

On: 30 April 2015, At: 01:29

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Heat Transfer Engineering

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/uhte20>

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Accepted author version posted online: 29 Apr 2015.



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To cite this article: Valeria Oldani, Claudia L. Bianchi, Serena Biella, Carlo Pirola & Giuseppe Cattaneo (2015): Perfluoropolyethers coatings design for fouling reduction on heat transfer stainless steel surfaces, Heat Transfer Engineering, DOI: [10.1080/01457632.2015.1044417](https://doi.org/10.1080/01457632.2015.1044417)

To link to this article: <http://dx.doi.org/10.1080/01457632.2015.1044417>

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Perfluoropolyethers coatings design for fouling reduction on heat transfer stainless steel surfaces

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ABSTRACT

The scope of this research is to obtain a film coating on stainless steel surfaces in order to reduce the interaction between the metal surface and the precipitates, so to mitigate fouling in heat exchangers. Perfluoropolyethers were used to obtain nano-range fluorinated layers in order to make hydrophobic the stainless steel surfaces. A pilot plant with two identical heat exchangers was built to investigate the ability of the hydrophobic coating of preventing fouling. The heat exchangers, installed in parallel, operated at the same temperature and pressure conditions, i.e. laminar flow regime and inlet flow temperatures of 291-293 K for cold streams and 313-333 K

for hot streams. We compared the heat transfer performance of the two heat exchangers. After a five months operation the decrease in the heat transferred was 56% for the coated heat exchanger and 62% for the uncoated heat exchanger. Moreover, the increase of heat transfer resistance due to scale on the uncoated heat exchanger, with respect to the coated one, was three times higher.

INTRODUCTION

The term fouling is usually referred to the accumulation of unwanted deposits on solid surfaces. Regarding the heat exchangers, fouling phenomenon occurs specially on heat transfer surfaces and the consequences are not negligible. The presence of the deposits, in fact, represents a further resistance to heat transfer and it is also responsible for the increase of the pressure drop. The result is the loss of efficiency, more consumption of energy, and a higher operating cost [1].

Several fouling mitigation techniques were adopted and great attention was paid in the past for the on-line physical mitigation of fouling in the heat exchangers. Physical mitigation techniques try to reduce fouling phenomenon modifying the interaction of the fouling precursors with the heat transfer surfaces [2].

According to Malayeri et al. [3], considering the physical and geometrical properties of a surfaces, the foulant deposition process can be altered in two ways, by reducing the work of adhesion between the surface and the fouling precursor or by increasing the shear stress. Key elements for these operations are the surface roughness, the surface free energy and surface geometry both at micro- and macroscopic scale.

In this research we used hydrophobic coatings to modify the surface energy of stainless steel so to reduce the interaction between the fouling precursor and the heat transfer surface. Several researches show that lower surface energies can reduce the propensity of the surface to foul; Förster and Bohnet [4] demonstrated that the nucleation rate and the adhesion of crystals on the heat transfer surfaces decreases for low energy surfaces with an increase of the length of the fouling induction period. Zhang et al. [5] confirmed the ability of super-hydrophobic surfaces (i.e., very low surface energy) to delay bio-fouling phenomena, on the basis that the air bubbles

entrapped in micro and nano-pores on the super-hydrophobic surface can create a barrier preventing the adsorption of micro-organisms. Modified polytetrafluoroethylene (PTFE) composite coatings, characterized by non-stick properties and low surface energy, were developed with good results in fouling protection. Zhao et al. [6] developed graded Ni-Cu-P-PTFE coatings for minimizing adhesion of both micro-organism and scale, showing minimal adhesion of *E. Coli* bacteria and CaSO_4 at the lower surface free energy values. Rosmaninho et al. [7] attested easy removal of non-microbiological milk deposits on stainless steel surfaces covered with Ni-P-PTFE coatings. Other materials have been used in order to obtain anti-fouling coatings. Wang and Liu [8] used nano-scale TiO_2 layers on copper surfaces, obtaining hydrophobic surfaces able to enlarge the fouling induction period for scale formation. Martinelli et al. [9] used amphiphilic polymer coatings in order to reduce both the hydrophobic and hydrophilic interactions between bio-foulants and solid surfaces. Results show weaker adhesion of some micro-organism on the amphiphilic films.

In this work we used α,ω -functionalized perfluoropolyethers (PFPE) for obtaining hydrophobic coatings. Typical properties of PFPE are high thermal stability, chemical inertness, hydrophobicity, oleophobicity and very low surface energy; moreover the presence of functional groups strongly changes chemical reactivity of the polymer, allowing for example the formation of chemical bonds with chemical sites present on metal surfaces, such as $-\text{OH}$ sites [10]. Fabbri et al. [11] attested high hydrophobicity and low surface energy for coatings obtained from different functionalized PFPE, specifically triethoxysilane and hydroxy α,ω terminated poly(caprolactone-*b*-PFPE-*b*-caprolactone).

Coatings features and surface energy were studied by XPS and contact angle analysis. Moreover coatings resistance against different liquid environments was investigated.

In order to demonstrate the anti-fouling efficacy of the fluorinated coatings developed, a pilot plant with two identical shell and tube heat exchangers was built. Shell and tubes heat exchangers are the most common heat transfer equipment used in chemical industries, due to their versatility, robustness and reliability. However, this type of heat exchangers is involved in fouling phenomena if the design practice is not proper [12]. Internal and external tubes surfaces of one of the pilot heat exchangers were treated with a PFPE solution in order to obtain a protective coating. The performance of the heat exchangers was monitored and fouling resistance was determined along a period of five months.

EXPERIMENTAL PROCEDURE

Coating deposition procedure

PFPE's used for obtaining the coatings have a general formula $X-[OCF_2]_n[OCF_2CF_2]_p-X$, where X is a functional polar group and the sum $n+p$ is between 9 and 15, while the ratio n/p is between 1 and 2.

Fluorinated coatings were prepared on stainless steel (AISI 316) surfaces. Stainless steel samples of dimensions 2 cm x 1 cm and thickness 0.5 cm were used for coating characterization and resistance determination. In order to remove the rough impurities, the samples were washed with water and brushed, before applying the coatings. For obtaining ideal surfaces suitable for XPS analysis, some samples were cleaned also by the use of organic solvents (acetone).

The coating was applied also on heat exchanger stainless steel tubes, for anti-fouling activity determination. The tubes had internal diameter of 8 mm, 1 mm thickness and 500 mm length. A careful washing of the tubes was made with water; however tubes surfaces were not specifically treated with chemicals or mechanical equipment.

The coatings were obtained dissolving in water or in a mixture of water and 2-propanol the functional PFPE derivatives. The weight percentage of the fluoropolymer in each solution ranges from 0.5% wt to 10% wt; the solution may include also a catalytic amount of acetic acid in the same weight percentage of the fluoropolymer; the acetic acid facilitates in fact the cross-linking process of some types of PFPE derivatives. The coating deposition on stainless steel surfaces consisted in immersing the samples in the PFPE solution; the immersion time can vary from 10 minutes to several hours. Finally a heat treatment was performed in a stove at temperatures varying from 353.15 K to 423.15 K, for 3 to 24 hours.

