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Evaluation of a Robust, In-Situ Surface Treatment for Pipeline Solids Deposition Mitigation in Flowing Systems

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Abstract

The formation/precipitation and deposition of pipeline solids, such as gas hydrates, asphaltenes, and waxes have long plagued production fields. Given the vast differences in chemistries of these solids, any current prevention or mitigation strategy, particularly for cases where multiple issues are a concern, is likely to involve an extensive assortment of undefined chemical additives that are both costly and add complexity to the system. Surface treatments (coatings), on the other hand, present a relatively new viable option for management strategies. A chemically and physically robust surface treatment with the ability to address deposition issues for multiple pipeline solids could not only decrease the operating expenditures for a field through material cost savings and obviation of downstream separation, but could also simplify produced fluids by eliminating additional chemicals from the mixture.

The purpose of this study is to explore the feasibility of a particular surface treatment as part of a solids management strategy. This work utilizes an omniphobic surface treatment to probe its effects on gas hydrate, asphaltene, and wax deposition. Specifically, high pressure rocking cells are employed to study gas hydrate nucleation and deposition. A bench-scale flowloop filled with crude oil and heptane is used to quantify the deposition of crude oil and asphaltenes after a set time period. Lastly, a mechanical shear device measures the adhesion force of wax deposits on untreated/treated surfaces.

The gas hydrate rocking cell tests demonstrate an increase in induction time and occasional elimination of hydrate nucleation with the surface treatment. Moreover, the same apparatus indicates that the critical shear to avoid hydrate deposition may be lowered in the presence of the surface treatment compared to untreated pristine carbon steel coupons. A custom-built asphaltene flowloop then establishes that this surface treatment is effective in dramatically reducing the deposition of the aliphatic components of a crude oil, with a moderate reduction in the asphaltene fraction. Finally, mechanical adhesion force measurements for solidified paraffin wax display trends in agreement with the asphaltene results. The surface treatment on both pristine and corroded surfaces is able to reduce the adhesion of wax deposits to values below a pristine, untreated surface.

Introduction

Flow assurance has been coined as a type of engineering specifically tasked with ensuring a safe and steady production from systems such as oil or gas fields. Particularly for crude oil, production fluids can be quite complex, comprising a large number of components. Many issues, which can hinder or arrest flow, derive from these. This includes the formation of pipeline solids, most notably gas hydrates, asphaltenes, and waxes. Overall, these species contribute to alterations in fluid properties (viscosity changes), multiphase flow (slugging events), and flow area (stenosis through deposition) (Ahmed, 2007).

Gas hydrates are crystalline water compounds capable of formation above the ice point. At high pressure and low temperature conditions, water molecules orient into cage structures, collecting gas molecules within them (Sloan & Koh, 2007). After formation, these compounds have been observed to progress towards aggregation and deposition where accumulation and jamming ensue (Aman et al., 2018; Nicholas et al., 2009; Srivastava et al., 2017; Turner et al., 2005). Current mitigation strategies focus on complete prevention through chemical and/or thermal measures (Sloan & Koh, 2007). Recent studies have examined the application of management strategies for systems facing OPEX constraints (or unplanned shutdowns), utilizing internal properties and external means to retard nucleation and promote a stable slurry flow (Creek et al., 2011; Kinnari et al., 2015; Turner et al., 2015).

Asphaltenes constitute the most polar element of crude oil. They are defined as the fraction insoluble in paraffinic solvents such as n-pentane or n-heptane, yet readily disperse in aromatic compounds like toluene (Langevin & Argillier, 2016). While hydrates may be considered the most dangerous pipeline solid due to their plugging timescales, asphaltenes may be the most challenging. The composition and properties of the asphaltene fraction vary widely depending on the crude oil studied, often leaving discrepancies in their reporting. For example, order of magnitude differences are stated for properties as fundamental as molecular weight (Mullins, 2011). As a result, attributes of asphaltenes and the mechanisms of their deposition remain unclear. Nevertheless, prevention and remediation methods have been developed. Chemical inhibition has been attempted, although not with much success (Montesi et al., 2011). More reliable methods of remediation revolve around polar solvent injection (xylene) and routine pigging (Mansoori, 2010).

