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Scale-Up and Modeling Efforts Using an Omniphobic Surface Treatment for Mitigating Solids Deposition

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Abstract

Gas hydrates, waxes and asphaltenes represent some of the most significant flow assurance challenges, especially in subsea lines, where treatment options can be limited. Currently, complete avoidance is the primary strategy for hydrate management, while chemical or mechanical flushing/pigging may be utilized for other solids. Each system must also be treated with individualized solutions, as there have been no proved one-size-fits-all technologies demonstrated to date. As an alternative to constant chemical injection or thermodynamic controls such as insulation or heating, a robust omniphobic surface treatment material has been developed which has been shown in previous studies to significantly reduce the adhesion of flow assurance solids, resulting in lower risk for deposition and plugging of gas hydrates, waxes, and asphaltenes. As part of a Department of Energy study, laboratory scale tests were performed on a variety of apparatuses ranging from micromechanical force (micron scale) to laboratory flow loop testing (meter scale). While the results from these tests have been promising, there can be some disconnects between lab-scale observations and field-scale testing.

Several factors can result in discrepancies between small-scale bench-top studies and deployment-scale efforts. These include flow conditions (Reynolds number, flow regime), chemistry (synthetic vs. crude oils, gas composition, and additives), physical differences (pipeline material, size, and geometry), etc. This work will describe the actions taken to better understand the deployment and performance of a material such as this omniphobic surface treatment in field scenarios, and to build confidence for deployment in a production scenario. These efforts include modeling field production scenarios using models developed from lab observations, application of the material to field-scale equipment to better understand application challenges, and expanded survivability and longevity testing. Understanding the bridge between laboratory testing and full-scale deployment allows for better technique and risk mitigation for field scale testing.

Introduction

In the production of oil and gas, many strategies have been applied to avoid the deposition of solid compounds such as hydrates, waxes and asphaltenes. These compounds can be formed under a variety of thermodynamic and chemical conditions and are some of the top challenges in flow assurance, as they can cause stenosis of the pipeline if allowed to deposit unchecked. Gas hydrates, crystalline compounds which form when water and a suitable "guest" molecule are brought together under appropriate thermodynamic (temperature and pressure) conditions, can threaten oil, natural gas transmission and production, and carbon sequestration injection lines, for example. Waxes and asphaltenes exist as natural components in some oils, but changes in the composition, pressure, or temperature of the oil phase can cause them to precipitate as a solid phase which can adhere to the insides of production and transmission lines. Each of these compounds can form blockages in pipelines, resulting in costly maintenance, shut-downs, or potential pipeline blockage.

Commonly, solutions to flow assurance challenges include frequent pigging to mechanically remove deposited solids, thermodynamic controls such as heating or insulation, or chemical injection (Cochran 2003, Kinnari 2015, Rashidi 2015). For hydrates, for example, estimates for the cost of mitigation can be upwards of $1M/mile of pipeline (Sloan 2010). However, the most ideal solution in these cases is a "do nothing" approach where active mitigation strategies become unnecessary. One such option is a low surface energy surface treatment or coating material which resists the deposition of these solids. By lowering the adhesion, deposition can be slowed, lowering the frequency of necessary maintenance. Alternately, low adhesion surfaces can allow deposits to slough once they become large enough to be removed by the shear force caused by the fluids in the line (Aman 2018). While coating materials have been a subject of consideration in the past, limitations have included challenges with in-situ application, compatibility with temperatures, pressures, and chemical components, and costs to scale technology to commercial levels (Smith 2012, Sojoidi 2015). This paper details efforts to scale up one such material, the DragX surface treatment, which has been previously shown to resist hydrate deposition and plugging in rocking cell and flowloop testing, as well as demonstrating resistance to wax and asphaltene deposition in lab-scale tests (Brown 2017, Pickarts 2020–2022). This omniphobic surface treatment (OST) works to reduce both surface roughness and surface energy with minimal thickness modification to the pipe walls.