The PFPE solution used for coating the heat exchanger tubes was obtained by formulating 1% wt of a PFPE derivative and 1% of acetic acid in water. Tubes were consequently dipped into the solution, by using a tank of appropriate dimensions, for 20 minutes and dried in an industrial stove for 19 hours at a temperature of 353.15 K. Following this procedure both the internal and external surfaces of the tubes were coated.

Characterization of fluorinated surfaces

X-ray photoelectron spectroscopy (XPS) spectra were obtained by using M-probe apparatus (Surface Science Instruments). Monochromatic Al K α radiation (1486.6 eV) was used as source. Analyses were performed on spot of size 200 μm \times 750 μm and pass energy was 20 eV. Survey analysis in the whole range of X-ray spectra and high-resolution analyses in the

typical zone of C-bonds, F-bonds and O-bonds were performed. Fittings were performed using pure Gaussian peaks, Shirley's baseline and no constraints.

Contact angle (CA) measurements were performed by a Krüss Easy Drop instrument. For water contact angle determination a Milli-Q apparatus was used to prepare the testing liquid. The surface free energy of the coated samples was determined by using Lewis acid-base approach. Three pairs of SFE-Theta values were obtained for each analysis by using as test liquid diiodomethane (Sigma-Aldrich, purity 99%), distilled water and formamide (Sigma-Aldrich, purity $\geq 99.5\%$). CA values here reported are the average values obtained from at least five different determinations, obtained by the deposition of the liquid drops at different sample locations.

Coating resistance tests

One of the main problems related to the use of organic coatings for fouling protection is the poor stickiness and the low resistance against erosion, above all if coating thickness is below $5\ \mu\text{m}$ [13]. For this reason before testing the effective anti-fouling activity of the hydrophobic coating on the pilot plant, we have investigated the coating resistance against aggressive liquid environments. The PFPE coated stainless steel plain samples were dipped into different solutions, for a period of one week; specifically the testing liquids were: tetrahydrofuran (THF), acetone, Milan municipal water, synthetic seawater (pH 8.2), sodium hydroxide solution (NaOH, pH 9), hydrochloric acid solution (HCl, pH 2) and chloramines solution ($\text{NH}_2\text{Cl-NHCl}_2$, 300 ppm). During the tests the solutions were continuously stirred and chemicals concentration was kept constant. Moreover the coating resistance was studied at room temperature or by using thermostatic bath at higher temperatures (323.15 K; 353.15 K). The coating resistance was quantified by comparing the water contact angle values measured before and after 7 days test.

The decrease in surface hydrophobicity represents the index of coating deterioration. All of the chemicals used for coating preparation, characterization and testing were purchased from Sigma Aldrich.

Heat exchanger pilot plant

A heat exchanger pilot plant was built in order to verify the antifouling properties of the fluorinated coating developed for stainless steel. The experimental equipment consisted of two shell and tubes heat exchangers AEW TEMA type. Shells had horizontal orientation and internal diameter of 90 mm. Tubes were plain type, the outside diameter was 10 mm and the thickness was 1 mm. The length of tubes was 500 mm, the layout angle was 30° and the pitch was 12.5 mm. Tubes material was stainless steel AISI 316, while shells were realized in glass. Both heat exchangers had 18 tubes, one shell-pass and six tube-passes. Flows were countercurrent. The only difference between the two heat exchangers was the presence of a PFPE coating on the tubes surfaces of only one of them.

The schematic diagram of the pilot plant is shown in Figure 1; the coated heat exchanger is named with the letter A (HX A), while the uncoated heat exchanger is named B (HX B).

Municipal water of the city of Milan was used as operating fluid, Table 1 reports the chemical composition of the water used during the experimental work. The cold stream, introduced in shell, had average temperature of 293 K, while hot stream was preheated in a tank at a temperature between 313 and 333 K, before being introduced into the tubes. Temperatures of inlet and outlet fluids were determined by flexible thermocouples, positioned at the inlets and outlets of the tube-side and shell-side. The thermocouples sensibility is between 10 and 50 $\mu\text{V}/^\circ\text{C}$. The experimental flow rates were 184 kg/h for tube side and 45-60 kg/h for shell side.

Shell and tubes flow rates were regulated by the use of massive flow meters (standard accuracy $\pm 5\%$ of full scale flow), placed before the tube-side and shell-side flows entrance.

During all the experimental work the shell and tubes flow rates of the two heat exchangers were kept similar; inlet flows temperatures in tube and shell were the same for the two heat exchangers, fed in parallel.

The experimental work ran for a time period of five months and during the experimentation the pilot plant worked in continuous conditions. Temperatures and flow rates values were recorded 6 times per day, at time intervals of 2 hours.

Theory for heat transfer coefficient and fouling resistance determination

The performance of heat exchangers usually diminishes with time as a result of the accumulation of fouling deposits on the heat transfer surfaces. Such an effect can be represented by a fouling resistance R_f (see Eq. 3), which is a measure of the thermal resistance induced by fouling. In order to evaluate the coating effect on foulants deposition on the heat transfer surfaces of the pilot plant, the fouling resistance was determined for both the coated and uncoated heat exchangers and compared.

By knowing the flowrates and the inlet and outlet temperatures of the operating streams, it was possible to determine the overall heat transfer coefficient U .

The cold-side, or shell-side, heat transfer coefficient h_C , was determined by the following relation, [14]:

$$Nu = \frac{h_C D}{k} = 0.664 Re_G^{0.5} Pr^{\frac{1}{3}} \quad (1)$$

The experimental Reynolds numbers, as defined by Gnielinski [14] (Re_G), ranged from 3000 to 6000, while Prandtl number varied in the range 5.9-6.2.

The hot-side, or tube-side, heat transfer coefficient h_H was determined by the Sieder-Tate relationship (Eq. 2), valid for laminar flow regimes, i.e., $Re \leq 2000$ and $1/Gz \leq 0.01$:

$$Nu = \frac{h_H D}{k} = 1.86 Gz^{\frac{1}{3}} \left(\frac{\mu_b}{\mu_w} \right)^{0.14} \quad (2)$$

Experimental value calculated for $1/Gz$ is 0.003, Re number is 1113; the ratio μ_b/μ_w , which depends on the temperature, varied in the range 0.69-0.78.

Considering Eq. (3), representative of the overall thermal resistance in heat exchangers, it is possible to determine the fouling resistance R_f by knowing U , h_C and h_H :

$$R_{total} = \frac{1}{U} = \frac{1}{h_C} + \frac{1}{h_H} + \frac{D_{out} \ln \left(\frac{D_{out}}{D_{in}} \right)}{2k} + R_f \quad (3)$$

where:

$$\frac{D_{out} \ln \left(\frac{D_{out}}{D_{in}} \right)}{2k} = R_{wall} \quad (4)$$

In this work it was considered a general fouling resistance R_f , given by the sum of the fouling resistance at the inner and outer tubes surfaces. Moreover the overall heat transfer coefficient U was calculated considering the logarithmic mean value of the heat transfer surface area (A_{mlg}), determined between the inner and the outer tubes surface area. For this reason in the following pages the overall heat transfer coefficient is expressed as U_{mlg} .

