

USE OF PERFLUOROPOLYETHER COATINGS TO MITIGATE FOULING ON HEAT EXCHANGER METAL SURFACES

V. Oldani¹, C.L. Bianchi¹, S. Biella², C. Pirola¹ and G. Cattaneo³

¹ Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy & Consorzio INSTM, Via Giusti 9, 50121 Firenze, Italy
valeria.oldani@unimi.it

² Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

³ ST special tanks S.r.L., Via Ai Pascoli snc, 23841 Annone di Brianza (LC), Italy

ABSTRACT

Scope of this research is to have a film coating on steel surfaces in order to reduce interaction between the metal surface and the precipitates, so to reduce the effect of the fouling in heat exchangers.

Perfluoropolyethers are used to obtain nano-range fluorinated layer in order to make steel surfaces hydrophobic. A pilot plant with two identical heat exchangers AEW TEMA TYPE was built to investigate the ability of the hydrophobic coating to prevent fouling. The heat exchangers, installed in parallel, were operating at the same temperature and pressure conditions. The thermodynamic performance of the two heat exchangers was compared. After a five months operation the results obtained demonstrate a significant increase of heat transfer resistance due to scaling on the uncoated heat exchanger respect to the coated one.

INTRODUCTION

The term fouling is usually referred to the accumulation of unwanted deposit on solid surfaces. Related to heat exchangers, fouling phenomenon occurs specially on heat transfer surfaces and the consequences are not negligible. The presence of the deposit, in fact, represents another resistance to heat transfer and it is also responsible of the increasing of the pressure drop. The results is the loss of efficiency thus and a more consumption of energy and an higher operating cost (Bott, 1995).

Several fouling mitigation techniques have been adopted and a great attention has been paid in the past for the on-line physical mitigation of the fouling in the heat exchangers. Physical mitigation techniques try to reduce fouling phenomenon modifying the interaction of the fouling precursors and the heat transfer surfaces. (Müller-Steinhagen et al., 2011).

According to Malayeri et al. (2009), if we consider the physical and geometrical properties of the surfaces, the foulant deposition process can be altered in two ways, or by reducing the work of adhesion between the surface and the fouling precursor or by increasing the shear stress. Key

elements for this is the surface roughness, surface free energy and surface geometry both at micro- and macroscopic scale.

In this research the use of hydrophobic coatings was made in order to modify the surface energy of 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 et al. (1999) demonstrated that the nucleation rate and the adhesion of crystals on the heat transfer surfaces decreases for low energy surfaces. Zhang et al. confirmed the capacity of superhydrophobic 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 superhydrophobic surface can create a barrier preventing the adsorption of micro-organism. Modified polytetrafluoroethylene (PTFE) composite coatings, characterized by non-stick properties and low surface energy, have been developed with good results in fouling protection. Zhao et al. (2005) developed graded Ni-Cu-P-PTFE coatings for minimize adhesion of both micro-organism and scale, showing minimal adhesion of *E. Coli* bacteria and CaSO₄ at lower surface free energy values. Rosmaninho et al. (2007) 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 et al. (2009) used nanometer TiO₂ layer on copper surfaces, obtaining hydrophobic surfaces, able to enlarge the fouling induction period for scale formation. Martinelli et al. (2008) used amphiphilic polymer coatings in order to reduce both the hydrophobic and hydrophilic interactions between organisms responsible of bio-fouling and the surfaces. Results show weaker adhesion of some micro-organism on films reach in the amphiphilic polymer.

In this work functionalized perfluoropolyethers (PFPE) are used to obtain 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 –OH sites (Tonelli et al.). Moreover Fabbri et al. 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 have been studied by XPS and contact angle analysis. Coatings resistance to different liquid environment was tested.

