A HOLISTIC APPROACH TO HEAT EXCHANGER PLATE SURFACE DESIGN

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ABSTRACT

To develop a robust heat exchanger surface with excellent mechanical strength and outstanding resistance to fouling and corrosion, while maintaining optimal thermal performance, a series of dynamic procedures were followed. Because conventional procedures often focus on only one or two of the desired surface properties, a completely functional surface is not always achieved. In this work, a holistic approach was applied, which focused on optimizing several desired properties often observed in either metal or polymer coated heat surfaces; our goal being to combine these properties in a single surface. Exposing our heat exchanger surface to sour crude oil at 120°C over a period of more than six months confirmed the robustness of the surface, with sustained thermal performance, significantly less fouling and improved resistance to chemical attack compared to conventional surfaces.

INTRODUCTION

High efficiency heat transfer, from the heat exchanger surface, to the process fluids is of great importance in the industrial operations of heat exchangers. But these industrial operations are frequently affected and interrupted by fouling; a process which results in the buildup of unwanted material on heat exchanger surfaces.

Typical metal based heat exchanger surfaces, such as carbon steel and stainless steel are susceptible to fouling and corrosion, particularly stress cracking corrosion at high temperatures and pressures. The high surface energies of these metal based equipment also make them prone to attract foulants, particularly viscous polyaromatic asphaltenes which readily form on the walls.

Although polymeric based heat exchangers provide an alternative and are considered advantageous over their metal counterparts, in that they are less expensive, lighter in weight, resist corrosion, with minimal fouling, they exhibit inferior mechanical and thermal properties.

Heat exchanger plate surfaces in service are susceptible to the effects of the process fluid they are exposed to. With exposure to the process fluid, surfaces are prone to corrosion, as chemical reactions occur on the surface of the metal. However, the main deficiency arises when a foulant layer is formed from particulates and chemicals in the processing fluid which bind to the surface. As fouling occurs, the thermal conductivity is diminished and the efficiency of the process is impeded, which leads to increased energy consumption, decreased hydraulic performance and inevitable economic losses due to the necessity to have the equipment cleaned regularly.

As a whole, the concept of fouling is a poorly understood phenomenon, primarily because it involves more than one mechanism. Most solutions currently proposed and implemented focus on improving only one or two aspects of the mechanism.

Several methods to mitigate fouling abound in the literature, including process fluid modification, control of process conditions and surface modification processes. Of the different methods employed to mitigate fouling, heat exchanger surface modification processes are the focus of this work.

The most dominant property reported in the literature for modified surfaces is their ability to resist foulant adhesion and buildup. Creating a surface which mitigates fouling will result in improved operation costs (Magens et al., 2015). However, research has established that an optimal surface modification is thermally stable, maintains adhesion to the metal substrate, and reduces fouling, all while maintaining efficient thermal performance. (Gomes da Cruz et al., 2015; Oldani et al., 2013, Santos et al., 2013, Santos et al., 2015). Thus a holistic approach is required to create a robust surface that combines the resilience of a

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polymeric surface with the effectiveness of a metal based exchanger surface when exposed to high temperatures and process fluids.

This work provides as complete a process as possible to bring about a heat exchanger surface with all these desired properties. We report the characterization techniques to validate the expected results, and provide data on long term testing to investigate performance in simulated heat exchanger processes.

EXPERIMENTAL TECHNIQUES

The heat exchanger plate was prepared by modifying the surfaces of aluminum, carbon steel and stainless steel plates. Unmodified plates served as reference surfaces.

The surfaces were modified by spraying a proprietary polymeric material, which was prepared in the laboratory, to a thickness of no more than 89 micrometers, followed by curing at room temperature. Maximum chemical resistance and mechanical properties were achieved after 5 to 7 days. Figure 1 depicts the holistic approach tailored to overcome the current limitations on surface modified heat exchanger surfaces.

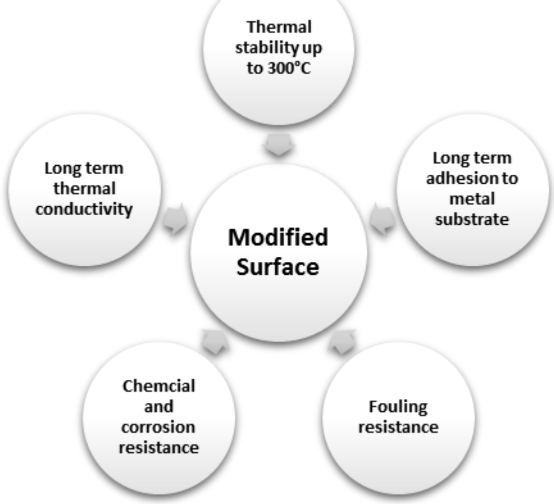


Fig. 1 Holistic process design to ascertain how a robust heat exchanger surface is obtained.