EXPERIMENTAL RESULTS

Coating characterization

Contact angle measurements were performed in order to assess the hydrophobicity of the stainless steel surface after the coating deposition. Figure 2 shows typical images of water drops deposited on uncoated and coated stainless steel samples, while Table 2 reports the contact angles and free surface energies that were determined on different type of fluorinated samples. We observed a consistent decrease of free surface energy for fluorinated coated samples compared to the uncoated sample (Table 2). Coating formulations named as A and C are referred to those in which 2-propanol was used as solvent, while for B and D water was used as solvent. The difference between A and C formulation from B and D, is the presence of perfluoropolyethers with different α - ω terminations. The deposition and drying procedure for these samples were the same, i.e., 20 minutes immersion and 20 hours drying at 353.15 K.

Samples E and F were coated by using the same PFPE water formulation, coating was obtained by immersing for 5 hours the samples inside the polymeric solution and drying for 20 hours at a temperature of 403.15 K. Sample E was cleaned before the coating deposition by using organic solvents, while surface of sample F was only washed with water. There are no significant differences in contact angle values or surface free energy between these two samples. Thereby it is possible to suppose that a specific step of pre-washing, by chemicals or mechanical equipments is not necessary for the obtainment of hydrophobic surfaces, as long as new materials are used and a careful washing with water is performed before the coating deposition.

Samples A and C are characterized by lower surface energy than B and D, due to a better solubility of the fluoropolymers in the organic media. Nevertheless we noticed that, increasing immersion time and drying temperature, it is possible to obtain high water contact angle values

and low surface energies also for coatings obtained from completely water PFPE formulations (samples E and F).

XPS analyses were performed in order to understand the chemical features of the fluorinated layer on stainless steel surfaces. These analyses (Figure 3) highlighted a high content of fluorine on the coated surfaces (atomic percentage 41.6%). Iron was not detected from XPS analysis, confirming the presence of fluorinated layer greater than 50 Å (depth of investigation of the instrument). From high resolution analysis performed in the typical zone of C-bonds and O-bonds it was possible to assume the formation of a cross-linked fluorinated layer on stainless steel surface. Molecules create in fact a cross-linkage each other mainly through C-F and C=O bonds, forming a stable and resistant grid on the metal surface.

Coatings chemical resistance

To assess the stability of the coatings and the formation of chemical interactions between the functionalized PFPEs and the stainless steel surfaces, coated samples were dipped into THF and acetone. After 1 hour immersion at room temperature, no significant changes in contact angle values were detected, confirming the formation of chemical bonds between the coating and the stainless steel surface.

Preliminary investigations of the resistance of the coatings against erosion in liquid environments were performed by immersion of the samples in different chemical solutions (Table 3). We observed that coatings are resistant to water and disinfectant agents (chloroamines) at both mild and high temperatures (the decrease of CA is about 5% with respect to the starting value); acidic solutions erode more the fluorinated films, at room temperature the CA decrease in 7 days is 19%, while at 353.15 K is 26%. However the final CA angle value

measured for each sample is greater than 90° , identifying hydrophobic surfaces. Surfaces remain hydrophobic also after immersion in synthetic seawater, as long as the temperature is under 323.15 K. Alkaline environments are more aggressive for the PFPE coatings and at high temperature coatings quickly deteriorate.

Pilot plant experimentation

Heat exchanger pilot plant was built for determining anti-fouling properties of the fluorinated coating developed. The plant operated in a laminar flows regime and with small temperature differences, in order to asses at first the ability of the hydrophobic layer to reduce foulant adhesion on the heat transfer surfaces. Specifically the average fluid velocity for the shell side was 0.0086 m/s, while for the tube side was 0.1100 m/s. The corresponding Reynolds number for the tube side flow is 1113, attesting a laminar flow inside the tubes.

Data presented in this work were collected from the 60th operating day until the 172nd. The thermodynamic coefficients reported in the article (U_{mlg} , h_H , h_C and R_f) were obtained by considering the average flow conditions and the average temperatures of the inlet and outlet fluids for each working day. Moreover data reported in this article were affected by a systematic error related to the accuracy of the instruments used for the determination of the parameters; the continuous variation of the flowrates and temperatures, in the ranges previously introduced, for both heat exchangers, caused the obtainment of scattered values.

In order to verify the heat transfer efficiency of the two heat exchangers, the overall heat transfer coefficient was calculated. Supposing that the presence of the fluorinated coating, at nanometer thick level, does not cause any variation to flow regime or neither represents a further thermal resistance, it is possible to compare the results obtained for coated and uncoated heat

exchangers. In Figure 4 the trend of the overall heat transfer coefficient (U_{mlg}) is reported, with respect to the time. For both heat exchangers U_{mlg} decreased with time, but values determined for the coated heat exchanger were always higher than the ones obtained from the monitoring of the uncoated heat exchanger. Considering the trend of the values collected as linear, it is possible to underline a difference between the two slopes calculated, which is -0.71 for the coated heat exchanger and -0.91 for the uncoated one. Thus we can suppose a higher decrease of heat transfer efficiency with respect to the time for the uncoated heat exchanger. Table 4 reports a direct comparison of the heat transfer capacity of the two heat exchangers; the whole working period was divided in 4 sub-periods of about 30 days, an averaged value of heat transfer coefficient U_{mlg} and of the fouling resistance R_f is presented for each period. We noticed a significant difference (about 60 W/m²K) between the U_{mlg} values of the two heat exchangers, for all the considered periods.

The decrease of U_{mlg} values with time can be correlated to an increase of the thermal resistance. The overall thermal resistance depends on shell side and tube side heat transfer coefficients and on fouling resistance.

Figure 5 highlights that shell side and tube side heat transfer coefficients are almost the same between the two heat exchangers, but they are not identical. The heat transfer coefficients depend on the pilot plant design and on the flowrates and temperatures; while the two first parameters were kept identical between HXA and HXB, during all the experimentation, the temperatures of the outlet fluids of the coated heat exchanger are different from those of the uncoated heat exchanger, for this reason the heat transfer coefficients can not be identical.

Moreover due to a variation of the inlet flowrates and the inlet temperatures of shell fluids with time, the cold heat transfer coefficients are very scattered.

Nevertheless the similar values obtained for cold side and hot side heat transfer coefficients of the two heat exchangers suggest a very similar working condition between the two heat exchangers; in fact the operating properties, such as flows, temperatures and velocities were kept similar between the heat exchangers. Also foulant concentration in operating fluids and flow geometries were the same. Similar working parameters between the two heat exchangers are essential for the obtainment of comparable fouling resistance values; the only variable between the heat exchangers was the presence of the hydrophobic coating on the tubes surfaces of only one of them.