In order to demonstrate the anti-fouling efficacy of the fluorinated coatings developed, a pilot plant with two identical shell and tube heat exchangers has been 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 are greatly involved in fouling phenomena if the design practice is not proper (Costa et al. 2008). Internal and external tubes surfaces of one of the pilot heat exchangers have been treated with a PFPE solution in order to obtain a protective coating. Heat exchangers performances were monitored and fouling resistance was determined along a period of five months.

1 EXPERIMENTAL

1.1 Preparation of fluorinated coated stainless steel surfaces by liquid phase deposition

The fluorinated coatings were first applied on stainless steel (AISI 316) samples, used for coating characterization. The size of that samples was 2 cm x 1 cm and 0,5 cm in thickness.

Samples used for XPS analysis have been submit to a cleaning treatment before depositing the fluorinated cover. Such treatment consists in a cleaning with water and acetone, in order to remove the rough impurities present on the samples.

For contact angle analysis fluorinated coatings were applied on both previously cleaned or un-cleaned surfaces.

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 $x+p$ is between 9 and 15, while the ratio x/p is between 1 and 2.

The coatings have been 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 used. The coating deposition on stainless steel surfaces has been obtained by dipping the samples in the PFPE solution, immersion time can vary from 10 minutes to several hours. Finally a thermic treatment has been performed in a stove at temperatures varying form 80°C to 150°C for 3 to 24 hours.

The tubes of the heat exchanger pilot plant were coated by using a solution obtained from a completely water formulation of a PFPE derivative, using 1% wt of the polymer. Tubes were consequently dipped into the solution for 20 minutes and dried in an industrial stove for 19 hours

at a temperature of 80°C. Tubes surfaces were not specifically treated (for example with some chemicals or mechanical equipment), before the deposition procedure, but only a carefully washing was made.

1.2 Characterization of fluorinated coated surfaces

X-ray photoelectron spectroscopy spectra were obtained by using M-probe apparatus (Surface Science Instruments). Monochromatic Al K α radiation (1486.6 eV) was used as source. Analysis were performed on spot of size 200 μ m \times 750 μ m and pass energy was 25 eV. Survey analyses 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. Free surface energy of coated samples has been determined by using Lewis acid-base approach. Three pairs of SFE-Theta values were obtained for each analysis by using di-iodomethane, water and formamide as solvent. CA values here reported are the average values obtained from at least five different determinations, obtained by deposition of liquid drops at different sample location.

1.3 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 tube and shell heat exchangers AEW TEMA type. Shells had horizontal orientation, with an internal diameter of 90 mm. Tubes were plain type, the outside diameter was 10 mm and the thickness was 2 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. 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 tailor made PFPE coating on the tubes surfaces of only one of them.

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

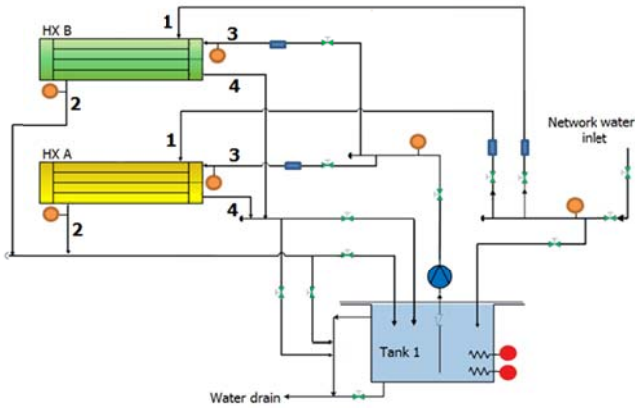


Fig. 1 Flow-sheet of the pilot plant: Heat Exchanger A (HX A); Heat exchanger B (HX B); --1-- Shell side inlet flows; --2-- Shell side outlet flows; --3-- Tube side inlet flows; --4-- Tube side outlet flows; ● Thermocouples; ■ Flow controllers; ▲ Valves; ● Heating units; ● Pump;

Municipal water of the city of Milan was used as operating fluid, in Table 1 is reported the chemical composition of the water used during the experimental work. The cold stream, introduced in shell, had a temperature of 21°C, while hot stream was preheated in a tank at a temperature between 45-60°C, before introducing into the tubes. Temperatures of inlet and outlet fluids of tube-side and shell-side were determined by flexible thermocouples, positioned at the inlets and outlets of the tube-side and shell-side. 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, placed before the tube-side and shell-side flows entrance.