Simulated conditions were achieved through exposure to sour crude containing a high water cut. Sour crude oil is crude oil containing a sulfur content greater than 0.5%. Deionized water was added at a 1:4 ratio with the crude oil in order to further simulated harsh field process fluid.

Methods of Analyses

Thermal stability was determined using thermogravimetric analysis (TGA) methods on a TA Instruments Q500 thermal analyzer. The procedure involved ramping the temperature from 30°C to 600°C at a heating rate of 10°C/min under an inert nitrogen atmosphere flowing at a rate of 60 mL/min. The integral of the weight loss with respect to time was analyzed to determine the rate of mass loss, which speaks to the degree of potential deterioration of the surface modification.

To verify long-term adhesion, tests were performed according to ASTM D3359 and ASTM D4541. The surface was cut using a sharp knife in a lattice pattern and pressure sensitive tape was applied and pulled off the surface. The amount of material delaminated from the surface was used to determine the degree of adhesion, with a 0B being assigned to very poor adhesion and 5B assigned to excellent adhesion. In addition, scribe creep was also tested for by cutting an "X" into the surface prior to exposure to hot sour crude oil. Any portion of the coating that lifted off was then measured.

The ability of the surface to resist fouling, was characterized by investigating the contact angle of water and crude oil droplets, along with the sliding angle of crude oil droplets on the surface using an FTA200 goniometer.

Surface repellency properties, especially surfaces for heat exchanger plates, are commonly characterized by the "permanent marker test" (Holberg et al., 2014; Santos et al., 2013). Given the lack of a standard test method for fouling, additional analysis was completed using, a modified version of ASTM D6943. Sour crude oil was used as the test fluid and the test was at T = 80°C and 120°C, and at t = 1week, 1 month, 5 months and 12 months with intermittent stirring on a weekly basis. This was a semi-static test with the crude oil containing up to 20% water content to simulate field runs and these modified plates were then compared against untreated plates which underwent the same exposure.

For the purpose of examining thermal performance, a quantified measure was obtained by estimating the thermal conductivity of the surface following ASTM E1530. The thermal conductivity was calculated by using heat flow, q and temperature difference, ΔT which were derived from differential scanning calorimetric tests.

The overall chemical resistance and barrier properties of the modified surface play important roles in maintaining the integrity of the modified surface. Electrochemical impedance spectroscopy, following ISO 16773, was employed to measure how effective the surface is as a barrier to corrosive species. The sample was presoaked in an electrolyte, composed of 5% NaCl, for 48 hours prior to testing. The surface was free from any defects including scratches, gouges or dents prior to testing. Bode plots were analyzed by extrapolation to acquire the impedance value at a frequency of 0.1Hz. Additional testing was also done to determine the importance of the condition of the modified surface. SEM analysis was used to note the effects of surface porosity, where the modified plates were exposed to a crude oil and water mixture for 2 weeks. Additionally, to determine the overall chemical resistance and the compact nature of the surface, visual defects such as delamination and surface degradation were measured after 12 months of exposure to process fluids in simulated conditions.

RESULTS AND DISCUSSION

Thermal Stability at High Temperatures

In formulating a thermally stable modified surface, a high crosslink density is desirable to create a network of high thermal stability in the polymer matrix. Therefore polymer building blocks with high functionality were used to generate a high cross link density, while using a blend to ensure enough flexibility is maintained to reduce brittleness.

TGA analyses of the material showed high thermal stability up to 150°C, and less than 5% loss at 300°C (Fig. 2). At temperatures up to 370°C the rate of material loss was still negligible. Furthermore, the unique nature of the polymeric blend prevents complete degradation of the surface material, leaving enough material to ensure further surface protection over the process duration and temperature range.