The fouling resistance variation with time is presented in Figure 6. According to the U_{mlg} trend (Fig. 4), also the fouling resistance (R_f) grew with time, but the values calculated for the uncoated heat exchanger were always greater than the ones evaluated for the coated heat exchanger. In Table 4 we underline a difference between the average R_f values obtained from the coated heat exchanger and the uncoated heat exchanger. In the first working period the fouling resistance of the uncoated heat exchanger was $0.002 \text{ m}^2\text{K/W}$ higher than the one of the coated heat exchanger. This difference increased up to $0.003 \text{ m}^2\text{K/W}$ in the last period. Moreover the average fouling resistance value of the last period, calculated for the uncoated heat exchanger, was lower than the average value calculated for the uncoated heat exchanger in the first period.

To more clearly observe the effect of the coating used, in Fig. 7 is represented the quantity of heat transferred with respect to the time by the two heat exchangers. The two heat exchangers worked in a very similar way, the quantity of heat transferred decreased with respect

to time for both plants. However q values calculated for the coated heat exchanger were higher than the ones obtained for the uncoated heat exchanger ($\Delta q \approx 150$ W). Both heat exchangers were therefore involved in the same type of fouling phenomenon, as shown by the continuous decrease of heat transferred, however the loss of efficiency in heat transfer due to fouling was inferior for the heat exchanger characterized by low energy heat transfer surfaces. We estimated a total decrease in heat transfer capacity of 56% for the coated heat exchanger and of 61% for the uncoated one, in the work period between the 60th working day to the 172nd. Therefore we suppose that the presence of the fluorinated hydrophobic coating on the heat transfer surfaces influenced the coating layer formation and growth on heat transfer surfaces.

After 5 months of operation, the pilot plant was shut down. Some tubes samples, covered by a foulant layer, were collected. SEM and EDX analysis were performed on these samples in order to determine the composition of the deposits (Electron microscopy Philips XL-30CP with RBS detector of back scattered electrons).

Images in Fig. 8 show the presence of crystalline deposits on both the internal tube surfaces, coming from the coated and uncoated heat exchangers. Fouling deposits formation cannot be completely avoided by using a PFPE hydrophobic coating, however there is a recognizable difference in crystals structure between Fig. 8a (referred to the PFPE coated heat exchanger) and 8b (referred to the uncoated heat exchanger). On the uncoated stainless steel surface the deposit seems to form a compact layer of little crystals, on the other hand, on coated surface, crystals are bigger and more dispersed. Such a difference between the two fouled surfaces could suggest a different mechanism of adhesion of the foulant particles, maybe influenced by the low surface free energy of the coated material.

EDX results pointed out to a high atomic content of carbon, magnesium, calcium and oxygen. Chromium and nickel derive from stainless steel (Table 5). Thus we can suppose that the type of fouling involved during the experimentation is scaling, probably due to calcium carbonate and magnesium oxide. Moreover no differences were detected between the deposits collected from the coated heat exchanger and from the uncoated one.

Eventually a cleaning procedure was performed by propelling foam projectiles inside some tubes of the two heat exchangers. It has been verified by this procedure an easier removal of the scale deposited inside the coated tubes than the uncoated one. The presence of the hydrophobic coating has therefore limited the scale adhesion and accumulation on the heat transfer surfaces.

CONCLUSIONS

Modification of stainless steel surface properties was obtained by the deposition of a fluorinated coating, by using α - ω functionalized perfluoropolyethers.

Low surface energy was evaluated for stainless steel samples coated with the PFPE derivatives (3.3-11.3 mN/m). The hydrophobicity was attested by water contact angle analysis; depending on the type of PFPE formulation and the deposition procedure, it was possible to obtain high contact angle values, from 100° up to 140°.

Immersion in THF or acetone did not affect the stability and the hydrophobicity of the coatings, consequently, we assume the formation of chemical bonds between the PFPE functional group and the chemical sites present on the stainless steel surfaces. Moreover we suppose the formation of a nanometer level thickness coating.

We studied also the chemical resistance of the coatings. Tests performed for 1 week immersion of coated samples in different chemical and aggressive environments, highlighted good resistance of the coatings against water erosion, both at high temperature (353.15 K) and room temperature. The surfaces remained hydrophobic also after immersion in acidic solutions and chlorine solutions.

The effective anti-fouling efficiency of the hydrophobic coating was tested by a pilot plant, constituted of two shell and tube heat exchangers; tubes of only one of them were coated: during 5 months experimentation it was possible to observe lower heat transfer resistance due to fouling for the coated heat exchanger compared to the uncoated one (the average values were 0.0018 vs 0.0051 m²K/W respectively, in the last working month). The fluorinated coating actually limited the scale formation on the heat transfer surfaces.

The coating influence on flow regime and on heat transfer is under investigation; resistance to abrasion and turbulent flow effects will be considered in future work and the anti-fouling activity of the PFPE coatings will be compared to that of anti-fouling commercial paints and coatings.

NOMENCLATURE

A	Heat transfer surface area, $2\pi DL$, m ²
CA	Contact angle, θ degrees
c_p	Specific heat of fluid, J/kg K
D	Diameter, m
Gz	Graetz number, $Re Pr D/L$, dimensionless
h	Heat transfer coefficient, W/m ² K

k	Liquid thermal conductivity, W/mK
L	Length, m
l_b	Baffle spacing, m
Nu	Nusselt number, hD/k , dimensionless
Pr	Prandtl number, $c_p \mu_b / k$, dimensionless
q	Heat quantity, J/h
R	Overall thermal resistance m^2K/W
Re_G	Reynolds number defined by Gnielinski, $W L / \varepsilon_F D l_b \mu_b$, dimensionless
R_f	Fouling resistance, m^2K/W
R_{wall}	Wall resistance, m^2K/W
U	Overall heat transfer coefficient, $W/m^2 K$
W	Total mass flowrate, kg/h

Greek Symbols

ε_F	Shell void fraction, m
θ	Contact angle, $^\circ$
μ	Fluid viscosity, Pa·s

Subscripts

b	Bulk
C	Cold
f	Fouling
H	Hot

ACCEPTED MANUSCRIPT

in Inner

mlg Logarithmic mean

out Outer

w Wall

REFERENCES

- [1] Bott, T.R., *Fouling of Heat Exchangers*, pp. 1-6, Elsevier Science & Technology Book, The Netherlands, 1995.
- [2] Müller-Steinhagen, H., Malayeri, M.R., and Watkinson, P., Heat Exchanger Fouling: Mitigation and Cleaning Strategies, *Heat Transfer Engineering*, vol. 32, no. 3-4, pp. 189-196, 2011.
- [3] Malayeri, M.R., Al-Janabi, A., and Müller-Steinhagen, H., Application of Nano-modified Surfaces for Fouling Mitigation, *International Journal of Energy Research*, vol. 33, pp. 1101-1113, 2009.
- [4] Förster, M., and Bohnet, M., Influence of the Interfacial Free Energy Crystal/Heat Transfer Surface on the Induction Period During Fouling, *International Journal of Thermal Sciences*, vol. 38, pp. 944-954, 1999.
- [5] Zhang, H., Lamb, R., and Lewis, J., Engineering Nanoscale Roughness on Hydrophobic Surface-Preliminary Assessment of Fouling Behavior, *Science and Technology of Advanced Materials*, vol. 6, pp. 236-239, 2005.
- [6] Zhao, Q., Liu, Y., Wang, C., Wang, S., and Müller-Steinhagen, H., Effect of Surface Free Energy on the Adhesion of Biofouling and Crystalline Fouling, *Chemical Engineering Science*, vol. 60, pp. 4858-4865, 2005.
- [7] Rosmaninho, R., Santos, O., Nylander, T., Paulsson, M., Beuf, M., Benezech, T., Yantsios, S., Andristos, N., Karabelas, A., Rizzo, G., Müller-Steinhagen, H., and Melo, L.F., Modified

Stainless Steel Surfaces Targeted to Reduce Fouling – Evaluation of Fouling by Milk Components, *Journal of Food Engineering*, vol. 80, pp. 1176-1187, 2007.