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

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 obviously the same for the two heat exchanger, fed in parallel.

The experimental work ran for a time period of five months, during while the pilot plant worked in continuous conditions. Temperatures and flow rates values were recorded 5/6 times per day, at time intervals of 2 hours.

By knowing the flow rates and the inlet and outlet temperatures of the operating streams, it was possible to determine the overall heat transfer coefficient U , according to the equation:

$$U = \frac{q}{\Delta T_{mlg} A_{mlg}} \quad (1)$$

A_{mlg} is the logarithmic mean of the external and internal heat transfer surface area, while ΔT_{mlg} is the logarithmic mean temperature difference. The expression for the logarithmic mean temperature difference used in Eq. 1 is the sequent:

$$\Delta T_{mlg} = \frac{(T_{in}^1 - T_{out}^2) - (T_{out}^1 - T_{in}^2)}{\ln \left[\frac{(T_{in}^1 - T_{out}^2)}{(T_{out}^1 - T_{in}^2)} \right]} \quad (2)$$

Equation 2 is characteristic for countercurrent flows; the apex 1 is referred to hot stream while the apex two is referred to cold stream. *In* and *out* subscripts are referred respectively to inlet flows and outlet flows.

The cold-side, or shell-side, heat transfer coefficient h_C , was determined by the following relation, valid for laminar flow regime:

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

The hot-side, or tube-side, heat transfer coefficient h_H was determined by the Sieder-Tate relationship, valid for laminar flow regimes:

$$Nu = \frac{h_H D}{k} = 1.86 Gz^{\frac{1}{3}} \left(\frac{\mu_b}{\mu_w} \right)^{0.14} \quad (4)$$

Considering the following Eq. 5, representative of the overall thermal resistance in heat exchangers, it was at least possible to determine the fouling coefficient h_f , by knowing U , h_C and h_H :

$$\frac{1}{U} = \frac{1}{h_C} + \frac{1}{h_H} + \frac{1}{h_f} \quad (5)$$

The fouling thermal resistance R_f was then calculated according to the sequent relation:

$$R_f = \frac{1}{h_f} \quad (6)$$

2 RESULTS AND DISCUSSION

2.1 Characterization of fluorinated coated stainless steel sample

Contact angle and free surface energy: In Figure 2 typical images of water drop deposition on uncoated and coated stainless steel samples are reported. In Table 2 the results of contact angle analysis and free surface energy determination, performed on different type of fluorinated-coated samples, are reported.

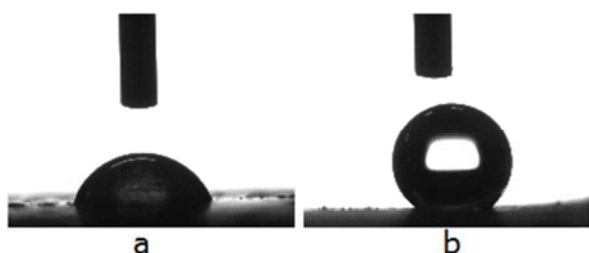


Fig. 2 Liquid droplet of distilled water deposited on uncoated stainless steel surface (a) and coated stainless steel surface (b).

Table 2. Surface characterization of coated stainless steel sample 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

From Table 2 is possible to observe a consistent decrease of free surface energy for fluorinated coated samples related to the uncoated sample. Coating formulations named 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 and B and D is the presence of PFPEs with different α - ω terminations. Deposition and drying procedure for this samples were the same, i.e. 20 minutes immersion and 20 hours drying at 80°C.