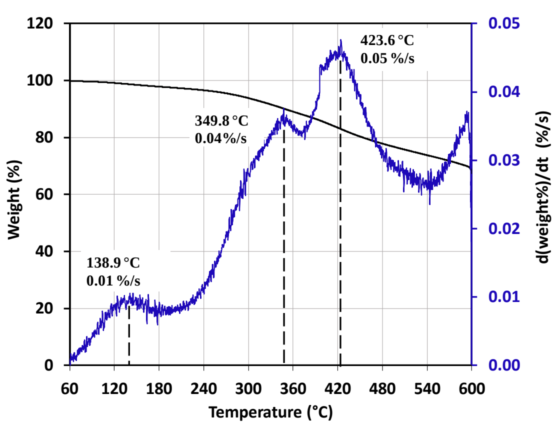


Fig. 2 TGA analysis using a platinum sample pan, at a heating rate of 10°C/min and nitrogen purge rate of 60 mL/min.

Long-Term Adhesion in Simulated Conditions

One major cause of corrosion and deteriorating performance in surface modified heat exchangers is the failure of adhesion to the substrate, especially after exposure to the process fluid.

The proposed modified surface was tested to characterize its adhesion to the substrate. After exposure to sour crude for 5 months at 120 °C, surfaces with stainless steel 316 substrates were found to have an adhesion of 3B, a decrease from 4B before exposure to the process fluid (Fig. 3 *right*). The non-stick properties of the modified surface prevented the use of pull adhesion as a method of evaluation, due to the fact that the specified adhesive would release from the modified surface after only 300 psi. Attempts were made to improve adhesion of the dolly adhesive by abrading the modified surface, however no change was observed. A scribe was cut into the surface of the coating before exposure to the process fluid. Scribe undercutting was measured and was less than 1 mm.

The surface therefore shows satisfactory adhesion to the substrate, even when exposed to the process fluid at elevated temperatures.

Fig. 3 Adhesion tests showing minimum scribe creep (*left*) and satisfactory adhesion (*right*) to the 316SS substrates.

Fouling Resistance in Simulated Conditions

With thermal stability and adhesion to the substrate established, the anti-fouling properties were investigated. Oil and water repellency capabilities were quantified by studying the contact angle properties of the surfaces. It is well established in the literature that contact angle measurements provide information on the wetting properties of a solid surface in contact with liquids. High contact angles (>90°) indicate low wettability or a phobic interaction between the surface and liquid; while low contact angles (<90°) indicate high wettability or a philic interaction between the surface and the liquid.

The measured contact angles of water droplets on the surfaces showed that the surface modification process improved the hydrophobic capacity from 73.53° to 100.07° (Fig. 4). Exposure of the surface to sour crude oil after 12 months showed a slight decrease to 98.24°. These values are comparable to those of antifouling coatings in the literature (Holberg et al, 2014).

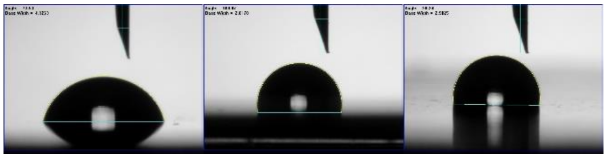


Fig. 4 Water droplet on stainless steel panel (*left = 73.53°*); water droplet on surface modified stainless steel panels before exposure to high temperature crude oil (*middle = 100.07°*) and after exposure to high temperature crude oil for 12 months (*right = 98.24°*).

However, it has been observed that oleophobic surfaces tend to hold tightly to oil droplets even at contact angles >150° and exhibit high sliding angles thus compromising oil repellency properties (Feng et al., 2006; Li et al., 2001; Steele et al., 2009). This defeats the purpose of oleophobicity for the current application as it actually encourages foulant buildup. Thus, the goal in terms of oil wetting is to achieve a surface for which the sliding angle to promote oil flow will be low enough to enhance oil flow across the surface, but for which the contact angle is high enough to exhibit surface oil repellency. The modified surface showed low sliding angles of no more than 3°.

In a static test, where plates were exposed to crude oil for a week at 120°C, it was seen that the oil adhered strongly to untreated stainless steel plates; but this was not the case with the proposed modified surface (Fig. 5). Moreover, exposure to crude oil for 1 month showed that the low surface energy of the modified surface prevented oil from adhering to or accumulating on the surface.

Fig. 5 Unmodified stainless steel surface after dipping in oil at 120°C for 1 week (*left*); modified stainless steel surface after dipping in oil at 120°C for 1 week and a cleaned modified stainless steel surface after immersion in hot crude oil at 120°C for 1 month (*right*). Surface modification results in improved oil repellency.