While lab-scale and mid-scale experiments have shown the OST to be effective for a range of solids deposition scenarios, full-scale field trials require additional information to de-risk new technologies and validate that small scale data is applicable for deployment activities. In this work, simulations were performed which took parametric data from lab-scale results and applied them to a full-scale pipeline. Additionally, lab-scale survivability tests under a range of thermodynamic and chemical conditions were conducted, extending the range of conditions for which the surface treatment has been validated. Finally, application techniques were demonstrated on a 20" pipeline, showing that in-situ application including surface preparation and material application can be scaled up from lab scale without compromising coverage, adhesion, or surface roughness characteristics.

Simulated Treated Pipeline

Modeling was conducted using the CSMHyK (CSM Hydrate Kinetic) film growth model, which is utilized as part of a full-scale transient multiphase flow simulator (Qin 2020). The simulation is based on an existing field known to have hydrate formation challenges which includes a 3.2 km long, 4-inch OD, uninsulated horizontal pipe. The operating pressure in the flowline is about 1,200 psia. The reservoir produces a black oil with 10 vol.% water cut and approximately 60 vol.% liquid loading. The average liquid velocity in the pipeline is set to 0.8 m/s (3 kg/s) for this simulation. Both steady state and transient (shut in followed by a restart) simulations were performed, as historically transient conditions represent a minority of operations, but are the most high-risk scenarios from a hydrate-formation perspective (Makogan 1996). The transient state simulations included a 1-day shut-in and subsequent 7 days of restart with 4 hours of ramp up to return to the steady state flow rate. The steady state simulation was a 7-day constant flowing simulation. The ambient temperature outside the pipe was 5°C. While it has been shown that the treatment can operate both by reducing the surface roughness and the surface energy of the pipe wall, for this simulation, the surface energy was the main parameter of focus. To model the treatment on the pipe, the wettability of the pipe surface was modified to match experimental data. This modification led to changes in the deposition behavior of hydrates in the simulation. Sloughing events were not considered in this model.

Figure 1 shows the pressure drop across the 3.2 km pipeline as a function of time for untreated (restart and steady state) and treated scenarios. Both the untreated cases show an increase in pressure drop over the one week modeled timeframe, indicating that hydrate is building up over this time. A snapshot of the pipeline at the 7-day mark (Figure 2) shows that the hydrate deposit is thickest at the beginning of the pipe section but maintains a fairly consistent thickness of hydrate coating over the length of the pipeline.

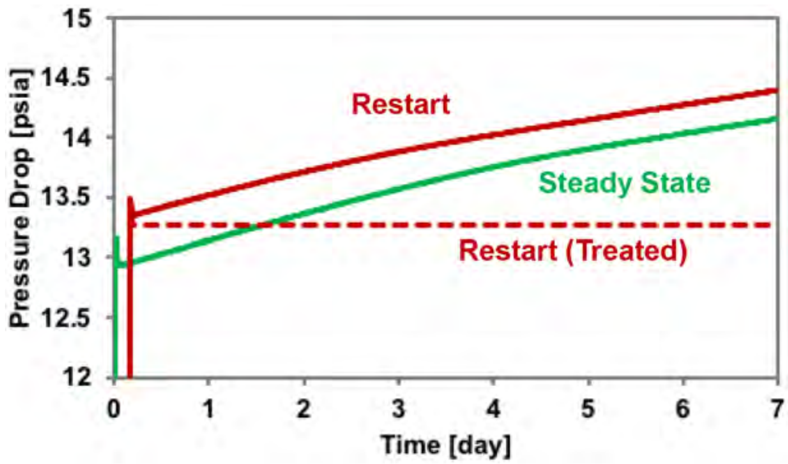

Figure 1—Pressure drop profiles for simulated field conditions.

