heptane/crude oil = 3.4 constant for all experiments). Pristine data collected from (Pickarts et al., 2020).

When compared to the pristine pipe, corrosion increased the amount of oil and asphaltenes deposited by approximately a factor of 4 and 10, respectively. This increase could be caused by two main mechanisms: 1) the increase in the surface roughness and 2) possible chemical interactions between asphaltene molecules and metal ions generated during the corrosion process. Both mechanisms have been proposed by several authors (Becker, 1997; Sung et al., 2016; Vargas, F. M., Tavakkoli, 2018). Most importantly, it augmented differences between untreated and treated cases, making the true effects of the surface treatment distinguishable.

It is worth noting the significant impact of the surface treatment in reducing the mass of oil and asphaltenes deposited especially in corroded pipes. This decrease was very dramatic in the corroded pipe, attaining a reduction of 80% for the total deposit and 85% for the extracted asphaltenes (an order of magnitude in each case). It was hypothesized that the presence of the treatment significantly reduced the surface roughness by creating a smooth film that inhibited asphaltene deposition. At the same time, the surface treatment may have acted as a solid barrier blocking the direct contact of the crude oil and metal pipe surface, which could reduce the asphaltenes-pipe wall interactions. In other words, the results suggested that the application of a surface treatment could attenuate the two potential contributing causes of asphaltene deposition on corroded metal surfaces.

This result has important practical implications, considering that pipes used in the oil and gas industry are generally corroded due to environmental factors (e.g. air humidity), or are easily susceptible to corrosion during the application of specific chemical treatments (e.g. oil recovery methods based on CO_2 injection) (DeBerry & Clark, 1979). Currently, further investigations are underway to increase the potential of the surface treatment as an asphaltene mitigation strategy.

Surface Treatment Survivability under Flowing Conditions

Along with functionality, coating durability holds critical significance with its successful application. Reports of pinhole bubbling and ribboning delamination have been all too common for those experienced with coating application under high pressure scenarios. With the potential for additional capital expenditure and/or introduction of plug-inducing materials into the production stream, the requirement for a physically-robust, strongly adhered coating that maintains these properties for extended time periods is necessary for the practical application of this technology.

The flowloop results presented above were part of a subset of tests that took place over a period of 1 year. During this time, the surface treatment in Deposit Leg #2 was subjected to approximately 4000 hours of high-pressure, solid particle (gas hydrate)/fluid flow. This also encompassed 2 full pressure cycles, where the flowloop was completely depressurized to atmospheric conditions. Throughout this time, the physical integrity of the treatment was inferred and monitored through several indirect observations detailed below.

First, it was noted that hydrate results (nucleation and growth rates) remained positive over the course of this testing sequence. In past rocking cell tests, improperly adhered treatments were revealed when treated results closely matched untreated cases, since hydrate were no longer interacting with the treated surface. Hydrate nucleation delays were not observed and growth rates were identical to bare carbon steel coupons. The observation that positive results regarding both hydrate nucleation and growth were maintained in the flowloop even after several pressure cycles was a strong indicator that the surface treatment had not been compromised.

Furthermore, in the event of damage/delamination, one would expect corrosion to occur on the underlying carbon steel surface as has been observed in past rocking cell tests. This, in turn, would have discolored the process fluid in the loop and been readily visually apparent. However, circulation with DI water at the end of the testing period revealed no evidence of corrosion products in the loop. Along with the positive hydrate results, this was a strong indicator that the treatment is strongly bound to the surface, preventing process fluids from contacting the underlying carbon steel pipe surface.

While these initial results appear promising, it must be noted that the only solid particle flow tested in this investigation were gas hydrates. Field systems typically encounter additional materials such as sand particles and other erosive conditions during production. These scenarios lie outside of the current scope of this work.

Conclusions

To address issues of pipeline solids deposition, this study explored the application of an omniphobic surface treatment as a potential mitigation technology in fully flowing systems. Both gas hydrates and asphaltenes were comprised in a scope of work on two flowloops. These included a high-pressure lab-scale apparatus for gas hydrates and benchtop loop for asphaltenes.

First, high pressure flowloop trials performed without the aid of the memory effect probed the effects of the treatment on gas hydrate nucleation. Induction times were recorded for a condensation-based film growth process, and the results mirrored that seen previously for oil-dominated rocking cell tests. Untreated surfaces formed hydrate rather quickly, within a day of entering the hydrate stability zone. On the other hand, omniphobic treated surfaces never nucleated hydrates. This metastability was observed over extended periods of time, including more than a week. This data illustrated that the surface treatment can aid in hydrate nucleation prevention.

Subsequent tests at identical conditions were then performed, but utilized the hydrate memory effect so that growth could be observed in the presence of the surface treatment. Hydrate growth rates differed quite dramatically between the two cases. Comparison between them quantitatively showed that the untreated surface grew hydrates at a rate that was about 1.5 times that of the treated case. Together with the nucleation results, this study has revealed several complementary benefits of the treatment in regard to hydrates beyond adhesion reduction. This type of analysis highlighted how altering surface properties can measurably impact several factors; more than what might be readily apparent.

Next, crude oil and asphaltene deposition tests occurred for corroded carbon steel surfaces. The principle here was to ensure large differences for deposited materials existed between untreated and treated trials. Similar to hydrates, the results were striking. Deposited amounts for both the total crude oil and asphaltene fraction alone decreased by an order of magnitude in the presence of the treatment. Unlike the previous study with pristine pipe surfaces, the positive impact of the surface treatment was very clear.