Samples E and F were coated by using the same PFPE water formulation, immersing for 5 hours and drying for 20 hours at a temperature of 130°C. The only difference between the two samples is that surface of sample E was previously cleaned before the coating deposition, while surface of sample F was not cleaned. It is interesting to note

that there are no significant differences in contact angle values or surface free energy between this two samples. Thereby is possible to suppose that a specific step of pre-washing, by chemicals or mechanical equipment, is not necessary for the obtainment of hydrophobic surfaces.

Coatings obtained by PFPE formulation A and C are characterized by lower surface energy than coating obtained by B and D formulations, due to a better solubility of the fluoropolymers in the organic media. Nevertheless it was noted 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 water PFPE formulations (samples E and F).

Coating nature and homogeneity: XPS analysis were performed in order to rationalized the chemical features of the fluoropolymer layer on stainless steel surfaces. The results of these analysis (Figure 3) show the presence of a high content of fluorine on the surface investigated (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). The results obtained from high resolution analysis are presented in Figure 4 and 5. In Figure 4 is shown the high resolution spectrum in the typical zone of C-bonds. The predominant part of the fitted spectrum is referred to C-C and C-F bonds. In Figure 5 is presented the high resolution spectrum in the O-bonds zone. Peaks in the carbonyl and carboxylic bonds zone are predominant.

From the observing of XPS results is possible to assume the formation of fluorinated layer on stainless steel surface. Molecules create a cross-linkage each other mainly through C-F and C=O bonds, forming a stable and resistant grid.

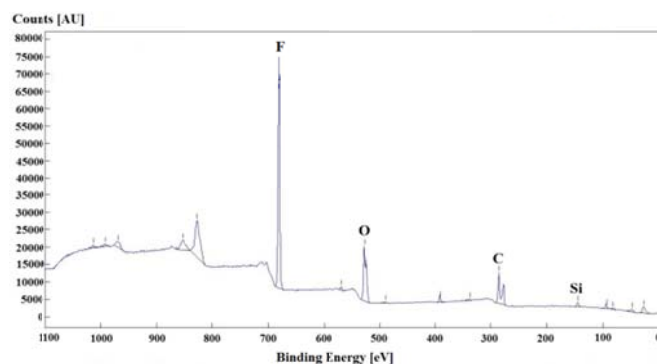


Fig. 3 Survey analysis in the whole range of X-ray spectrum; composition table: Si = 3,6 % at; C = 31,4 % at; O = 23,5 % at; F = 41,6 % at.

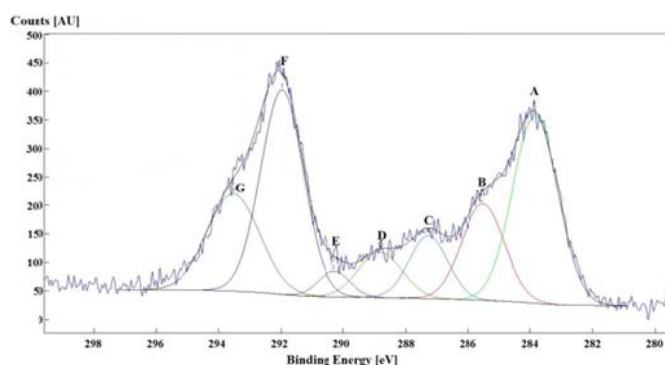


Fig.4 High resolution XPS analysis in the C bonds zone: A = 283,83 eV (C-C bonds); B = 285,50 eV (C-H); C = 287,26 eV (C-O); D = 288,81 eV (C=O); E = 290,30 eV (CF₂-CH₂); F = 291,97 (CF₂/CF₃); G = 293,52 eV (CF₂/CF₃).

