Development of Thin Sol-Gel Coatings for Heat Exchanger Fouling Mitigation at Elevated Temperatures

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ABSTRACT

Fouling of heat transfer surfaces can be a significant challenge for oil and gas operators, requiring regular maintenance and cleaning procedures to ensure efficient, safe and reliable operation. Polymer coatings have been used to some extent to mitigate fouling in shell-and-tube (S&T) exchangers, but these coatings have historically suffered from poor reliability – especially at temperatures above 150 °C – and compromised heat transfer efficiency owing to their thick, insulating nature. Alternatively, hybrid organic/inorganic sol-gel (SG) coatings can be formulated to exhibit repellency towards a broad range of organic and inorganic fouling species encountered in crude oil and hydrocarbon processing. Primary attributes of the spray-applied SG coatings include low surface energy, chemical- and wear-resistance, flexibility, and low thickness ensuring high heat transfer efficiency as well as mechanical and chemical durability. Here, we describe the development, test and application of high-temperature sol-gel (HTSG) coatings onto stainless steel materials , and demonstrate their stability at temperatures exceeding 315 °C in crude oil, and in saturated steam at 185 °C. Crude oil fouling rates for HTSG coated tubes are significantly lower than those for uncoated tubes and, more importantly, accumulated deposits are removed at shear stress values corresponding to typical operating conditions in commercial heat exchangers. We also report and describe efforts to scale-up the technology for deployment to the field, on commercial S&T exchangers.

INTRODUCTION

S&T heat exchangers are used in a wide range of applications in contact with crude oil. Fouling occurs via unwanted deposition of particulates, impurities, salts and various organic species onto heat transfer surfaces during processing of crude oil and other fluids. Fouling reduces the overall heat transfer efficiency thus increasing energy consumption of the unit. Severe fouling can lead to production interruptions and even equipment failure. To reduce energy loss, risk of production interruptions, and maintain efficiency of heat transfer, frequent service processes are typically required.

To avoid fouling issues in plate and frame heat exchangers thin oil repellent coatings have successfully been utilized and show excellent stability and repellency in crude oil coolers (Santos et. Al., 2013, Holberg and Bischoff, 2014). More recently, the coating technology has been qualified for use in S&T exchangers (Bischoff et. Al., 2015), with a field trial being tested at present. However, for operating at higher temperatures, the coating must be tailored to overcome these new demands. One of the main limitations of classical organic-inorganic hybrid sol-gel coatings are their relative low temperature resistance, this is because at temperatures around 200 °C the organic components of the hybrid system start to decompose. Contrary to the hybrid systems, pure inorganic sol-gel coatings have a better thermal resistance but they are very brittle, require relative high curing temperatures (500-700 °C), and typically cannot be applied much thicker than 2 μm without cracking. Such thin coatings therefore require a very controlled surface preparation to ensure tubes have sufficiently low surface roughness for the coating to evenly cover the substrate. The HTSG coating that we present here, is an organic-inorganic hybrid coating prepared through a sol-gel method that complies the thermal resistance characteristics of pure inorganic systems but without the thickness and brittleness constraints. The coating is easily applied by spraying and able to coat complex geometries. Furthermore, the repellent properties of the HTSG coating are achieved without the addition of high cost, environmentally-sensitive fluoro-derivatives.

METHODS

The HTSG coating was applied onto either 1) AISI 316L stainless steel (AISI 316L) coupons cut to size by either a saw or using a pneumatic scissor or 2) stainless steel 316 (SS316) tube sections supplied in the required length.

The HTSG coating was applied by conventional High Volume Low Pressure (HVLP) air spray using a SATA mini-jet 4 spray gun equipped with a size 0.8 mm nozzle and pressurized air at 2.5 bar. Following application, the HTSG coating was allowed a brief 10 minute solvent flash-off before the coating was cured for 10 minutes at 80 °C and subsequently 3 hours at 300 °C.

Coating thickness was measured on flat samples with a Bykotest 7500 (Byk-Gardener).