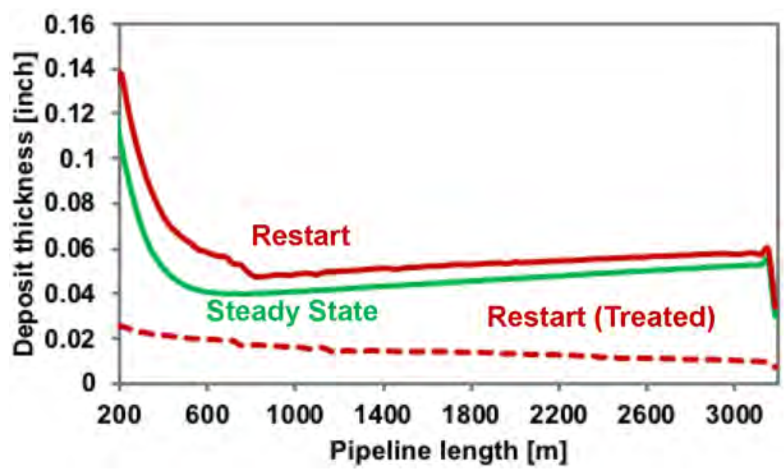

Figure 2—Hydrate deposit thickness at the end of the 7 day simulation as a function of the location along the pipe length.

In contrast, for the treated scenario, the pressure drop remains constant with time, and although some hydrate does deposit on the pipe wall, it appears to not increase the pressure drop. Flowloop tests have also indicated that hydrate does still form in treated systems, but both the nucleation and the deposition may be delayed due to the lowered surface energy of the treated surface (nucleation events for this simulation were not modified). This simulation indicates a much lower risk of developing hydrate plugs than the untreated scenario. Further simulations for higher risk plugging scenarios will be conducted in the future, as more experimental data can be incorporated into the modeling tools.

Survivability testing

Previous publications have shown test results indicating adhesion strength, chemical compatibility, and thermal stability of the surface treatment material (Brown 2017, Pickarts 2020–2022). In order to expand the parameters of these tests, third party Atlas cell testing was used to determine the performance of the material under harsher conditions that more closely mimic subsea pipeline conditions. Atlas cell testing is a standard method for evaluating films and coatings which will be utilized in oil and gas lines. Pressurized testing exposes a coupon to elevated pressures in the presence of three phases (gas, hydrocarbon, and aqueous) of material and holds for a period of time before rapid depressurization. Cold wall testing simulates the temperature gradient that can be experienced across a pipe wall, especially in subsea conditions. Hot fluids which are produced from the wellhead are separated from cold seawater by the pipe wall; this differential can induce a thermal gradient which can cause adhesion loss, blistering, and disbondment of coatings and linings in pipes. In the cold wall test, 3 phases of fluid are held at a high temperature against the treated coupon surface, while the opposite side of the coupon is cooled.

Coupons were shot blasted and prepared to NACE 3 standards prior to application of the treatment material. Quality control was performed using Dry film thickness measurements to verify the material application was consistent. Pinhole detection was performed using a low voltage holiday test, which uses a small current to test whether any pinholes in the treatment exist. Average thickness was 52µm for the pressurized test coupons and 47µm for the cold wall coupons.

For both the cold wall and the pressurized tests, the cells were filled approximately 1/3 with synthetic seawater and 1/3 with a 50/50 mix of toluene and kerosene as a hydrocarbon phase. Finally, the cell was pressurized with nitrogen at 300 psi for the pressurized test, and air at atmospheric pressure for the cold wall test. The Atlas Cell high pressure tests were performed via ASTM D6943-15(2019) "Standard Practice for Immersion Testing of Industrial Protective Coatings and Linings" Method C. Coupons were left for 7 days before depressurization and analysis. For the cold wall tests, ASTM D6943-15(2019) "Standard Practice for Immersion Testing of Industrial Protective Coatings and Linings" Method B2 was used. For these tests, the treated test section was the hot side, which was maintained at 65 °C, while the cold side was maintained at 10 °C. Results from the testing is shown in Figure 3.