[8] Wang, L.L., and Liu, M.Y., Antifouling Properties on Surfaces of TiO₂ Nanometer Films Coated With Liquid Phase Deposition, *Proc. International Conference on Heat Exchanger Fouling and Cleaning VIII*, Schladming, Austria, Published Online www.heatexchanger-fouling.com, 2009.

[9] Martinelli, E., Agostini, S., Galli, G., Chiellini, E., Glisenti, A., Pettit, M.E., Callow, M.E., Callow, J.A., Graf, K., and Bartels, F.W., Nanostructured Films of Amphiphilic Fluorinated Block Copolymers for Fouling Release Application, *Langmuir*, vol. 24, pp. 13138-13147, 2008.

[10] Tonelli, C., Gavezotti, P., and Strepparola, E., Linear Perfluoropolyethers Difunctional Oligomers: Chemistry, Properties and Applications, *Journal of Fluorine Chemistry*, vol. 95, pp. 51-70, 1999.

[11] Fabbri, P., Messori, M., Pilati, F., and Taurino, R., Hydrophobic and Oleophobic Coatings Based on Perfluoropolyethers/Silica Hybrids by the Sol-gel Method, *Advances in Polymer Technology*, vol. 25, No. 3, pp. 182-190, 2007.

[12] Costa, A.L.H., and Queiroz, E.M., Design Optimization of Shell and Tubes Heat Exchangers, *Applied Thermal Engineering*, vol. 28, pp. 1798-1805, 2008.

[13] Müller-Steinhagen, H. and Zhao, Q., Investigation of Low Fouling Surface Alloys Made by Ion Implantation Technology, *Chemical Engineering Science*, vol. 52, pp. 3321-3332, 1997.

[14] Gnielinski, V., Equation for Calculating Heat Transfer in Single Tube Rows and Banks of Tubes in Transverse Flow, *International Journal of Chemical Engineering*, vol. 19, pp. 380-400, 1979.



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Table 1. Chemical analysis performed on water used as operating fluid for the pilot plant. Results are supplied by Metropolitana Milanese S.p.A.

Parameter	Value	Measure Unit
pH	7.9	pH
Conductivity 20°C	615	µS/cm
Dry residue at 180°C	400	mg/L
Hardness	23	°F
Ca	82	mg/L
Mg	18	mg/L
Na	15	mg/L
K	1	mg/L
Fe	12	mg/L
Mn	1	mg/L

Table 2. Surface characterization of coated stainless steel flat samples by water contact angle measurements and surface free energy determination.

Coating formulation type	Water contact angle (θ degree)	Surface free energy (mN/m)
Uncoated sample	76 ± 5.5	45.7 ± 2.0
A	132 ± 3.4	4.6 ± 0.9
B	117 ± 9.2	7.8 ± 1.0
C	128 ± 5.3	7.1 ± 1.6
D	114 ± 4.2	11.3 ± 1.2
E	135 ± 1.9	3.7 ± 0.3
F	138 ± 4.0	3.3 ± 1.0

Table 3. Results of resistance tests performed on coated stainless steel plain samples. The working temperature is specified for each test.

Conditions	Initial water CA values (θ degree)	Final water CA value (θ degree)
THF – 298.15 K	126 ± 3.7	123 ± 7.5
Acetone – 298.15 K	131 ± 8.8	131 ± 4.8
Municipal water – 323.15 K	143 ± 3.7	134 ± 3.9
Municipal water – 353.15 K	126 ± 5.2	121 ± 3.7
Seawater – 323.15 K	132 ± 9.0	102 ± 12.7
HCl solution – 323.15 K	132 ± 4.9	107 ± 2.9
HCl solution – 353.15 K	137 ± 1.81	102 ± 5.1
Chloroamines – 313.15 K	135 ± 4.0	129.2 ± 5.9
NaOH solution – 323.15 K	129 ± 3.2	105 ± 2.6
NaOH solution - 323.15 K	129 ± 2.8	62 ± 5.6

Table 4. Comparison between the averaged overall heat transfer coefficients and the averaged fouling resistance values calculated monthly for the two heat exchangers.

Period	Coated heat exchanger		Uncoated heat exchanger	
	Overall heat transfer coefficient U [W/m ² K]	Fouling resistance R_f [m ² K/ W]	Overall heat transfer coefficient U [W/m ² K]	Fouling resistance R_f [m ² K/ W]
1	279	0.00098	217.4	0.0025
2	237	0.0017	177.9	0.0036
3	228	0.0018	167.3	0.0051
4	220	0.0021	146.1	0.0053

Table 5. EDX analysis results; atomic % contents of the main elements are reported.

Element	Atomic content [at. %]	
	Sample from coated heat exchanger	Sample from uncoated heat exchanger
Sulfur	0.2	0.04
Magnesium	8.5	8.2
Potassium	0.01	0.04
Calcium	2.18	1.41
Iron	2.9	6.3
Chromium	9.1	9.3
Nickel	1.5	3.1
Silicon	5.6	5.2
Carbon	14.4	10.6
Oxygen	54.9	54.0
Lead	0.0	0.11