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Adhesion was tested by cross-cut/tape test according to ISO 2409 but with two differences: Tesa Krepp 4331 by Tesa was used as tape and the tape tear-off was repeated three times. The test was rated from 0 (best) to 5 (worst) both after cross-cut and after subsequent tape tear off. Dolly pull-off strength test was also used for assessing adhesion. This test measures the force required to pull a specific diameter of coating off the substrate using hydraulic pressure. Adhesion values were estimated using a Pneumatic Adhesion Testing Instrument PosiTest AT-1 automatic (DeFelsko, USA) in accordance to ASTM D 4541 using dollies (Ø 20 mm) that were affixed to flat coupons using a two-part epoxy adhesive (UHU Plus ENDFEST 300).

Surface energy was measured using a series of polar test inks (Plasmatreat, Series C - Ethanol) with known surface tensions ranging from 28-72 mN/m. The principle of using test inks relies on the observation that a liquid with a lower surface tension than the coating will wet the sample, whereas a liquid with a higher surface tension than the coating will not. Test inks were applied to cleaned samples using a fine brush. If the ink wetted the sample for more than 2 s, the ink was removed and the next higher surface energy ink was applied. This process was repeated until the ink beaded within 2 s of application. This value is reported as the surface energy by the test ink method.

The thermogravimetric data was obtained from Thermogravimetry Analyzer (TGA, TA 951) performed in air over a temperature range of 25 °C to 900 °C at a heating rate of 5 °C / min. Weight-loss/temperature curve was recorded. Additionally, the thermal stability of the coating was analyzed at 300 °C by placing samples, for a defined period of time, in an oven with air circulation.

Coated AISI316L samples were exposed to steam at 185 °C and 150 psig pressure in an autoclave. These studies are intended to address a potential failure mode of the coating for S&T service, where approximately 1-2 hours of continuous steam exposure is anticipated prior to equipment removal from service. The sample was held in place using Teflon tubing and removed from the autoclaves after 2 h, 6 h and 12 h exposures. After each period of steam exposure surface energy was measured for the sample with polar test inks.

Fouling rate of the HTSG coating was measured in a test rig which comprises of a double pipe test section with process flow in the annulus and a constant internal tube wall temperature of 316 °C (600 °F). This is ensured by adjusting power dissipation in a cartridge heater installed inside the inner tube. The cartridge heater was equipped with numerous Resistance Temperature Detectors (RTDs) distributed uniformly within the heated zone which monitored Mean Temperature Difference (MTD) between the test tube and process fluid. Overall heat transfer coefficient U was calculated based on heat balance shown in Equation 1.

$$U = Q / (A*MTD) \tag{1}$$

where Q is absorbed heat measured from process fluid flow rate and temperature increase in the test section (Btu/h); and A is the wetted surface area of the test tube (ft^2).

Fouling resistance R_f was calculated by monitoring changes in U as shown in Equation 2.

$$R_f(t) = 1/U(t) - 1/U_{start} \tag{2}$$

R_f is fouling resistance (ft^2-hr-°F/Btu); and t is time (hr). U and MTD have units of Btu/ft^2-hr-°F and °F, respectively. A constant flow rate of 10mL/min (corresponding to a velocity of 0.3 cm/s; shear stress near zero) was kept through the test section. Test fluid was heavy crude with API (American Petroleum Institute) gravity of 14 and a sulfur content of 4 %. The unit operated at a heat flux of approximately 1000 W/m2 and pressure of 3,500 kPa. This was sufficient to assure no vaporization at the heat transfer surface. The rig ran in a circulating mode. However, because of a large process liquid storage vessel, circulation rate was only 3 times per the test duration.

