COMPARISON OF HEAT EXCHANGER FOULING TEST RESULTS FOR ONCE-THROUGH AND RECIRCULATING MODES OF OPERATION

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ABSTRACT

Most academic and industry research on crude oil fouling utilizes test rigs that recirculate a batch of crude oil through a test section. This mode of operation is the only practical way to carry out laboratory experiments that attempt to simulate velocity-temperature conditions similar to those in actual heat exchangers. In contrast, the heat exchangers that operate in refineries utilize a once-through mode, receiving a continuously fresh crude oil stream containing fouling precursor. There are two competing mechanisms hypothesized to affect the fouling behavior of the crude during a recirculating test: thermal stress and depletion of fouling precursor. Thermal stress from cycling through the test rig several times can contribute to destabilizing the crude sample which may contribute to fouling. Conversely, depletion of the fouling precursor during recirculating experiments could reduce the amount of material available to deposit on the heat transfer surface.

This paper compares the experimental fouling test results carried out for the same crude oil batch in two modes of operation: once-through and recirculating. The purpose of this study was to determine the effects each mode of operation has on several fouling parameters including: fouling resistance, weight, composition and morphology of the deposits, and the fluid characterization of the crude oil sample. It was determined that the stability criteria (P-value), which describes asphaltene stability of the feed after the experiments, in addition to several fouling parameters, are affected by the mode of operation.

INTRODUCTION

Laboratory fouling experiments are often carried out to predict fouling propensity of various crude slates (Smith, 2013, Bennett et. al., 2009) and develop threshold fouling models such as those by Ebert and Panchal (1996). Typically, fouling rates are defined as a measure of changes over time in overall heat transfer coefficients. Our observations of actual heat exchangers in industrial facilities indicate significant differences between the fouling thresholds observed in the field and those determined by laboratory experiments (Jackowski, et. al., 2017). Additionally, the effects of temperature cycling and foulant precursor concentration have yet to be studied in-depth relating to crude oil laboratory fouling testing. Most academic and industry led research utilizes recirculating test rigs to study heat exchanger fouling. In this method, feed is recirculated and passes through the test section several, maybe even several thousand times. It is also not unusual for researchers to re-use the same feed for multiple experiments. Consequently, any possible changes in feed characteristics due to exposure to hot surfaces of the test section and possible changes in feed composition due to leaving fouling deposits behind are not considered while reporting the fouling test results.

This study intended to compare the results of fouling experiments performed in both the recirculating and once-through modes of operation. The variables observed were fluid properties before and after testing, analysis of the deposits retrieved from the test tubes, and fouling resistance complemented by visual observation of fouling deposits.

EXPERIMENTAL SECTION

Fouling Test

Methodology

The fouling experiments were performed in a test rig that utilizes electrically heated vertical tube equipped with multiple stationary thermocouples measuring surface temperatures. The test tube is inserted into an outer tube with process fluid flowing upward in the annulus. The inner heated tubes are new for each experiment and deposit weights are determined by weight measurements of the test sections before and after the experiments. The overall heat transfer coefficients U are calculated based on heat balance where mean temperature difference is obtained from fluid inlet, fluid outlet, and heat transfer surface temperature measurements. The fouling experiments were performed at a constant surface temperature.

In the recirculating experiments, the fluid sample passes several times through the test section leaving behind some fouling deposit or , alternatively, removing some deposit from the previous cycle(s). In addition, the recirculating experiments impose thermal cycling (heating and cooling) that could impact P-value (stability).

In the once-through experiments, the concentration of fouling precursors, if present, is constant and the fluid is exposed to heating only, similarly as in the refinery preheat train exchangers.

Operating Conditions

The experiments were performed at constant surface temperature and the constant pressure that was selected to prevent vaporization in the test section. For the once-through test mode, the sample volume and flow rate were selected to maximize the run time. The test rig limitations allowed us to run the once-through mode for 17 hours at volume flow rate of 1.0 mL/min. In order to keep the test run duration the same and to accomplish a minimum of 4 thermal cycles, the recirculation test was performed at 1.5 mL/min, i.e., 50% higher volume flow rate than that for the once-through mode. Keeping the test duration the same for both modes of

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operation was selected as the main variable to allow for a proper comparison of collected deposit samples. Impact of the test run duration on the deposit sample characteristics was determined by running the recirculation test for 42 hours. Tables 1 and 2 summarize the test runs.