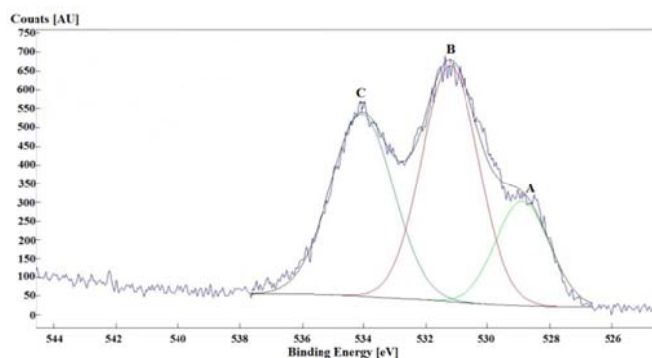


Fig. 5 High resolution XPS spectrum in the O bonds zone: A = 528,88 eV (O₂); B = 531,21 eV (C=O); C = 534,07 eV (C-O).

2.2 Coating chemical resistance

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

Preliminary investigations of the resistance of the coatings have been performed also by immersion of the samples in Milan municipal water, synthetic seawater, NaOH solution (pH 9), HCl solution (pH 2) and NHCl₂ solution (300 ppm). Tests were performed at room temperature or by using thermostatic bath at higher temperatures; samples were kept immersed for a period of 1 week, maintaining continuously stirred the solution. In Table 3 some results are presented.

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

Conditions	Initial water CA values (θ degree)	Final water CA value (θ degree)
THF	126 ± 3.7	123 ± 7,5
Acetone	131 ± 8.8	131 ± 4.8
Municipal water - 50°C	143 ± 3.7	134 ± 3.9
Municipal water - 80°C	126 ± 5.2	121 ± 3.7
Seawater - 50°C	132 ± 9.0	102 ± 12.7
HCl solution - 50°C	132 ± 4.9	107 ± 2.9
HCl solution - 80°C	137 ± 1.81	102 ± 5.1
NHCl ₂ - 40°C	135 ± 4.0	129.2 ± 5.9
NaOH solution - 50°C	129 ± 3.2	105 ± 2.6
NaOH solution - 80°C	129 ± 2.8	62 ± 5.6

The results show good coating resistance to water, chlorine solution and acidic solution at mild temperatures and high temperatures. Surfaces remain hydrophobic also after immersion in synthetic seawater, as long as the temperature is under 50°C. Alkaline environments are more aggressive for the PFPE coatings and at high temperature coatings seem to deteriorate.

2.3 Heat transfer coefficient and fouling resistance determination

Heat exchanger pilot plant has been built for determining anti-fouling properties of the fluorinated coating developed. Operative conditions of the pilot plant were kept mild, i.e. laminar flows and small temperature differences, in order to assess at first the ability of the hydrophobic layer to reduce foulant adhesion on the heat transfer surfaces.

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 level thickness, does not cause any variation to flow regime, it is possible to compare the results obtained for coated and uncoated heat exchangers. Data presented in this work are collected from the 60th operating day until the 172nd.

In Figure 6 the overall heat transfer coefficient (U) variation in function of the time is reported. For both heat exchangers U decreases with time, but values determined for coated heat exchangers are always higher than the ones obtained from the monitoring of the uncoated heat exchangers.

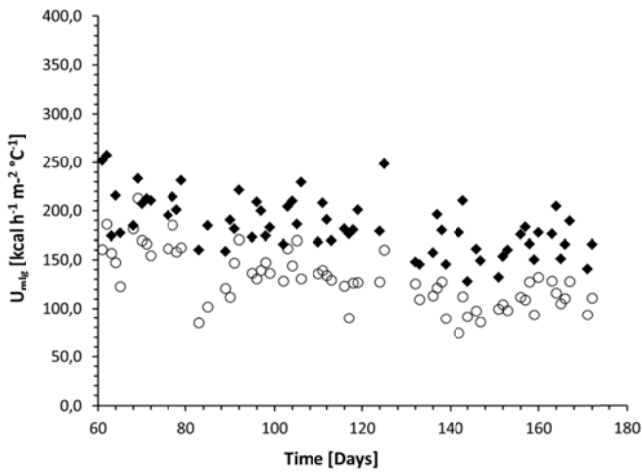


Fig. 6 Overall heat transfer coefficient vs time: \blacklozenge Coated heat exchanger; \circ Uncoated heat exchanger.