RESULTS AND DISCUSSION

Coating Characterization

Applying the HTSG coating on AISI 316L coupons yielded crack-free, smooth transparent coatings with a dry coating thickness in the range of 4-6 μm. Adhesion was evaluated by the cross-cut test to 0 (best adhesion value, no coating removed). Dolly pull-off strength was measured to 14.17 MPa. TGA analysis (air) of the HTSG coating showed that heating at 5 °C/ min the coating degradation begins at 488 °C, Figure 1

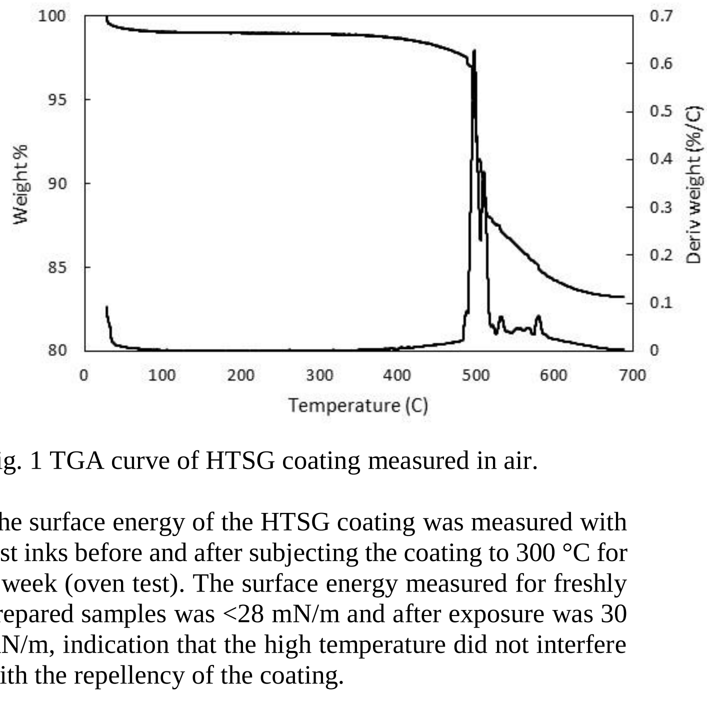

Fig. 1 TGA curve of HTSG coating measured in air.

The surface energy of the HTSG coating was measured with test inks before and after subjecting the coating to 300 °C for 1 week (oven test). The surface energy measured for freshly prepared samples was <28 mN/m and after exposure was 30 mN/m, indication that the high temperature did not interfere with the repellency of the coating.

Steam Out Test

Petrochemical plants steam out the tubes for 12-24 h to remove hydrocarbons. The exposure of the HTSG coating to the steam conditions showed a slight increase in surface energy with increasing exposure time, but generally

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outstanding retention of repellency throughout the 12 h test was observed (Figure 2).

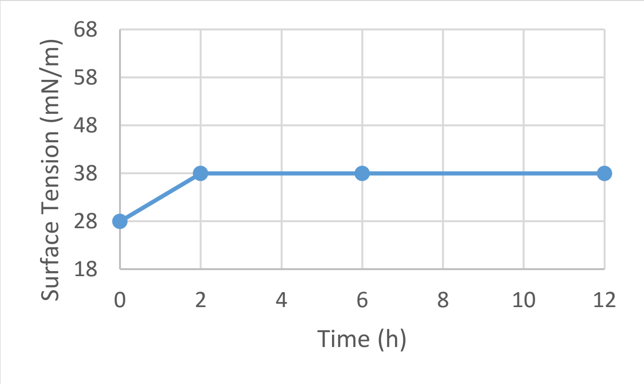

Fig. 2 Surface energy developments of the HTSG coating during steam out test (185 °C, 150 psig pressure).

Figure 3 shows the coating after 6h of steam exposure. No significant changes in the visual appearance of the HTSG coating or thickness as a function of steam exposure time was observed.