Waxes make up the heavier hydrocarbon components of crude oil. As the temperature decreases in a system, it may eventually cross the wax appearance temperature. Here, paraffin components crystallize out of solution where they may eventually deposit on the pipe walls (Lira-Galeana & Hammami, 2000). Similar to asphaltene remediation, both chemical and mechanical means are available to address wax deposits. While periodic pigging is perhaps the oldest and most commonly employed strategy, inhibitor and solvent chemicals have been also used (White et al., 2018).

As deduced from the above descriptions, methods to clear hydrate, asphaltene, and wax deposits are wide ranging, particularly for situations where chemical injections are involved. Should a production system face one or more of these issues, the remediation methods could quickly lead to expensive operating expenditures and further complicate an already complex system by the addition of chemicals. Another mitigation strategy that has typically only seen application in the laboratory yet has shown much promise for addressing these issues is coatings/surface treatments. Several studies focusing on hydrates have been published demonstrating how hydrophobic coatings may ease deposition and adhesion (Brown et al., 2017; Pelletier, 2017; Pickarts et al., 2019; Smith et al., 2012; Sojoudi et al., 2018; Sojoudi et al., 2015). Furthermore, waxes and asphaltenes have fallen into similar investigations as well (Bai et al., 2019; Pickarts et al., 2019; Rashidi et al., 2016). Particularly, one study suggests that the mechanism for wax adhesion focused on the surface roughness rather than the chemistry, where smoother surfaces reduce wax adhesion and avoid deposition (Hunt, 1962). This finding appears to be corroborated with a recent study of a smooth hydrophobic coating that reduces hydrophilic scale and hydrophobic waxes in flowloop and field trials tests (Bethke et al., 2018). Therefore, it appears that smooth coatings possessing hydrophobic properties may be able to address multiple flow assurance issues simultaneously, precluding/reducing the need for chemical injection and periodic mechanical removal. This could represent a major cost savings for production systems with successful implementation.

Unlike many previous studies, this ongoing work performs a comprehensive analysis, investigating gas hydrates, asphaltenes, and waxes with one surface treatment capable of in-situ application to corroded pipes. Its purpose is to bring laboratory results into reality by methodically working towards more industrially relevant testing scenarios (i.e. fully flowing, large-scale systems with multiple solids present). In this particular work, deposition and adhesion results for the three solids listed above are shown to demonstrate the extensive application potential of the surface treatment.

Methods and Materials

Omniphobic Surface Treatment

This work serves as an extension and expansion to a previous study, employing a surface treatment that has been described in detail earlier (Pickarts et al., 2019). In short, it can be characterized as a water-dispersible, low viscosity, nano-structure polymer topcoat capable of in-situ application to existing materials. It has demonstrated excellent physical integrity, with respect to industrial standards for erosion, adhesion, and wear, as well as broad chemical resistivity to compounds such as aliphatic and aromatic hydrocarbons. Finally, the application properties of this surface treatment are quite extensive where it may be sprayed, dipped, or flood-and-drained onto a number of surfaces including metals, concretes, and deposits.

Rocking Cells

The rocking cells utilized in this study are identical to those described in the prior work. The entire rocking unit contains three individual cells (3000 psig maximum operating pressure, ~30 mL each), which are composed of a stainless-steel body, sapphire glass windows, and a pressure transducer. See the previous work for a schematic of the individual cell (Pickarts et al., 2019). Together, these allow for visualization and quantification during high pressure, low temperature gas hydrate deposition tests. Hydrate subcooling and fluid shear are controlled through the cell's pressure-temperature conditions and the rocking rate applied by the motor, respectively. With these types of tests, the rocking cells may probe hydrate nucleation (through absolute pressure reduction) and deposition behavior (through visual observation) in the presence of untreated/treated coupons.

As before, tests are performed as an isochoric process. Untreated/treated coupons are inserted into each cell along with the desired amount of a model oil and deionized water and then pressurized at room temperature with a 74.7/25.3 mol.% methane/ethane mixture, typically to 500 or 1000 psig. Hydrates form as the temperature of the cooling bath surrounding the cells decreases at a set rate, and tests conclude either after a predetermined experimental testing time or when the deposition is observed.