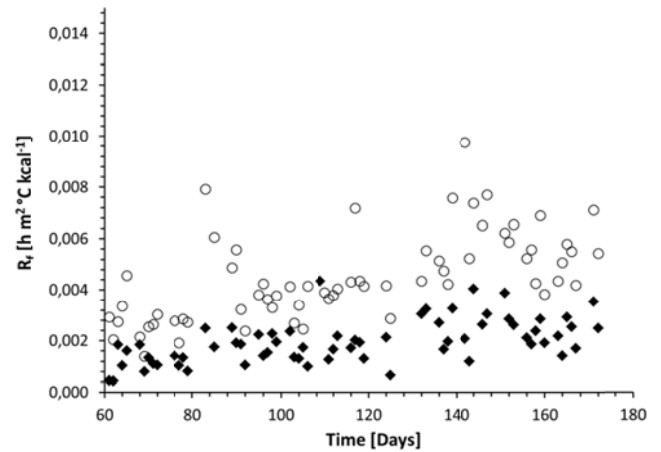


Fig. 8 Fouling resistance vs time: \blacklozenge Coated heat exchange \circ Uncoated heat exchanger.

The decrease of U values with time can be correlated to an increase of the thermal resistance. Overall thermal resistance depends on shell side and tube side heat transfer coefficient and on fouling coefficient.

In Figure 7 shell side and tube side heat transfer coefficient values are reported; it is possible to evidence that these values are almost the same between the two heat exchangers. Overall thermal resistance variation is consequently dependent only from fouling coefficient variation with time, or better from fouling resistance variation.

Parameters able to influence fouling rate and behavior in heat exchangers are the foulant concentration in operating fluids, the flow geometry and the operating properties, such as flows, temperatures and velocities. For the obtainment of comparable fouling resistance values between the two heat exchangers, all this parameters were kept similar for both of them, the only variable is the presence of the hydrophobic coating on tubes surface of one of them.

Fouling resistance variation with time is presented in Figure 8. It is possible to observe differences in fouling behavior between the two heat exchangers. The trend of the fouling resistance respect to time is comparable to the trend of overall heat transfer coefficient. Fouling resistance grow with time and R_f values calculated for the uncoated heat exchanger are always greater than the ones evaluated for the coated heat exchanger. Moreover, R_f value calculated for uncoated heat exchanger during the 60th working day is reach by the coated heat exchanger at day 140. These results demonstrate the ability of the hydrophobic layer to limit foulant deposition on heat transfer surfaces.

To more clearly observe the effect of the coating used, in Figure 9 is represented the quantity of heat transferred respect to the time by the two heat exchanger. One more time is possible to highlight a better performance for the treated heat exchanger after the 60th operation day. We suppose that a greater quantity of heat have been transferred at the same time by the coated heat exchanger respect to the uncoated one, due to the presence of a thinner fouling film or to an absence of it. This theory can be supported by the results obtained in the determination of the fouling resistance previously discussed.