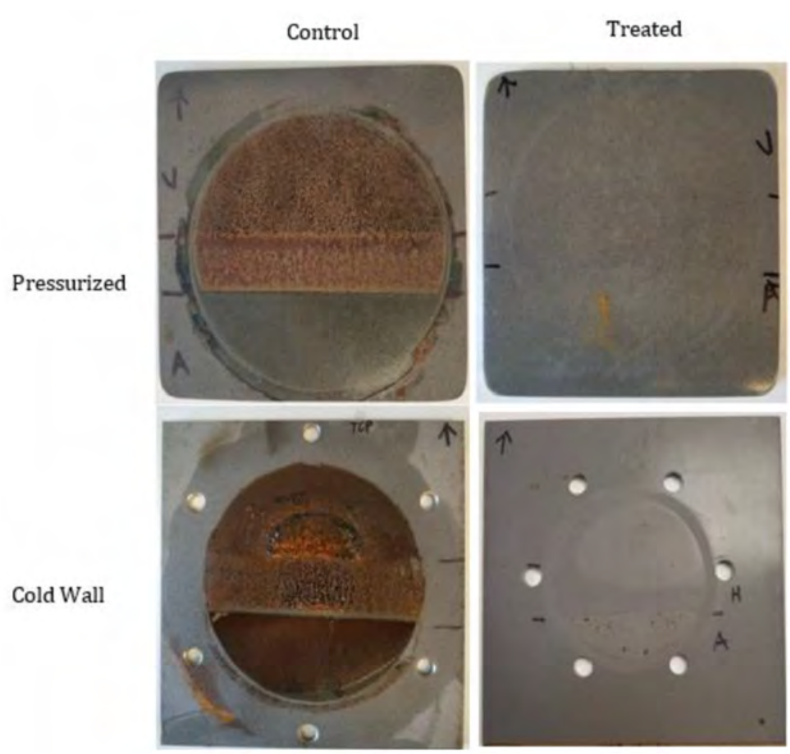

Figure 3—Control and treated coupons after high pressure (top) and cold wall (bottom) exposure.

Treated surfaces were compared with untreated surfaces; the untreated coupons showed significant corrosion in every phase (gas, hydrocarbon, and aqueous). As has been seen in previous trials on atmospheric pressure systems, the treatment material provides a significant barrier to corrosion. The top figure in Figure 3 shows that pressurized conditions had minimal effect on the treated surface. For the cold wall testing, the gas and hydrocarbon phases were unaffected over the test period, but the aqueous phase did show evidence of minor blistering. Holiday testing performed after the cold wall trials indicated that the treatment layer was intact even after the blistering, indicating that surface protection may continue even when the treatment becomes damaged in this method. Additional material optimization is underway to minimize the effect of significant temperatures in the aqueous phase.

Application Trial

The OST is capable of being applied using different methods based on the substrate and geometry. For lab scale trials, flat coupons were treated using spray or dip methods, while small tubes were treated using a fill and drain method. Surface preparation is also known to play an important role in optimizing the treatment effectiveness. This application trial demonstrates the ability to apply the treatment to larger diameter pipes while also meeting surface preparation requirements. For this trial, we partnered with a pipeline application expert to apply the surface treatment to 20" diameter pipes in 40' sections. Figure 4 shows an image of the pipe sections used in this trial.

Figure 4—20" pipes to be treated in the application trial.

The three major areas that were the focus of this application were the cleaning/surface preparation, material application, and evaluation of the results. For in-situ equipment, pigging is a common method used to clean and inspect pipelines. Pigs were used in this exercise for both the cleaning stage and the material application. In order to clean the pipes, brush pigs were used to clear off rust and debris before foam swabs were used to clean the surface of the pipeline. This initial cleaning is important to provide a more even surface and remove loose rust deposits before the material is applied to the surface. A cleaning surface treatment was then run through the pipe between two pigs to bring the surface to a NACE 4 standard surface preparation.