Bench-Scale Asphaltene Deposition Loop

Asphaltene deposition was investigated through a custom-built, atmospheric pressure, bench-scale flowloop whose design was inspired by previous asphaltene studies (Ghahfarokhi et al., 2017; Salimi et al., 2016). It is comprised of a fluid reservoir for the precipitation of asphaltene particles in a 12.5 mL/g heptane/crude oil mixture, a peristaltic pump for a fluid flow of 43.93 mL/min, and a carbon steel deposition testing section (43″ length, 0.12″ inner diameter, untreated/treated). Experiments are conducted for a predetermined experimental testing time of 4 days. The results obtained from this device include a quantification of the amount of total deposited material (all fractions of crude oil) and the asphaltene fraction alone. Ultimately, the purpose of the apparatus in this study is to explore the deposition tendencies of precipitated asphaltene particles without and with the surface treatment.

Solid Adhesion Testing Apparatus

The adhesion strength of solid paraffin wax was measured without/with the surface treatment on flat coupons. The experimental setup for this is constructed in a similar fashion to those used in ice and atmospheric pressure hydrate studies (Beeram, 2017; Meuler et al., 2010; Pelletier, 2017; Smith et al., 2012). A force meter with a solid probing arm is mounted on a manipulator stage, with the ability to move toward or away from the testing sample. In this case, the sample is approximately 0.5 grams of resolidified paraffin wax placed inside a square cuvette. As the probing arm is brought into contact near the base of the wax-filled cuvette, the force measured by the meter steadily increases. A sudden decrease in the measured force is observed at the point of failure and the maximum force preceding this event is taken as the adhesive force of the wax on the coupon. From this, critical shear values based on these force measurements are computed. At least 6 experiments were conducted for pristine untreated/treated and corroded untreated/treated coupons.

Results and Discussion

Gas Hydrate Nucleation

A "no-touch" time policy is often exercised by industry during unplanned shut-downs to determine the amount of time available before hydrate prevention/remediation strategies must be enacted (Hudson et al., 2000). Any possibility of increasing this time is of great interest as it would relieve time stresses and help avoid costly non-optimal strategies during turbulent times. The purpose of this part of the rocking cell study is to determine whether the surface treatment can have any positive impact in this respect. Since rocking cells operate as constant volume systems, a sudden and rapid decrease in the cell pressure indicates gas hydrate nucleation and growth. Consequently, rocking cell deposition tests are excellent tools that can provide insight into changes in hydrate induction times due to the surface treatment.

A subset of the hydrate nucleation results is delineated in Table 1. A total of three test series with 3 individual cells per test series are shown. Here, all experiments were conducted with 50% liquid loading (model oil + DI water) and 5% water content in the presence of untreated/treated steel coupons. Cell rocking was performed continuously throughout each test.

Table 1—Induction time data determined from cell pressure reduction for several test sequences. Results show the presence of the surface treatment may have a positive effect on induction times.

Test Series	Coupon Coated?		Induction Time [hr]	$T_{subcooling}$ [°C]	Comments
1	Cell 1	No	21.5-36	~13	Cell 3 No Nucleation
	Cell 2	Yes	21.5-36		
	Cell 3	Yes	>83		
2	Cell 1	No	7	~13	Cell 2 No Nucleation
	Cell 2	Yes	>147.5		
	Cell 3	Yes	67		
3	Cell 1	No	97	~8	Cell 3 No Nucleation
	Cell 2	Yes	104		
	Cell 3	Yes	>231		

As seen in Table 1, the presence of the surface treatment on the coupon clearly affected the induction times of gas hydrates positively. In each test series, the untreated coupon nucleated first, typically on the order of hours for high subcoolings (7, 21.5 hours) and within a few days (97 hours) for intermediate subcooling. Treated coupons, on the other hand, formed hydrates several hours (21.5 hours) to days (67, 104 hours) afterward. Furthermore, at least one of the two treated coupons in each test sequence never nucleated (>83, >147.5, >231 hours), despite sometimes spending over a week within the hydrate stability zone. While these results are very promising, further experiments at higher subcoolings are required to reduce stochastic effects and isolate the surface treatment's intrinsic effect on hydrate induction.