Table 1. Duration and fluid volumes for fouling tests.

Test Parameters	Sample Volume (mL)	Volume Tested (mL)	Flow Rate (mL/min)
Recirculation 42 H	1000	1000	1.5
Once Through 17 H	1300	1020	1.0
Recirculation 17 H	400	400	1.5

Table 2. Fouling test parameters

Test Rig Operating Conditions	
Velocity (mm/s)	0.9 and 1.4
Reynolds number at average bulk temp. (-)	1.2 and 1.8
Bulk Inlet Temperature (ºC)	58
Maximum Surface Temperature (ºC)	343
Heat Flux (kW/m^2)	45-65
Operating Pressure, MPa	3.5
Shear Stress, Pa	negligible

Fluids Characterization

Crude oils were characterized using conventional techniques. A list of characteristics and how they were measured are shown in Table 3. Additionally, compatibility parameters were determined for crude oils before and after the fouling testing.

Compatibility Testing

Table 3. Characterization of crude oil

Properties		ASTM Method
API gravity	32	D4052
Nitrogen (ppm)	1872	D5762
Sulfur (wt. %)	1.59	D1552
Asphaltene Content (wt. %)	3.23	D6560

Composition plays a significant role in the colloidal stability of petroleum systems (Hatke et al., 1993, Loeber et al., 1998, Taylor, 1998). The characteristics of the asphaltenes (Pfeiffer, 1940, Wiehe, 1996, Carbognani et. al. 1999, Rogel et al, 2003) and the solvent power of the oil are considered fundamental factors for the stabilization of asphaltenes in crude oil (Hatke et al. 1993). One way to evaluate the colloidal stability of crude oils is to use titration techniques to determine the amount of precipitant agent needed for destabilization. The amount of precipitant added is an indicator of the stability of the material. This onset of precipitation is related to the oil properties and the nature of the asphaltenes (Heithaus, 1962).

In this work, an automatic titration instrument is used to determine the characteristics of the asphaltenes (represented by P_a) and the solvent power of the oil or maltenes (represented by P_o). In this test, at least three solutions with different concentrations of the crude oil or blend are prepared in toluene. Each of these solutions is then titrated with heptane at a constant delivery rate. The titration is monitored continuously using ultraviolet- (UV) visible spectrophotometer. At the beginning of each titration, transmittance increases due to dilution with precipitant. At the flocculation onset point, the formation of asphaltene particles causes an immediate decrease in transmittance due to light scattering. For this reason, the curve in Figure 1 exhibits a maximum. This maximum is the flocculation onset (FR) and it is used to calculate the Heithaus compatibility parameters (P_a and P_o). FR is defined as:

$$FR = V_t / (V_t + V_h) \qquad (1)$$

The concentration of the solution (C) at the flocculation onset is given by:

$$C = W_a / (V_t + V_h) \qquad (2)$$

In a typical test, values of FR (equation 1) are plotted as a function of the concentration (equation 2) as shown in Figure 2. In this plot, the point at which the line intercepts the x-axis is defined as C_{min}, and the y-intercept is FR_{max}. C_{min} represents the onset of the precipitation when the crude oil is titrated without dilution. This value is frequently determined by extrapolation since an experimental value might not be available due to setup limitations.

The Heithaus compatibility parameters are calculated as:

$$P_a = 1 - FR_{max} \qquad (3)$$

$$P_o = FR_{max}[(1/C_{min})+1] \qquad (4)$$

$$P = P_o / (1 - P_a) \qquad (5)$$

P should be larger than 1 for the system to be stable.

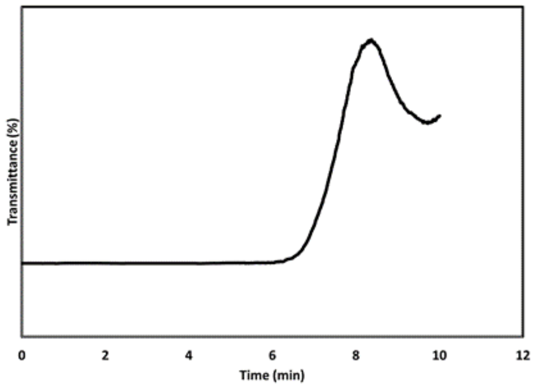


Figure 1. Titration curve obtained using an ultraviolet (UV) visible spectrophotometer