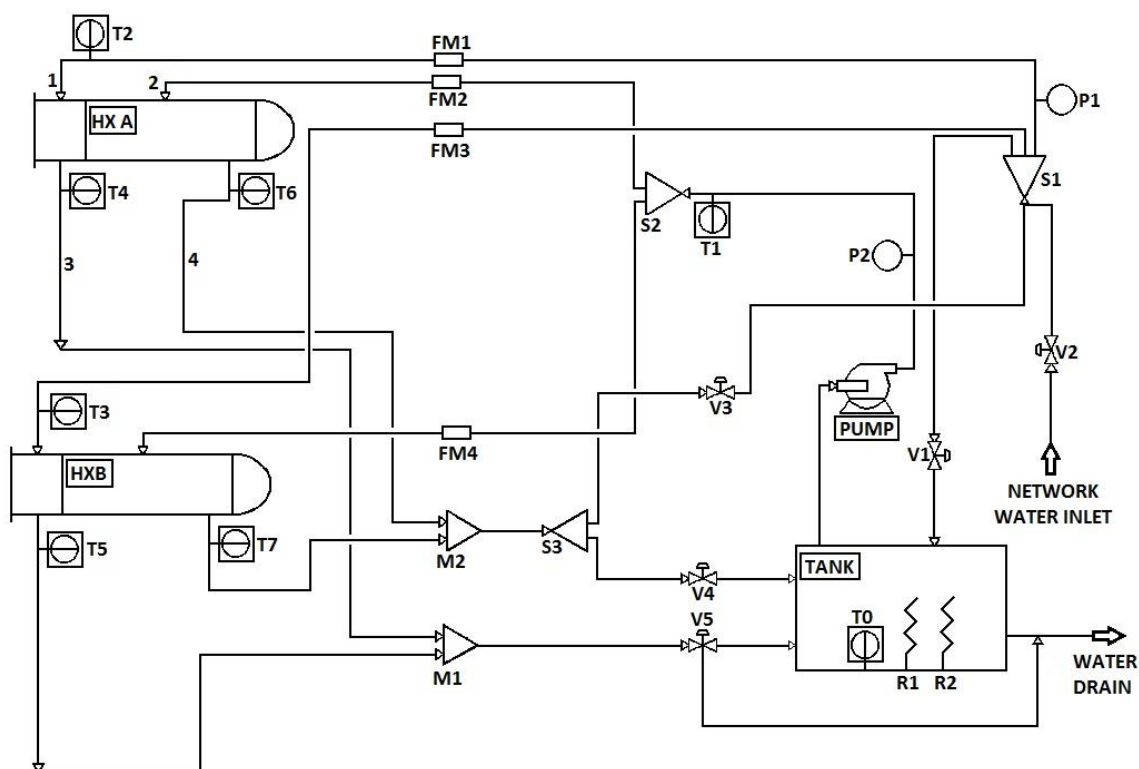


Figure 1 Flow sheet of the pilot plant. HX A: Heat Exchanger A; HX B Heat exchanger B; --1-- Shell side inlet flows; --2-- Tube side inlet flows; --3-- Shell side outlet flows; --4-- Tube side outlet flows; V: valves; T: thermocouples; FM: flow controllers; S: splitter; M: mixer; P: manometers; R1/R2: heating units.

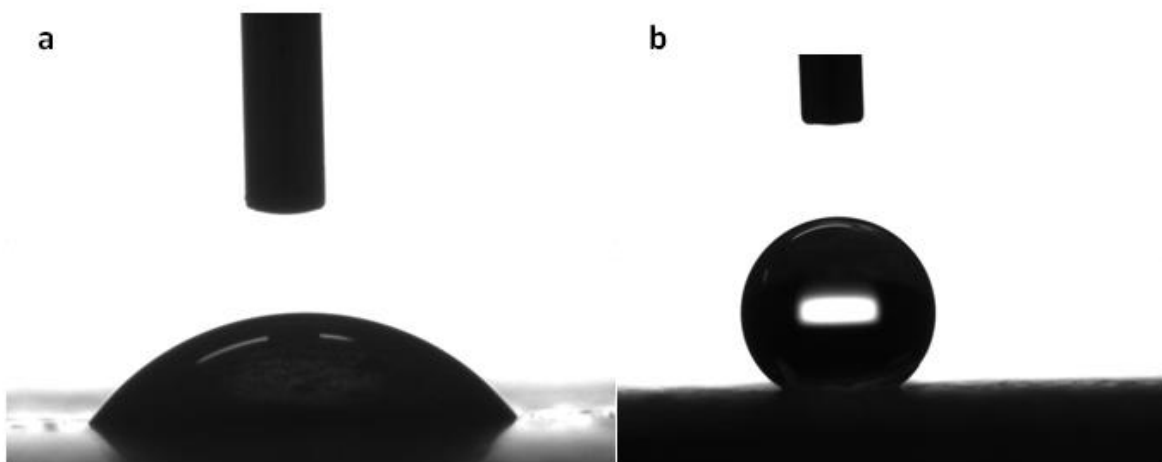


Figure 2 Contact angle measurements photos. Liquid droplet of distilled water deposited on (a) uncoated stainless steel surface and (b) coated stainless steel surface.

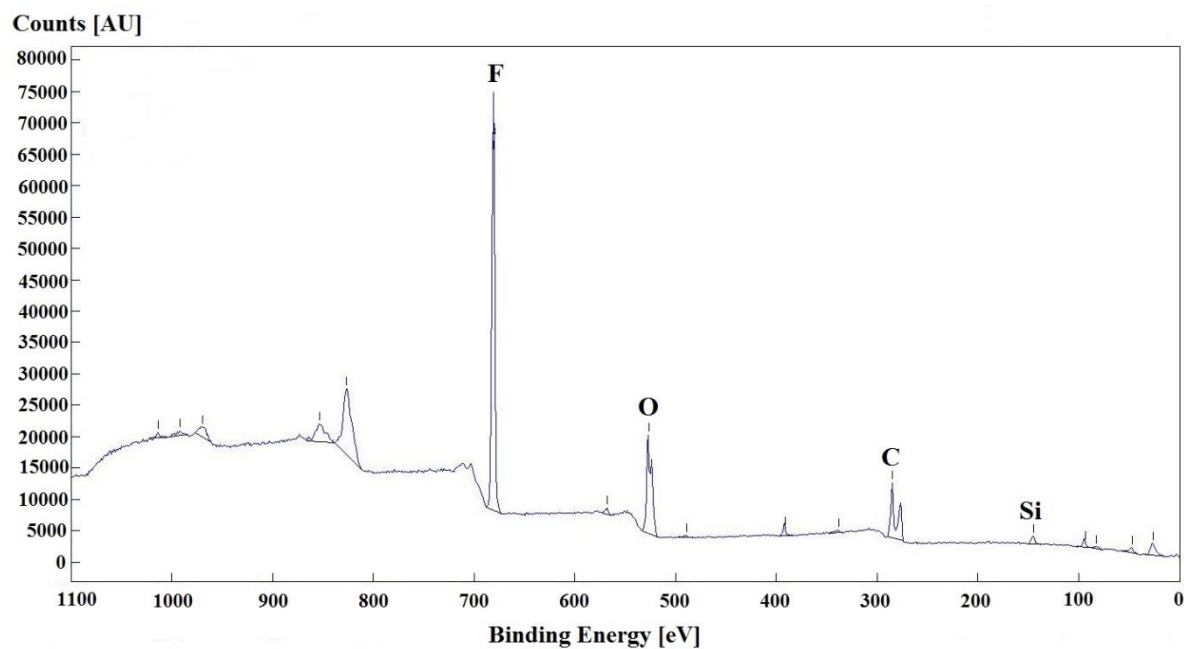


Figure 3 XPS survey analysis in the whole range of X-ray spectrum. Composition table: Si = 3.6 % at; C = 31.4 % at; O = 23.5 % at; F = 41.6 % at.