Finally, the surface treatment durability under flowing conditions was assessed during the full set of trials in the hydrate deposition loop, which occurred over a year long period. During this time, the treatment endured solid particle and fluid flow for an estimated 4000 operating hours and experienced 2 full pressure cycles. No indication of delamination or damage was detected during this time. Hydrate experiments continued to display dramatic differences between the treated and untreated trials. Furthermore, corrosion products were not found in the process fluid. Both of these indicated that the carbon steel surface was protected from the process fluids by the treatment. This positive result was particularly important because previous issues with coatings have not generally been related to their performance, but rather their robustness.

Overall, this omniphobic surface treatment continued to display promising results as experiments transition from controlled benchtop to the more industrially relevant fully flowing scenarios. Positive findings for all major flow assurance solids have enabled the continued progress of this ongoing comprehensive work. With completion of singular species studies, future efforts will encounter even more complex situations with multiple species testing in fully flowing systems.

Acknowledgement

The authors would like to acknowledge the support from the U.S. DOE-NETL, Award# DE-FE0031578 for funding this work, and William Fincham, DOE-NETL Program Manager for support and advice on this work.

References

Bai, J., Jin, X., & Wu, J. T. (2019). Multifunctional anti-wax coatings for paraffin control in oil pipelines. *Petroleum Science*, **16**(3), 619–631. https://doi.org/10.1007/s12182-019-0309-7

Becker, J. R. (1997). *Crude Oil Waxes, Emulsions, and Asphaltenes*. Pennwell Books. https://books.google.es/books?id=Qw9gwzzf4SAC

Bethke, G. K., Snook, B., Herrera, G., Kelly, A. E., Joshi, S., & Jain, S. (2018). A Novel Coating to Reduce Solids Deposition in Production Systems. Offshore Technology Conference.

Brown, E., Hu, S., Wang, S., Wells, J., Koh, C., Nakatsuka, M., & Veedu, V. (2017). Low-Adhesion coatings as a novel gas hydrate mitigation strategy. Proceedings of the Annual Offshore Technology Conference, **5**.

DeBerry, D, & Clark, W. (1979). *Corrosion Due To Use of Carbon Dioxide*.

Heydrich, M., Hammami, A., Choudhary, S., Mockel, M., & Ratulowski, J. (2019). Impact of a novel coating on inorganic scale deposit growth and adhesion. Proceedings of the Annual Offshore Technology Conference, 2019-May. https://doi.org/10.4043/29218-ms

Lachance, J. W., Talley, L. D., Shatto, D. P., Turner, D. J., & Eaton, M. W. (2012). Formation of hydrate slurries in a once-through operation. *Energy and Fuels*, **26**(7), 4059–4066. https://doi.org/10.1021/ef3002197

Misra, S., Baruah, S., & Singh, K. (1995). Paraffin problems in crude oil production and transportation: a review. *SPE Production and Facilities*, **10**(1), 50–54. https://doi.org/10.2118/28181-pa

Mullins, O. C. (2011). The asphaltenes. Annual Review of Analytical Chemistry, **4**(July 2011), 393–418. https://doi.org/10.1146/annurev-anchem-061010-113849

Pickarts, M. A., Brown, E., Delgado-Linares, J., Blanchard, G., Veedu, V., & Koh, C. A. (2019). Deposition mitigation in flowing systems using coatings. Proceedings of the Annual Offshore Technology Conference, 2019 - May. https://doi.org/10.4043/29380-ms

Pickarts, M. A., Croce, D., Zerpa, L. E., & Koh, C. A. (2020). Gas hydrate formation & transportability during transient shut-in/restart conditions. Proceedings of the Annual Offshore Technology Conference, 2020 - May. https://doi.org/10.4043/30857-ms

Pickarts, M. A., Delgado-Linares, J., Brown, E., Veedu, V., & Koh, C. A. (2020). Evaluation of a robust, in-situ surface treatment for pipeline solids deposition mitigation in flowing systems. Proceedings of the Annual Offshore Technology Conference, 2020 - May. https://doi.org/10.4043/30817-ms

Rashidi, M., Mombekov, B., & Marhamati, M. (2016). A study of a novel inter pipe coating material for paraffin wax deposition control and comparison of the results with current mitigation technique in oil and gas industry. Offshore Technology Conference Asia 2016, OTCA 2016, 4163–4169. https://doi.org/10.4043/26695-ms

Singh, P., Venkatesan, R., Fogler, H. S., & Nagarajan, N. (2000). Formation and aging of incipient thin film wax-oil gels. *AIChE Journal*, **46**(5), 1059–1074. https://doi.org/10.1002/aic.690460517

Sloan, E. Dendy, Koh, Carolyn, Sum, Amadeu K., Ballard, Adam L., Creek, Jefferson, Eaton, Michael, Lachance, Jason, McMullen, Norm, Palermo, Thierry, Shoup, George, Talley, L. (2010). *Natural Gas Hydrates in Flow Assurance*. Gulf Professional Publishing.

Sung, C. A., Tavakkoli, M., Chen, A., & Vargas, F. M. (2016). Prevention and control of corrosion-induced asphaltene deposition. Proceedings of the Annual Offshore Technology Conference, **2**(Creek 2005), 1589–1603. https://doi.org/10.4043/27008-ms

Vargas, F. M., Tavakkoli, M. (2018). *Asphaltene Deposition: Fundamentals, Prediction, Prevention, and Remediation*. CRC Press.