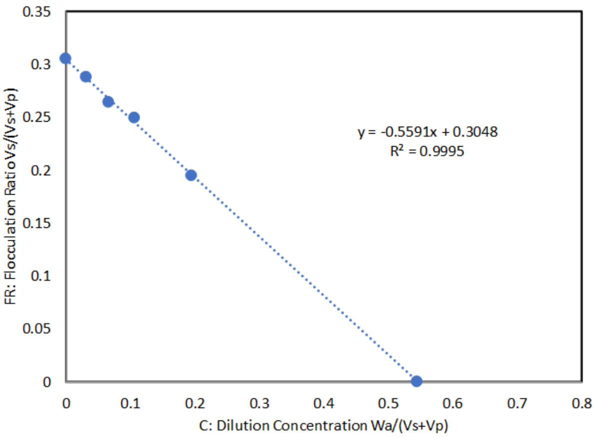


Figure 2. Flocculation Ratio as a function of crude oil concentration.

Deposit Characterization

After fouling testing, fouling tubes were recovered and washed with toluene until the washes were clear. Toluene solutions were evaporated to evaluate the soluble material entrained in the deposit. The fouling tube was dried in an oven at 100°C for 1 h and the insoluble material was scrape from the tube for further characterization.

Elemental Analysis.

Elemental analysis was carried out for the insoluble deposits using a Thermo Scientific Flash 2000. In these tests, the sample was combusted and the combustion products were separated and quantitatively determined with a thermal conductivity detector.

Asphaltene concentrations and asphaltene solubility profile.

Asphaltene concentrations and asphaltene solubility profiles were determined for the crude oil and the spent fluids, as well as for the soluble material recovered from the fouling tube using in-line filtration techniques (Rogel et al. 2015, 2016). In these techniques, a solution of the sample is injected into a flow of n-heptane as the mobile phase. This solvent induces the precipitation of asphaltenes and consequently their retention in the filter. To determine the asphaltene content the mobile phase is switched to a blend dichloromethane/methanol 90/10 v/v that re-dissolves the asphaltenes completely. Asphaltenes are quantified using an Evaporative Light Scattering Detector (ELSD). This technique produces results that correlate with the results obtained using the conventional gravimetric technique, ASTM 6560 (ASTM, 2005).

In the asphaltene solubility profile technique, after the initial injection and precipitation of asphaltenes, the mobile phase is changed gradually from pure n-heptane to 90/10 methylene chloride/methanol and then to 100 % methanol. This procedure gradually re-dissolves the asphaltenes from the easy to dissolve (low solubility parameter) to the hard to dissolve (high solubility parameter) producing a distribution that represents the range of asphaltenic species with different solubilities.

Infrared Spectra.

Infrared spectra were obtained in a Varian 7000e FT-IR infrared spectrophotometer. Transmission measurements were carried out on a Diamond Anvil Cell (DAC), which is used to compress the sample for transmission analysis. Spectra were measured from 4000cm^{-1} to approximately 400 cm^{-1} using a Deuterated Triglycine Sulfate (DTGS) detector as the average of 32 scans acquired at 4 cm^{-1}.

RESULTS AND DISCUSSION

The objective of this research was to compare the fouling behaviors of a crude batch tested in two modes of operation, one in which the crude ran once-through the test rig, and the other which had the crude recirculating throughout the duration of the test. The analysis embodied a holistic approach to fouling testing which took into account deposit and fluid characterization in addition to heat transfer data. Looking at the fouling resistance curves alone does not yield a firm conclusion on the effects of switching from a recirculating to a once-through mode of operation. However, the characteristics of the deposited material on the tube indicate that recirculating the crude sample results in more insoluble deposition. This can be observed visually in Figure 8 which compares the morphology of the deposits from the recirculating versus the once-through tests. The recirculating tests' deposits appear to have more solid material deposition that adheres to the tube compared to the once-through test. This is confirmed in Figure 3 which graphs the soluble and insoluble deposit weights for each test. The recirculating tests have noticeably more insoluble deposits. This conclusion is also supported by the theory initially stated which suggested that thermal stress affects the stability of the crude which may cause material to drop out of solution. Table 5 lists the compatibility parameters of the crude sample before and after the fouling test. The solvent power of the recirculated crude is greater than that of the once-through crude. This suggests that due to deposition of more foulant in the recirculating tests, the crude sample becomes more stable than the once-through crude sample which still contains more fouling precursor.