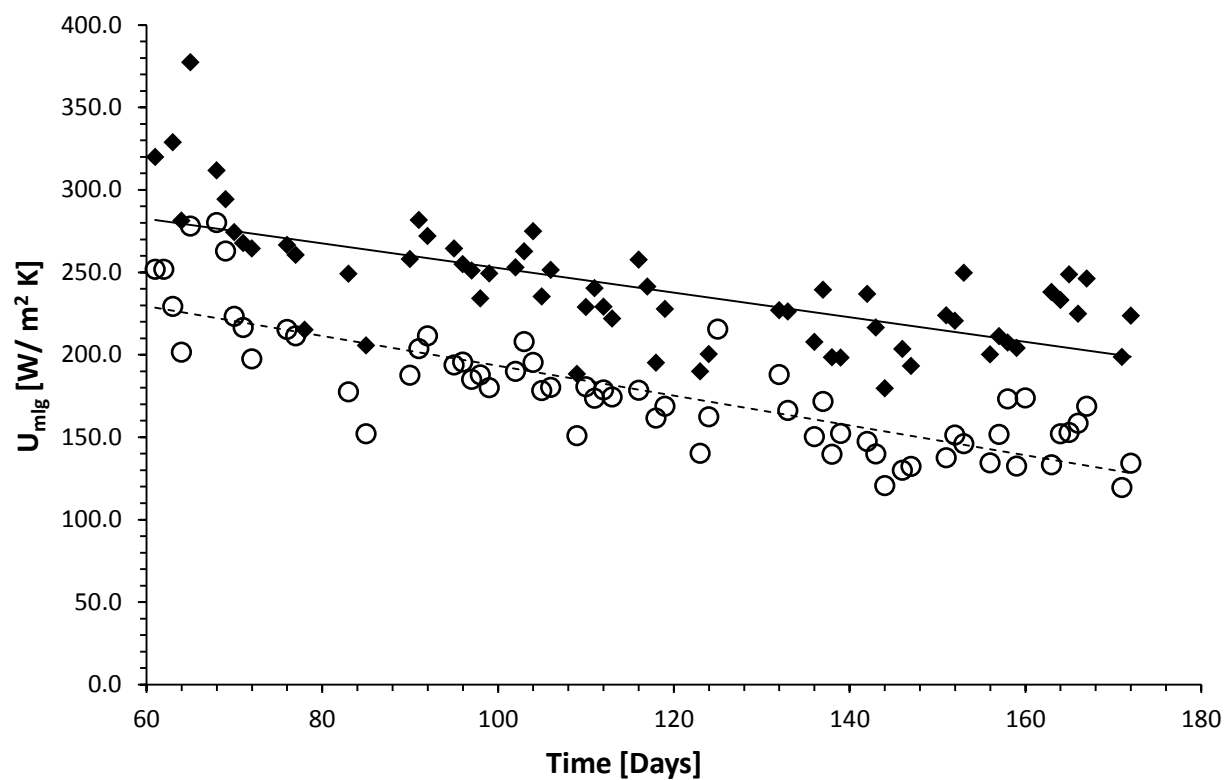


Figure 4 Overall heat transfer coefficient vs time. \blacklozenge Coated heat exchanger; \circ Uncoated heat exchanger.

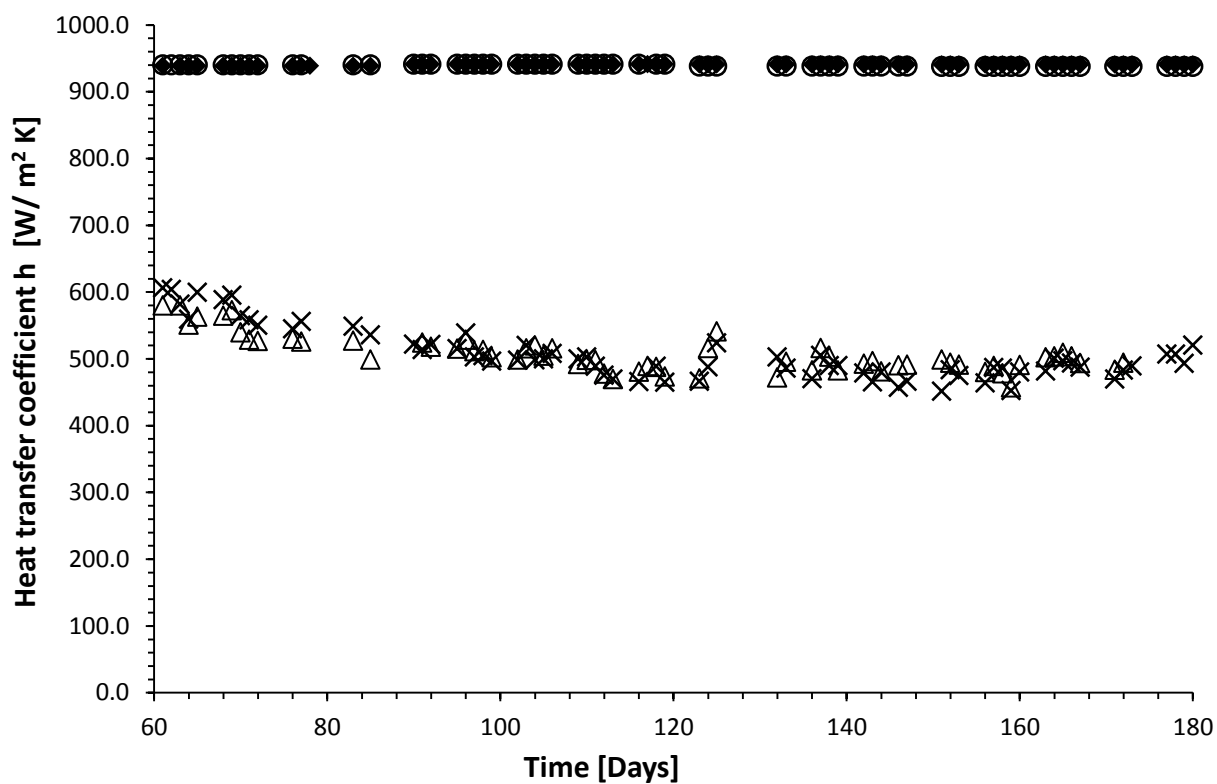


Figure 5 Comparison between shell-side and tube-side heat transfer coefficients of coated and uncoated heat exchangers. \blacklozenge h_H for coated heat exchanger; \circ h_H for uncoated heat exchanger; \triangle h_C for coated heat exchanger; \times h_C for uncoated heat exchanger