Gas Hydrate Deposition

In the previous work related to this surface treatment, rocking cell tests conducted at 1000 psig and 13 °C subcooling showed that treated steel coupons could repeatedly resist the deposition of hydrate agglomerates for the entire experimental length (24-72 hours), while untreated coupons failed (Pickarts et al., 2019). The second part of this recent rocking cell study delved into this further and focused on qualitatively ascertaining critical shear rates that prevent hydrate deposition for untreated and treated surfaces. A number of different parameters such as geometry, flow patterns & rates, and fluid properties can all affect the shear experienced at the pipe walls in a production system, with some areas having low shear, which makes them vulnerable to solids accumulation. The ability to reduce the shear required to prevent an irreversible adhesion of solids to the pipe surface would be greatly beneficial as it could reduce the amount of risk-prone areas in the system.

For rocking cells, the shear experienced at the surface of the coupon is inherently related to the rocking rate of these cells, which can be controlled by the speed of the motor. While an exact quantitative value of shear is nearly impossible to calculate for these devices, one can benchmark results through comparison of rocking rates required to avoid hydrate deposition for a set time period. Whether or not the surface treatment reduces the critical shear to avoid deposition compared to an untreated sample can be determined in this way.

As before, the rocking cell tests were performed with a model oil and DI water at 50% liquid loading and 5% water content. Cells were initially pressurized to 500 psig before cooling. Figures 1 and 2 illustrate the outcome (pass or fail) of each test for untreated and treated coupons at 25 and 30 rocks per minute.

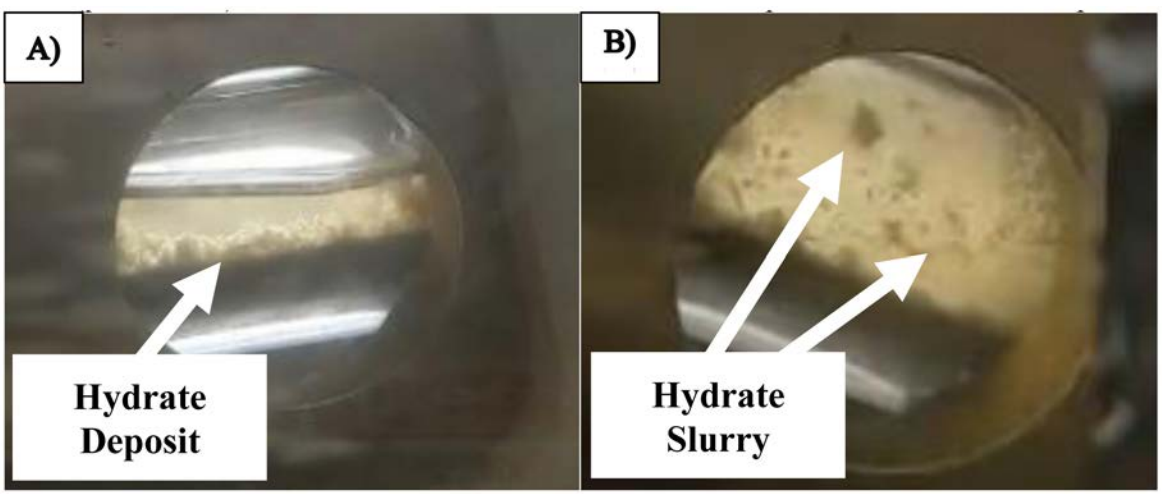

Figure 1—Hydrate deposition tests for untreated coupon. A) Deposit formation at 25 rock per minutes. B) Slurry without deposition formation at 30 rocks per minute.