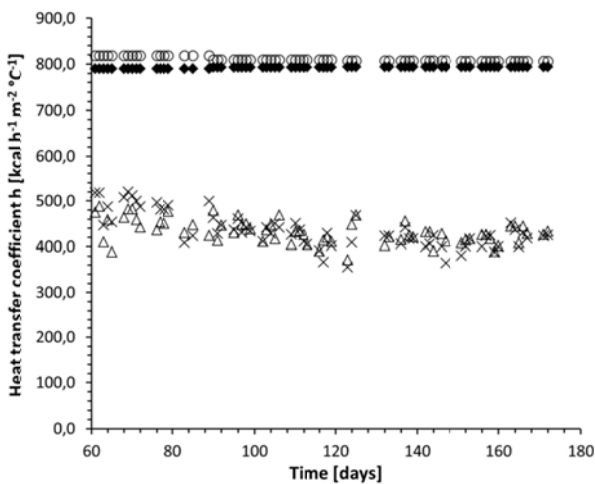


Fig. 7 Comparison between shell-side and tube-side heat transfer coefficients of coated and uncoated heat exchangers: \blacklozenge h_H for coated heat exchanger; \circ h_H for uncoated heat exchanger; \triangle h_C for coated heat exchanger; \times h_C for uncoated heat exchanger.

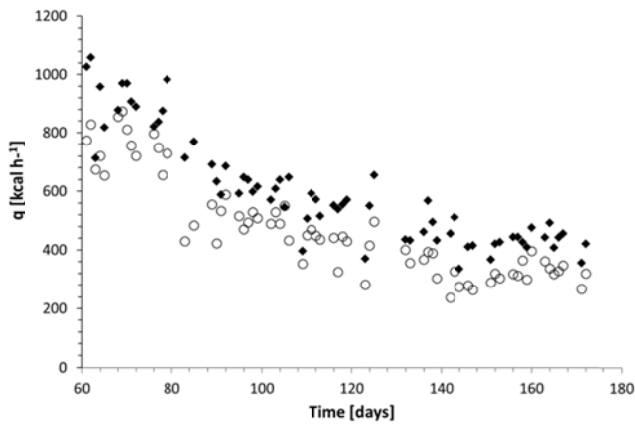


Fig. 9 Absolute value of the heat transferred vs time: ◆ Coated heat exchanger; ○ Uncoated heat exchanger.

A comparison between the progressive increase in time of fouling resistance of the two heat exchangers is presented in Figure 10. For each period of work considered, is reported the fouling resistance average value. R_f for the uncoated heat exchanger is about the double of the value calculated for the coated heat exchanger, moreover the increase in time of the fouling resistance seems to be higher for the uncoated heat exchanger than the coated one within 160 days.

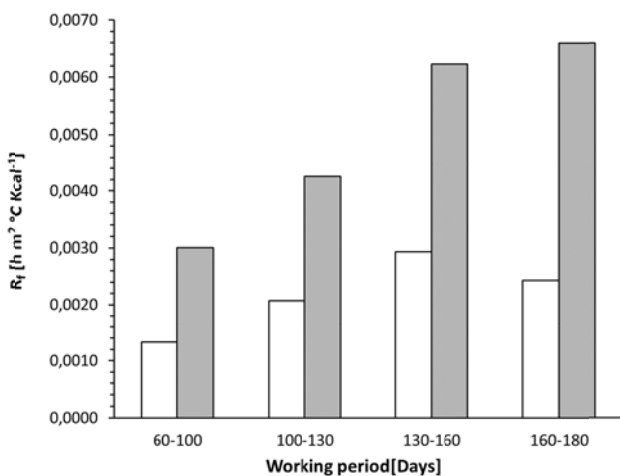


Fig. 10 Average fouling resistance values determined for increasing working period of the pilot plant: □ Coated Heat exchanger; ▒ Uncoated heat exchanger.

After 5 months operation, pilot plant was shut down. Some tubes samples, covered by a foulant layer, of the two heat exchangers, have been collected. SEM and EDX analysis were performed on this samples in order to determine the composition of the deposits.

Images in Fig. 11 show the presence of crystalline deposits on both the internal tube surfaces, coming from the coated and uncoated heat exchanger. EDX results point out

an high atomic content of carbon, magnesium, calcium and oxygen. Chromium and nickel derive from stainless steel (Tab. 4). 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 the uncoated one.