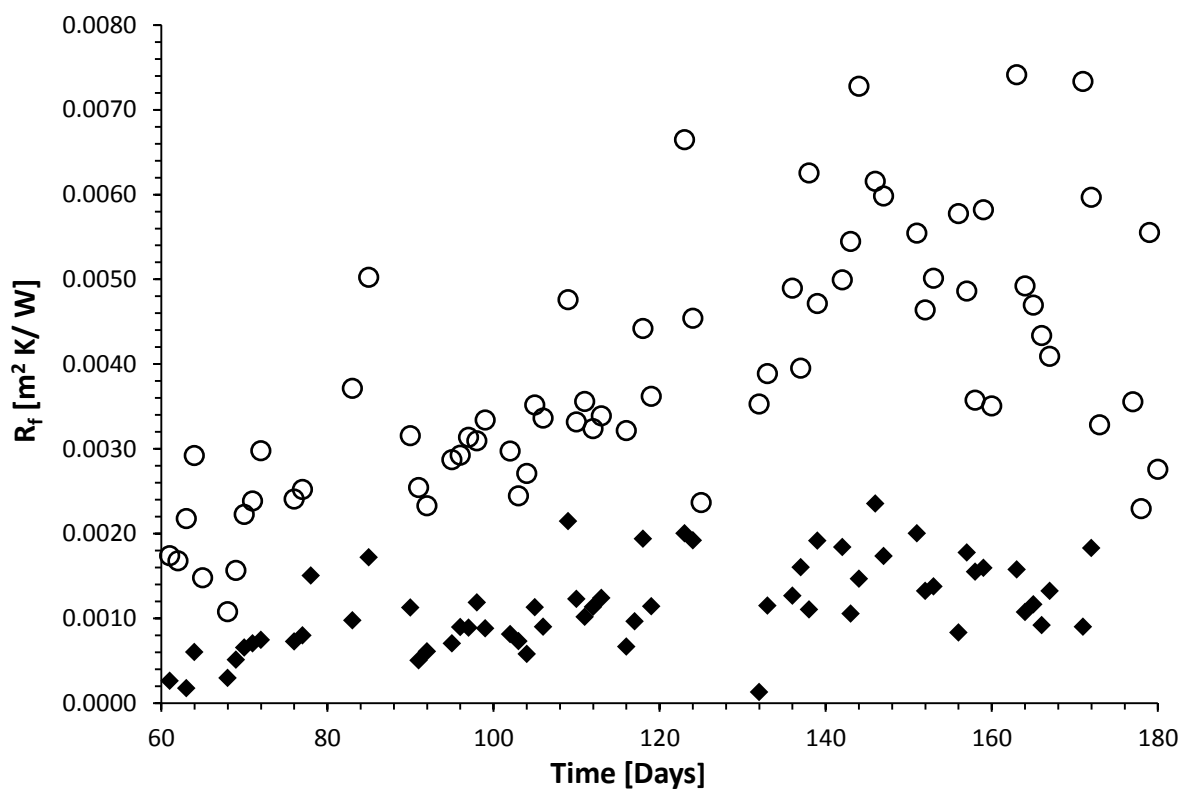


Figure 6 Fouling resistance vs time. \blacklozenge Coated heat exchange \circ Uncoated heat exchanger.

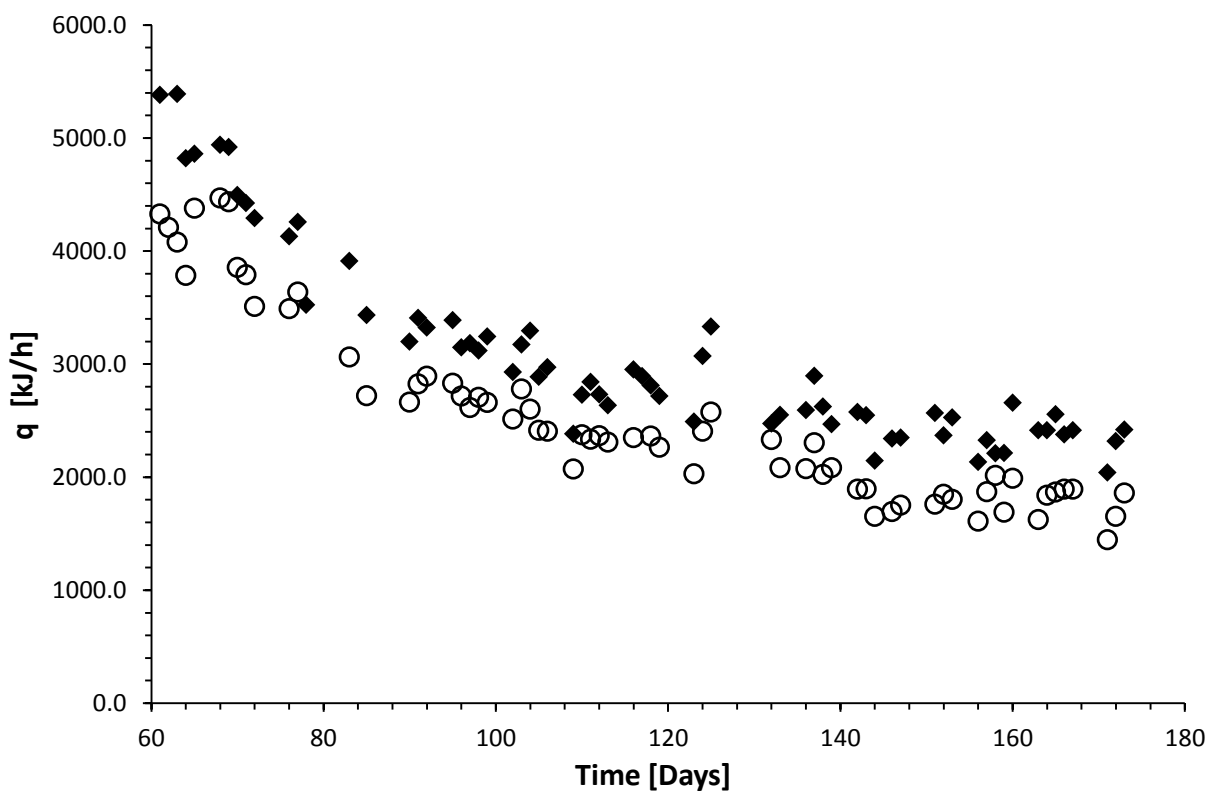


Figure 7 Absolute value of the heat transferred vs time. \blacklozenge Coated heat exchanger; \circ Uncoated heat exchanger.

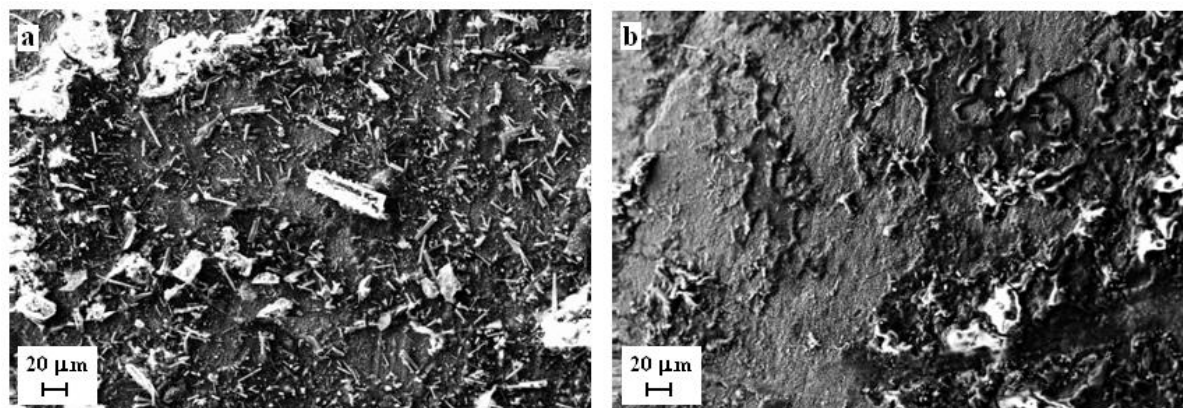


Figure 8 SEM images of fouling deposits formed on the internal tube surface of the (a) coated heat exchanger and (b) uncoated heat exchanger.