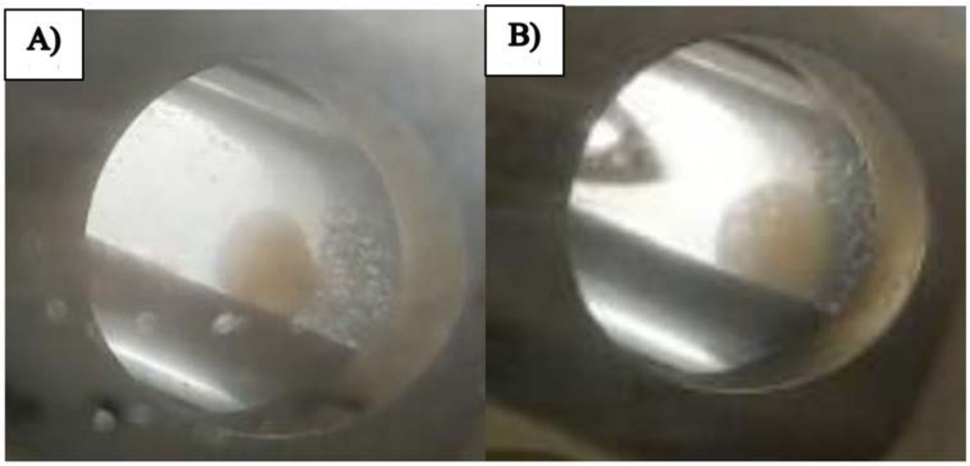

Figure 2—Hydrate deposition tests for treated coupons. A) Balled agglomeration without deposition at 25 rocks per minute. B) Balled agglomeration without deposition at 30 rocks per minute.

From Figure 1 B) and 2 B), it can be seen that the higher rocking rate of 30 rocks per minutes provided enough shear to avoid the deposition of hydrate particles and agglomerations for both untreated and treated surfaces. The results, however, diverged at 25 rocks per minute, Figures 1 A) and 2 A). The untreated sample in this case experienced significant deposition of hydrate particles on the face of the coupon, while the treated sample exhibited a similar behavior as that seen at 30 rocks per minute. These observations signal that a critical shear value exists between 25 and 30 rocks per minute for an untreated coupon, where hydrate deposition may be avoided. Moreover, the successful resistance of hydrate deposition by the treated samples at the same rocking rates also indicates that critical shear value to resist hydrate deposition is lowered compared to the untreated surfaces. Ongoing tests are being conducted to determine the rocking rate at which the treated samples may fail.

Precipitated Asphaltene Particle Deposition

While hydrates often garner significant attention due to the timescales at which they form, they do not represent the totality of flow assurance concerns, as other pipeline solids may be present. Asphaltenes are sometimes considered to be the most challenging pipeline solid, as much about them remains relatively unknown. Therefore, when developing a technology for field application, it is imperative to ensure its universal compatibility with other materials present to avoid potential deleterious effects. In other words, it is important to ensure a surface treatment developed to prevent hydrates does not promote asphaltene deposition.

Here, a bench-scale asphaltene deposition flowloop was used. Asphaltene particles were precipitated from a crude oil (28 API, 4.48% heptane asphaltenes) and deposited onto a carbon steel testing section. In total, 5 experimental trials were conducted for an untreated tube and 3 for a treated one. Total deposit amounts (all fractions of oil) and asphaltene alone are reported in Figure 3 below.