Further testing is needed to confirm these conclusions. Future testing shall investigate the effects of operating the test in the recirculating mode with more than 4 cycles, as well as keeping the flow rates constant (at the expense of the keeping the duration constant).

Figure 3 shows the weight of the deposit material recovered from the tubes after the fouling test. These results show that the once-through test has less insoluble material, although the total amount recovered is greater. Figure 3 shows an increase in the amount of insoluble material recovered as the duration of the run increases (in the recirculation tests) indicating accumulation of foulant. For the purpose of this study, the insoluble deposit weight is more significant than the soluble deposit weight because soluble material recovered is difficult to distinguish from hydrocarbon remnants leftover from the run due to low flow rate, and these remnants are expected to be easily removed when shear stress is applied.

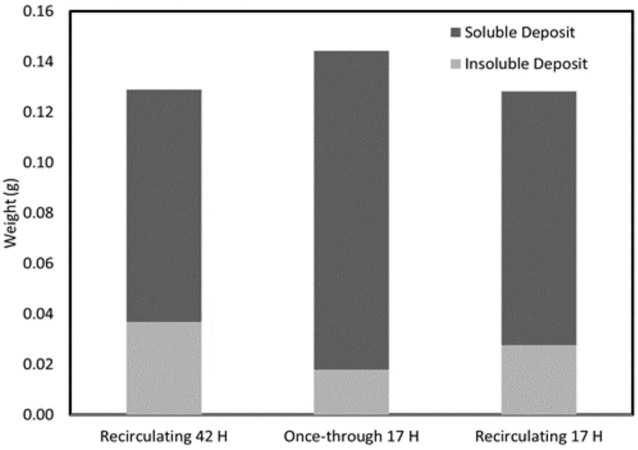


Figure 3. Weight of soluble and insoluble deposits recovered from tubes for each test.

Table 4 shows the elemental composition of the insoluble material recovered from the deposits. These results indicate that both deposits show a similar H/C ratio. The comparison of the infrared spectra of the insoluble material in Figure 4 shows the similarities between them, except for the peak observed at 1150 cm^{-1} that it is associated with the presence of sulfates. This peak is larger in the sample that recirculates for the longer duration, indicating the possible accumulation of sulfates as the time of the test increases. This result corroborates the increase in insoluble material present shown in Figure 3.

Table 4. Elemental composition of the insoluble deposit.

Test	C (wt.%)	H (wt.%)	N (wt.%)	H/C
Recirculation 42 H	69.35	5.19	1.40	0.90
Once through 17 H	72.90	5.42	1.71	0.89
Recirculation 17 H	66.94	4.84	1.53	0.87

The evaluation of the compatibility of the fluids before and after (spent fluid) the fouling tests were carried out to determine the effect of thermal stress on the crude oil properties. According to these results shown in Table 5, there is a decrease in stability resulting from the thermal stress induced in the sample. Results show that the asphaltene peptizability (P_a) remains practically constant. This is expected as it has been established (Heithaus, 1962) that the P_a is reasonably independent of the concentration of asphaltenes, so a small decrease in concentration should not affect its value. On the other hand, the solvent power (P_o) decreases in all of the samples. Studies of asphaltenes show that processing induces rather small changes in P_a as observed here, while causing more notable changes in P_o (Heithaus, 1962). Thermal conversion of the most aromatic portion of maltenes into asphaltenes or fouling precursors is the likely cause. It is interesting also to point out that the P-value for the fluid that passes once-through the heating element is lower than that of the fluids that recirculate several times. This presumably depends on whether the conversion of the most aromatic portion of the maltenes converts to foulant or asphaltenes, which decreases the solvent power and is offset by the aromatization of other components in the maltenes which increases the solvent power. In this set of experiments, it seems that the aromatization of some components of the maltenes might occur in the recirculating tests as the exposure time to thermal cycling increases due to the fluid passing several times though the heated test section several times. It has also been observed that for crude oils that have border line stability (P-value close to one), the P-value increases after the fouling test probably as a consequence of the depletion of foulant.