To closely simulate heat exchanger processes, long term exposure to oil, with intermittent stirring and added water content was performed. The water to oil ratio was set at 1:4 and this was maintained throughout the test period. After 5 months in sour crude oil, it was evident that the surface modification of the metal substrate improved the oil repellency, hence fouling resistance, of the surface. All surfaces exposed to the crude oil were washed with warm soapy water for cleaning. While the unmodified surfaces retained a foulant layer as thick as 47 μm after vigorous scrubbing, the modified surfaces had no added layer and did not require any scrubbing to clean.

After 12 months of exposure to the crude oil, the modified surfaces still showed no adhered foulant layer (Fig. 6).

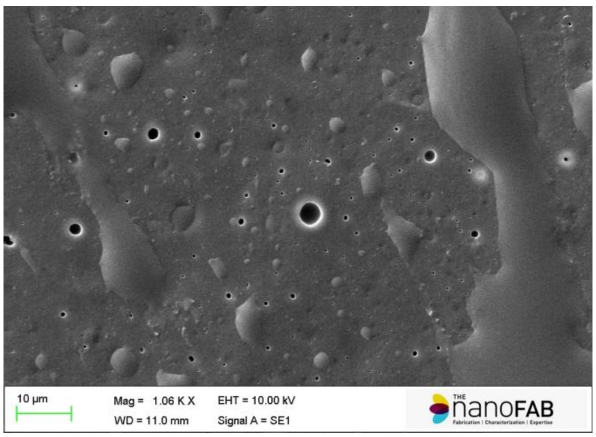
Fig. 6 Modified stainless steel surface after immersion in hot crude oil at 120° C for 5 months (*left*), a modified aluminum surface after immersion in hot crude oil at 120°C for 12 months (*middle*) and an unmodified stainless steel surface after immersion in hot crude oil at 120°C for 5 months (*right*)

Corrosion and Chemical Resistance Performance

For a comprehensive analysis, comparisons were made between a porous surface and a compact surface, both of which were on steel substrates and were subjected to wet sour crude oil (1:4 water to oil ratio) for a period of 2 weeks. SEM analyses of the porous surface (Fig. 7) exhibited poor resistance to fluid interactions with the substrate, resulting in delamination and the onset of corrosion. Conversely, the compact surface with no porosity maintained good adhesion to the substrate and showed no signs of corrosion.

Quantitative analyses of the anticorrosive properties of the compact surface was carried out by means of electrochemical impedance spectroscopy (EIS) studies in which the surface electric resistance (or impedance) was analyzed. At a frequency of 0.1Hz, the impedance value obtained was 10^{10} Ω cm^2. Skerry et al. (1987) report that surfaces of such high impedance exhibit excellent protection properties and are expected to retain these properties over long term exposure to the corrosive environment.

In addition to possessing anticorrosive properties, it is important that the modified surface be chemical resistant. Porosity can form from chemical degradation of the surface modification, making resistance to chemical attack essential to providing a long service life for the heat exchanger. The modified surface was applied to steel and immersed in crude oil at 120°C for 12 months. After exposure, the modified surface was found free of any defects, blisters, cracking, checking, softening, delamination and pinpoint corrosion.



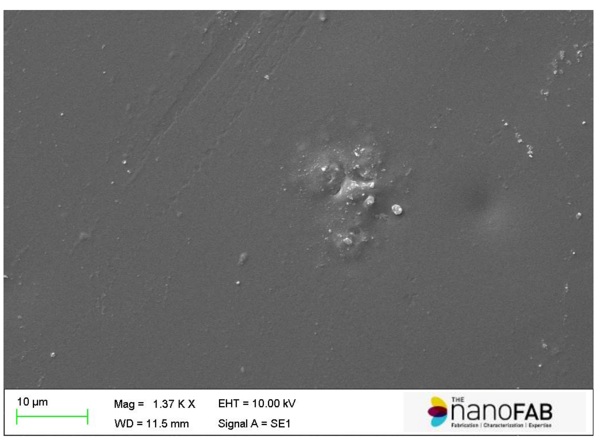


Fig. 7 Surface analyses studies by SEM showing a porous surface (*top*) which eventually fails in static crude oil tests and showing a compact surface (bottom) which retains all properties after exposure to high temperature crude oil for 12 months.