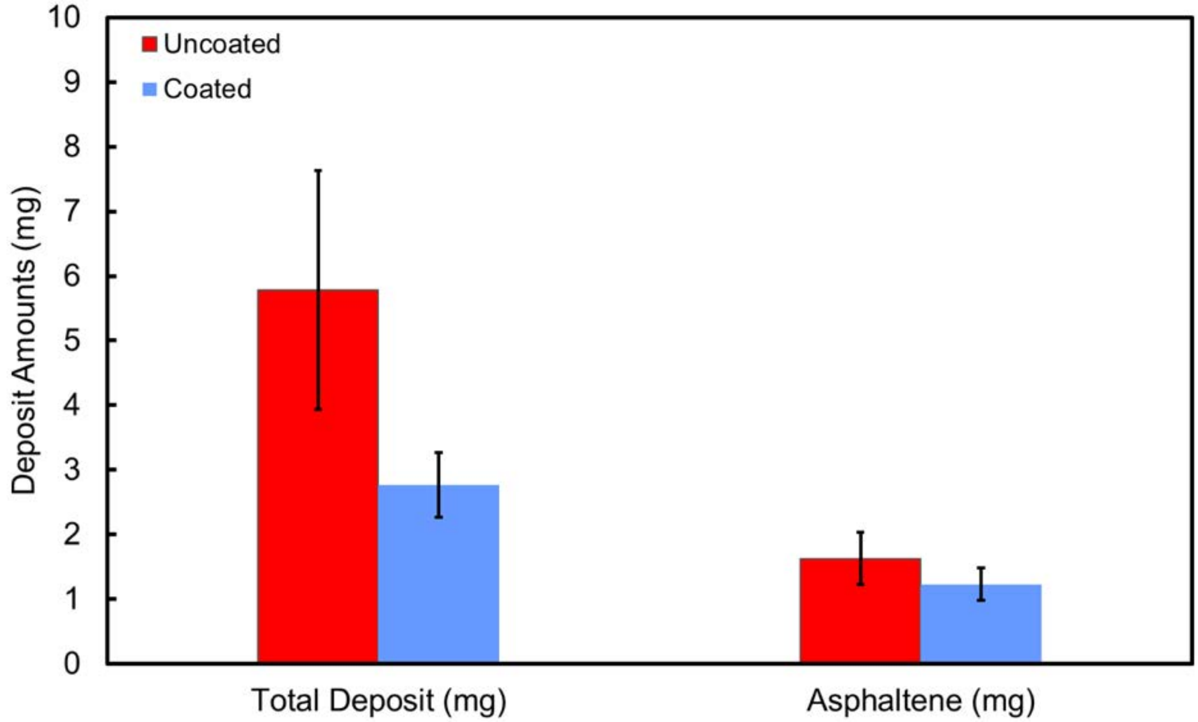

Figure 3—Asphaltene flowloop results showing the amount of total deposit (left) and asphaltenes alone (right). The surface treatment appears to reduce most significantly the amount of the total deposit.

It is clear from Figure 3 that the total amount of deposited material decreased due to the coating by about half, falling outside the experimental error, and is far more significant that the amount of deposited asphaltene particles. While the set of bars on the right indicate that a small reduction is observed, this change falls within the experimental error and is therefore not entirely conclusive. Additional trials are necessary to substantiate any conclusion drawn about asphaltene deposition. In light of these results, positive takeaways about the surface treatment include: (1) it shows resistance to the deposition of aliphatic compounds (crude oil fractions not only including asphaltenes) and (2) at the very least, it does not display an antagonizing effect with respect to asphaltene deposition (i.e. the worst case scenario is that asphaltene deposition remains unchanged with the surface treatment). The next steps would be to perform testing on corroded untreated and treated surfaces, which may display greater differences for the total/asphaltene deposit (as shown for hydrates and wax).

Wax Adhesion Testing

In addition to the interesting findings from the asphaltene study, waxes were considered in this study. Similar to the reasoning described in the gas hydrate deposition section, paraffin wax adhesion measurements were taken using a mechanical scraping device first before moving towards deposition testing to see if the surface treatment could reduce the critical shear necessary to prevent wax deposit formation. Testing conditions included both untreated and treated pristine and precorroded surfaces for 4 total surface conditions. Critical shear values were determined by dividing the measured adhesion force by the contact area of the deposit and are shown in Figure 4.