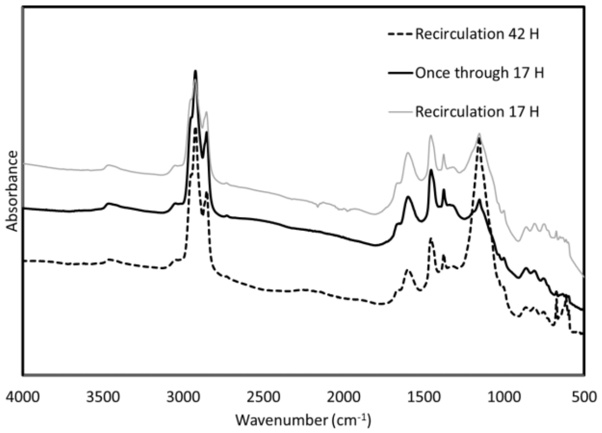


Figure 4. FTIR spectra for insoluble components of the deposits.

Table 5. Evaluation of compatibility parameters before and after (spent fluid) fouling testing.

Fluid	P_o	P_a	P-value
Crude Oil	0.42	0.70	1.41
Spent Fluid			
Recirculation 42 H	0.38	0.71	1.31
Once through 17 H	0.33	0.71	1.15
Recirculation 17 H	0.36	0.70	1.23

Asphaltene solubility profiles are shown in Figure 5 for the soluble portion of the deposits. The comparison of these profiles with those obtained for the crude oil indicate that the asphaltenes remaining in the soluble portion of the deposit have not suffered significant changes due to thermal degradation. This corroborates with the small change in the peptizability values shown in Table 5 for the spent fluids. It also indicates that the soluble portion of the deposit resembles the fluid before the test.

Based on these results, the small amounts deposited do not significantly impact the characteristics of the asphaltenes remaining in solution, but they do affect the characteristics of the maltenes.

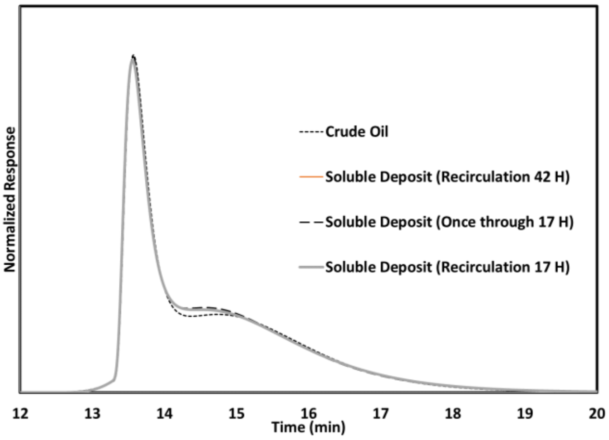


Figure 5. Solubility profiles of crude oil and spent fluids

In general, the recirculation of fluid seems to increase the amount of insoluble material recovered although their properties seem to be similar. From the compatibility point of view, the thermal stress on the fluids mainly affected their solvent power and this decrease might contribute to a larger deposition of insoluble materials. However, these results also need to be analyzed in the context of the initial compatibility characteristics of the sample. This is an important variable that was not considered in the present study.

Fouling resistance plots for each run are plotted in Figures 6 and 7. Equation (6) calculates fouling resistance, R_f by:

$$Rf(t) = \frac{1}{U_{(t)}} - \frac{1}{U_{(0)}} \tag{6}$$

Figure 6 shows the fouling resistance plots of all three experiments. All three tests begin with relatively similar fouling behavior until the 5 hour mark. Observing the fouling resistance curve for the 42 hour recirculating test, after 5 hours the fouling resistance drops off which may signify removal of deposit. After the dip the fouling resistance increases at a lower rate but exhibits more linear behavior. Figure 7 shows only the two 17-hour tests. The once-through test has a more steady trend in fouling resistance compared to the recirculating run which is expected. The recirculating curve is initially steeper, speculated to be caused by foulant in the feed being deposited early on before the feed cycles through several times. Note that for the once-through test, data was only plotted up to 15 hours due to an instrument error.