Thermal Conductivity

The foulant layer that builds up on unmodified surfaces during heat transfer processes introduces added thermal resistance to the heat exchanger equipment. This effect is dependent on the thickness of the foulant layer, δ_f, and is quantitatively represented by the fouling resistance, R_f. These quantities are mathematically related as follows with the assumption that the layer is a thin slab:

$$R_f = \delta_f / \lambda_f \tag{1}$$

The efficiency of a heat exchanger can be evaluated by the heat transfer coefficient, U. Based on Fourier's law of heat conduction, the rate at which heat flows across the process fluid, through the heat exchanger plate is given by:

$$q = UA\Delta t_m = \Delta t_m / R_o \tag{2}$$

Where Δt_m is the true mean temperature difference, and the inverse of the overall thermal conductance, UA is the overall thermal resistance R_o and therefore:

$$UA = 1 / R_o \tag{3}$$

Because R_f affects the overall heat transfer coefficient, U, based on equation (1) and (3), it is desirable to significantly reduce the thickness of the foulant layer δ_f, hence decreasing the R_f and increasing U.

Based on the schematic in Fig. 8, the overall thermal resistance of a heat exchanger with a modified surface is calculated according to Eq. (4) as follows:

$$R_o = R_h + R_{m,h} + R_w + R_{m,c} + R_c \tag{4}$$

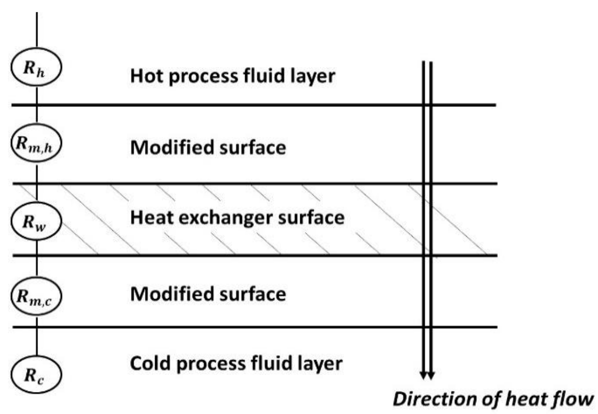


Fig. 8 Schematic of heat flow of a heat exchanger with a modified surface.

Based on calculations from differential scanning calorimetric studies, the thermal conductivity of the modified surface was found to be 2.8 W/K m. Li et al. (2014) found that modified surfaces with thermal conductivities greater than 2 W/K m were more likely to result in improved *(U)*, compared to those with thermal conductivity values less than 2 W/K m.

The antifouling properties of the robust surface, coupled with the overall thermal conductivity of the surface and the substrate, ensure that U_m will be at a constant value throughout the lifetime of the heat exchanger. This is desirable when compared to an unmodified surface which shows a continuous drop in U as the foulant layer builds up, leading to inefficient operation of the heat exchanger.

CONCLUSIONS

Heat exchanger plate lifetime can be increased by surface modification methods. A robust surface with antifouling properties and long term corrosion and chemical protection makes it possible to use less expensive material for heat exchanger construction (Gomes et al, 2015). By following a holistic process, such a surface was achieved and the following conclusions were obtained from surface characterization:

1. Heat exchanger plate surface modification reduces foulant binding and accumulation, while maintaining a constant thermal conductivity over the lifetime of the heat exchanger.
2. Only modifying the heat exchanger surface by lowering the surface energy is not sufficient to produce a robust surface. Thus tailoring the surface to promote better adhesion to the metal substrate, superior fouling resistance, high thermal stability, excellent chemical resistance, and sustainable thermal conductivity will prolong the efficiency and service life of heat exchangers in industrial settings.
3. Long term exposure of the modified surfaces to sour crude oil at high temperatures (up to 12 months at 120°C) showed that the surface had excellent chemical stability as the crude oil had no negative effect on surface properties.
4. Although unmodified steel surfaces exhibit a higher initial thermal conductivity, the efficiency is not sustained due to fouling. The initial thermal conductivity of modified surfaces may be lower, however, this value is maintained throughout the lifetime of the heat exchanger plate, thus giving it a long term advantage over steel surfaces.

NOMENCLATURE

A	cross-sectional transfer area, m^2
Q	heat transfer rate, W
R	thermal resistance, K/W
T	temperature
U	heat transfer coefficient, W/K m^2
Δt_m	true mean temperature difference, °C
δ	thickness, m
λ	thermal conductivity, W/K m

Subscripts

c	cold fluid
f	foulant
h	hot fluid
m	modified surface
o	overall
w	heat exchanger

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