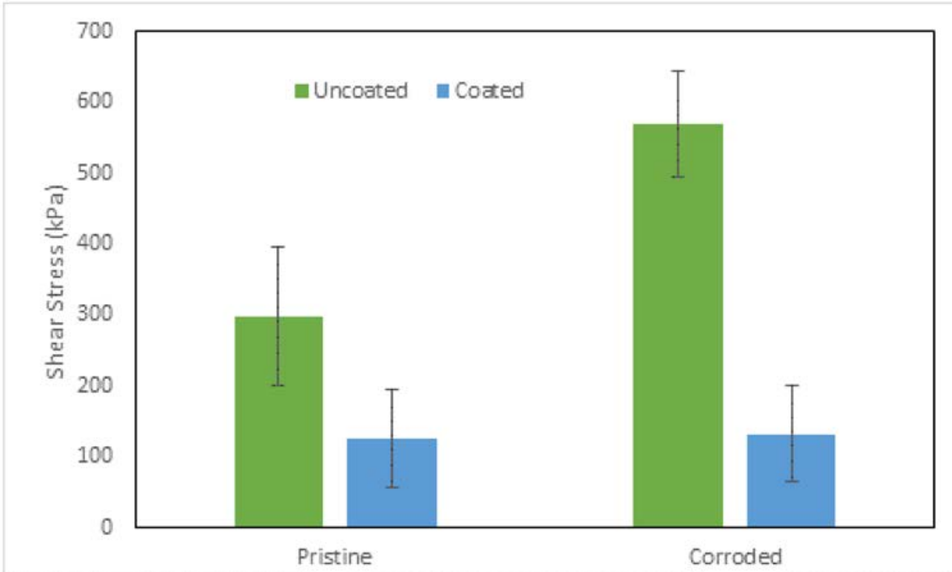

Figure 4—Shear removal calculations from measured adhesion force of paraffin wax on pristine and corroded untreated and treated surfaces. A reduction in the shear is observed when comparing treated to untreated for both cases: 3x for pristine and 5x for corroded.

It was observed that the treatment on both pristine and corroded surfaces led to a reduction in the required shear to remove a wax sample from the surface. For untreated cases, pristine coupons needed shears around 300 kPa. Corrosion of these surfaces subsequently almost doubled the required shear to 570 kPa. After treatment, these coupons were restored to better than new conditions. Pristine samples reduced by almost a factor of 3 to 125 kPa, while corroded samples decreased fivefold, reaching similar values as the pristine at 130 kPa.

Further visual analysis of the surfaces after testing provided more insight into the shearing behavior of the wax deposits. For untreated cases, wax deposit removal was typically a combination of wax-wax (cohesive) and wax-steel (adhesive) breakage. This suggests that the wax-steel interaction may be even stronger than what has been measured here (Figure 4). Furthermore, if applying this observation to a flowing system, it appears that attempted shearing off of a wax deposit (perhaps through increased fluid flow rate) may not completely solve this issue as residual wax deposits may remain. On the other hand, treated coupons experienced complete wax removal with no residue remaining, suggesting that shearing would lead to a complete elimination of accumulated waxes.

Conclusions

The management of pipeline solids, such as hydrates, asphaltenes, and waxes, is a critical focus of the flow assurance community, particularly with processes like deposition. The fact that one, some, or all of these could be occurring simultaneously in a system and all possess great differences in chemical makeup and properties leads to a complex array of possible combinatorial chemical additions as prevention and/ or mitigation strategies. Therefore, having the technology to resist even just more than one of these solids with only one in-situ material (such as a surface treatment) would represent a huge leap forward for flow assurance concerns by simplifying management strategies and amplifying savings through operating cost reduction. This study investigated the use of an omniphobic surface treatment as a possibility for such an application. The scope encompassed several major pipeline solids that are relevant to industry, which include gas hydrates (high pressure rocking cells), asphaltenes (bench-scale deposition loop), and waxes (mechanical shear apparatus).

From the high pressure rocking cells, the results suggest that hydrate nucleation may be severely delayed and critical shear values to avoid particle deposition may be lowered by the application of the surface treatment to a carbon steel coupon. Together, these result in a possible synergistic effect where "no-touch" times could be increased for unplanned shutdowns due to increased induction times and in the case of formation, greater operating confidence inside the hydrate stability zone can be achieved through less deposition risk in low shear areas.

Then, the asphaltene deposition loop showed a clear and significant reduction in the overall deposition of crude oil with the surface treatment. A positive yet smaller impact on the asphaltene fraction alone was also observed. Although additional tests are required to confirm this trend, it was unequivocal that asphaltene deposition was not exacerbated by the surface treatment.

Finally, a mechanical wax adhesion study demonstrated that the surface treatment could dramatically reduce the shear required to remove paraffin wax from pristine and corroded surfaces, transitioning them into better-than-new conditions. This trend agrees with the results obtained from the asphaltene work where aliphatic groups of the crude oil did not deposit as readily in the presence of the surface treatment.

While the previous study showed promise for surface treatments decreasing hydrate deposition, the recent results for this surface treatment have shown even more promise in the laboratory setting, this time in an expanded scope of several major pipeline issues beyond gas hydrates. This signifies another positive step forward in this comprehensive solids management study. Future actions will focus on pipeline solids testing in industrially relevant scenarios, particularly high pressure flowloop and multiple species testing.

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