After the cleaning, the OST material was applied using a pig train (Pretorius 2006). The pigs used and the configuration are shown in Figure 5 and Figure 6 below. Material was loaded into the pipeline such that it filled the space between two pigs, which draw closer together as the material is deposited to ensure that the material always fills the entire pipe diameter. This pig train allows for a thin film of material to be deposited on the walls of the pipeline as the pigs are propelled from the launcher to the receiver. After the pig train has reached the receiver, the pigs and leftover material are collected; the pot life of the material is 72 hours and can be reused for subsequent layers as long as the pipeline was cleaned sufficiently beforehand (i.e., no debris has accumulated in the material). Dry air through the pipeline between layers allows the material to fully cure. While the number of layers may depend on parameters including initial surface roughness and the intended fluid in the pipeline, each layer cures quickly, allowing for efficient thickness building as necessary. Two passes were applied for this trial to ensure complete coverage.

Figure 5—Pigs used for treatment application in pipelines.

Figure 6—Illustration of the pig train used to apply material in-situ.

During this process, the surface of the pipeline was characterized at each step for surface roughness, and the thickness of the OST material was measured after each layer had dried completely. Table 1 shows a summary of these measurements, indicating a significant decrease in the surface roughness of the pipe wall from the original state to the completed treatment. Inspection of the pipelines after the treatment was completed concluded that no apparent holidays or bare areas could be detected. Finally, the adhesion of the treatment was evaluated using ASTM D-3359-95 Method A- X-cut, wherein a blade is used to score the treatment in an X-pattern down to the pipe surface. A NACE-approved tape is adhered to the surface above the cuts and then subsequently removed. Adhesion of the treatment to the surface is characterized on a scale ranging from 0A (complete removal of the material) to 5A (no detectable peeling). Tests in multiple areas on the surface were characterized as 5A for this trial.

Table 1—Quality control parameters for the trial application.

Stage	Surface Treatment DFT (mil)	Surface Roughness (µinch)
Pre-cleaning	-	≥2000
Before Treatment	-	420-500
1st treatment	0.18-0.43	180-330
2nd treatment	0.56-1.14	160-260

Based on the results observed in this application trial, it was estimated that sections of at least 20 miles in length could be prepared and treated using this method. Scaled up application such as using these established industry methods, lowers the implementation risk for this technology, while foreknowledge of application challenges allows for a higher chance of success once this technology is field trialed.

Conclusions

Connecting tests performed on lab scale apparatuses such as rocking cells and flowloops with larger-scale deployment data is an important step towards field deployment of this surface treatment technology. Modeling efforts which incorporate lab data into commercial scale scenarios showed that hydrate blockages are less likely when the surface treatment has been applied based on a reduction in wall wetting and hydrate adhesion caused by the OST. Hydrate risk is highest in the field during shut-in scenarios, but these modeled cases indicated that application of a surface treatment may be a suitable replacement for costly chemical injection or thermal management. As the "do nothing" approach is the most ideal management scenario for hydrates, it is an important step toward risk management and safety standards to have a solution which has shown itself to passively mitigate hydrate risk even during a shut-down and restart.

While it is not possible to perform lab compatibility tests under every possible chemical and thermodynamic scenario, scaling technologies by looking at possible failure modes is an important step to reducing deployment risks and estimating the possible lifespan of new materials. Atlas cell testing showed that the surface treatment was able to weather extreme conditions and provide protection for the pipe surface even when compromised.

Finally, application trials demonstrated the ease of application for even large-scale deployments. While application methods had to be modified to meet the challenges of full-scale pipeline sizes rather than the lab-scale that it was previously demonstrated on, quality control measures indicated that the preparation and treatment were highly successful at a scale 10x larger than the lab-scale flowloop which has been used previously to demonstrate the surface treatment's performance. Taken together, these efforts are important steps in technology maturation and scale up. Each step taken to de-risk the technology and provide better background expectations helps as the surface treatment moves towards field trial and eventually full-scale deployment.

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