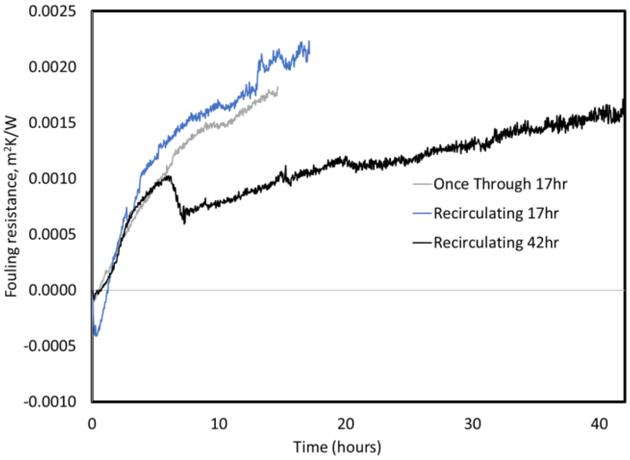


Figure 6. Fouling resistance comparison for each test.

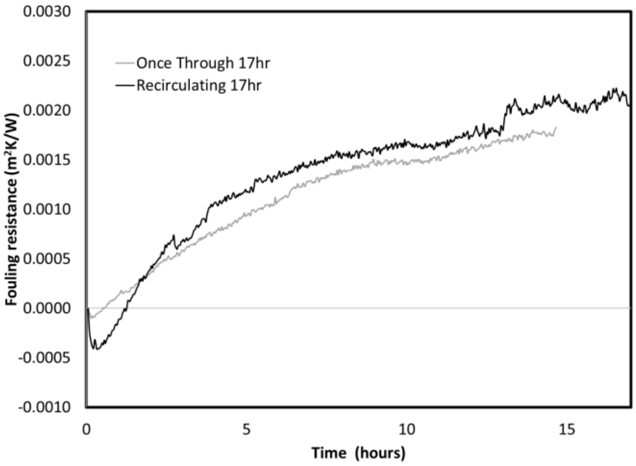
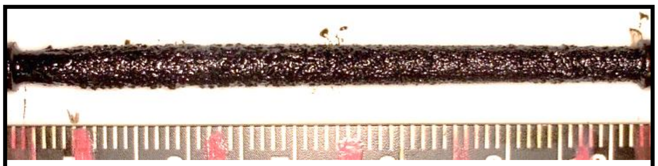


Figure 7. Fouling resistance comparison of 17 hour recirculating vs 17 hour once-through tests.

In addition to analyzing heat transfer data, visual inspection of the tubes was performed. Figure 8 shows images of all three tubes after each test concluded. The test section was carefully removed from the test rig, the tubes removed, and the images were taken on a digital microscope. Visually there is a difference in the morphology of between the deposit left from the recirculating tests versus once-through test. This corroborates with the weight and characterization of the insoluble and soluble portions of the deposits, where the once-through test produced more soluble deposit and less insoluble deposit than the recirculating tests.



(a) Recirculating 42 H

(b) Recirculating 17 H

(c) Once-through 17 H

Figure 8. Images of tubes extracted from the test section after conclusion of each test, respectively. Scale is in mm.

CONCLUSION

This study was the first of its kind investigating the impact the mode of operation has on a variety of fouling parameters related to crude oil fouling. Running the test in the recirculating mode was hypothesized to induce two competing mechanisms: thermal stress on the sample which could contribute to fouling, and depletion of precursor which could reduce fouling compared to the once-through mode.

Experimental results indicate that thermal stress induced from running the test in the recirculating mode took precedent over the depletion of fouling precursor. This conclusion is supported by the results from the deposit analysis and fluid characterization.

Future testing to confirm these conclusions will investigate the effects of holding the flowrate constant for both modes of operation, as well as increasing the number of cycles in the recirculating test.

NOMENCLATURE

FR	Flocculation ratio
FR_{max}	Y-intercept of the Flocculation Ratio
Vt	Volume of toluene, mL
Vh	Volume of heptane, mL
C	Concentration of solution, g/mL
C_{min}	The onset of precipitation when the crude oil is titrated without dilution
Wa	Mass of crude oil, g
Pa	Peptizability of asphaltenes
Po	Solvent power of maltenes
P	Overall compatibility of the system
Rf	Fouling resistance, m^2K/W
$U_{(t)}$	Overall heat transfer coefficient at time t, W/m^2-K
$U_{(0)}$	Overall heat transfer coefficient at time 0, W/m^2-K

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