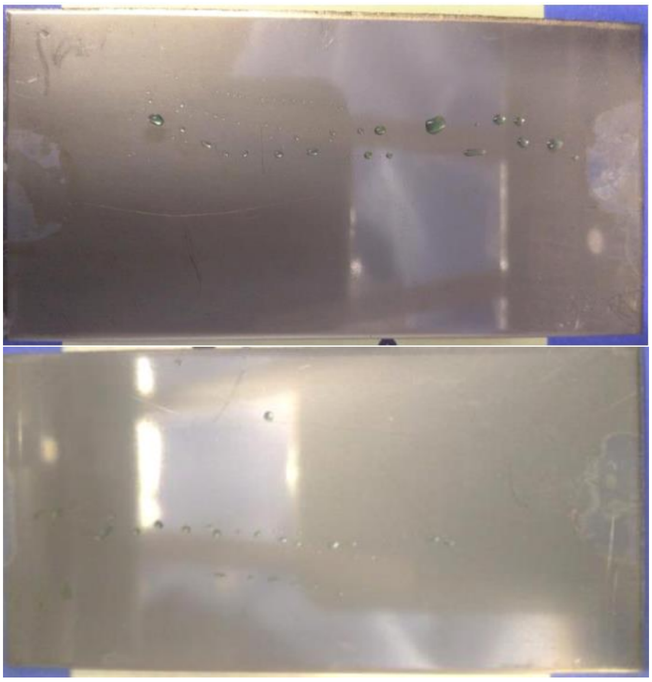

Fig. 3 Samples of HTSG coating after 6 h steam exposure Drops on the sample are from the test ink.

The very promising results regarding steam exposure demonstrate the robustness of the coating as well as its favorable adhesion to the AISI 316L material. The HTSG showed excellent performance and passed the test which is an important parameter for use in S&T exchangers.

Prolonged Fouling Resistance Test

Steam out testing demonstrated that the HTSG coating could withstand the very serve steam environment and also retain its low surface energy. To get a more precise understanding of the coating's repellent nature under operational conditions, the HTSG coating was tested in a dedicated fouling rig. This test simulates the fouling performance in the presence of specific process fluids at elevated temperatures and pressures. Figure 4 shows fouling performance data for the HTSG-coated SS316 tube relative to a bare SS316 tube. Experiments were performed at 316 °C (600 °F) in flowing crude oil.

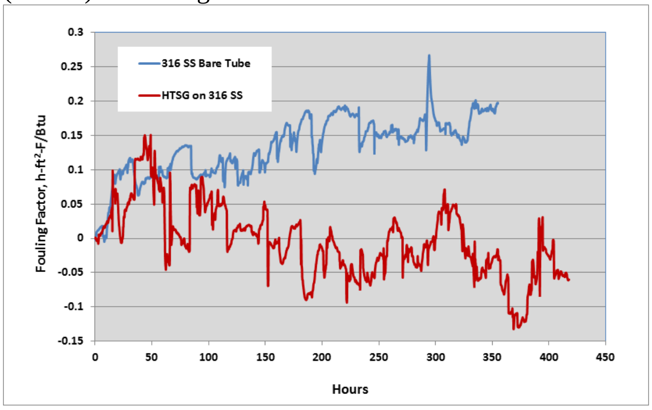

Fig. 4 Comparison of fouling rate for bare SS316 tube (blue) and tube coated with HTSG (red) at 600 °F in flowing crude oil

The fouling rate for the HTSG coated tube is appreciably lower than the uncoated tube after 350 h.

Scale-up for Deployment on Commercial S&T Exchangers

In order to bring the HTSG coating from a laboratory trial stage to commercial manufacturing processes in real S&T exchangers, it is vital to successfully scale-up. A low-temperature sol-gel (LTSG) coating has previously been through rigorous laboratory tests before proceeding to field trials. Prior to the field trials metal surface pre-treatment methodologies and coating application parameters were investigated and evaluated to identify a commercial process that yields consistent thickness, properties, and performance throughout the entire heat exchanger bundle. As of now, the same procedure is starting up for the HTSG coating with an aim for a field trial by the second half of 2017.

CONCLUSIONS

1. The potential for using a newly developed sol-gel coating for fouling mitigation in S&T exchangers operating at 300 °C has been investigated.
2. The HTSG coating showed excellent performance following 12 h test in high pressure steam at 185 °C.
3. Quantitative lab studies show that crude oil fouling rates for a stainless steel coated tube is significantly lower than for an uncoated tube and, as importantly, accumulated deposits are removed at shear stress values corresponding to typical operating conditions in commercial heat exchangers.
4. Based on the promising results development of a reliable manufacturing process for applying the coating to a commercial U-tube exchanger is now in progress.

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