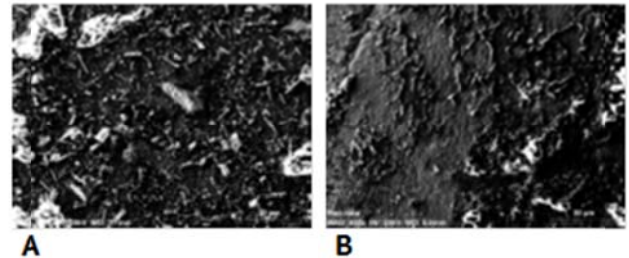


Fig. 11 SEM images (electron microscopy Philips XL-30CP with RBS detector of back scattered electrons) of fouling deposits on the internal surfaces of the pilot plant tubes: A tube from coated heat exchanger; B tube from uncoated heat exchanger. MAG: 802x, HV: 20 kV, WD: 7.1 mm.

Tab. 4 EDX analysis results; atomic % contents of the main elements are reported.

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

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 has been obtained by the deposition of a fluorinated coating, by using a α - ω functionalized perfluoropolyether compound.

1. Low surface energy was evaluated for stainless steel samples coated with the PFPE derivatives (3.3-11.3 mN/m). Hydrophobicity was attested by water contact angle analysis; depending on the type of PFPE formulation used and coating deposition procedure, it possible to obtain high contact angle values, from 100° up to 140°;
2. Immersion in THF or acetone didn't affect the stability and the hydrophobicity of the coatings, consequently, the formation of chemical bonds between the PFPE functional group and the chemical sites present on the stainless steel surfaces was assumed. It is supposed the formation of a nanometer level thickness coating.
3. Coating chemical resistance has been studied. Tests performed for 1 week immersion in different chemical and aggressive environments highlighted good resistance of the coatings.
4. The effective anti-fouling efficiency of the hydrophobic coating has been tested by a pilot plant constituted of two shell and tube heat exchangers, tubes of 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 (0.0024 vs 0.0066 h m² °C / kcal). The fluorinated coating actually limited the scale formation on the heat transfer surfaces.
5. 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.

NOMENCLATURE

A	Heat transfer surface area, $2\pi DL$, m ²
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 conductivity, W/m K
L	Length, m
l_b	Baffle spacing, m
Nu	Nusselt number, hD/k , dimensionless
Pr	Prandlt number, $c_p \mu_b/k$, dimensionless
q	Heat quantity, J/h
Re_G	Reynolds number defined by Gnielinsky, $W L / \epsilon_F D l_b \mu_b$, dimensionless
T	Temperature, K
U	Overall heat transfer coefficient, W/m ² K
W	Total mass flowrate, kg/h
ϵ_F	Shell void fraction, m
θ	Contact angle °
μ	Fluid viscosity, Pa·s

Subscript

b	Bulk
C	Cold
f	Fouling
H	Hot
in	Inner
mlg	Logarithmic mean
out	Outer
w	Wall

REFERENCES

- Bott T.R., 1995, Fouling of heat exchangers, ISBN 0444821864, Elsevier Science & Technology Book.
- Costa A.L.H., Queiroz E.M., 2008, Design optimization of shell and tubes heat exchangers, *Applied Thermal Engineering*, Vol. 28, pp. 1798-1805.
- Fabbri P., Messori M., Pilati F., Taurino R., 2007, 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.
- Förster M. Bohnet M., 1999, 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
- Malayeri M.R., Al-Janabi A., Müller-Steinhagen H., 2009, Application of nano-modified surfaces for fouling mitigation, *International Journal of Energy Research*, Vol. 33, pp.1101-1113.
- 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., 2008, Nanostructured films of amphiphilic fluorinated block copolymers for fouling release application, *Langmuir*, Vol. 24, pp. 13138-13147.
- Müller-Steinhagen H., Malayeri M.R. and Watkinson P., 2011, Heat exchanger fouling: mitigation and cleaning strategies, *Heat Transfer Engineering*, Vol. 32(3-4), pp. 189-196.
- 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., 2007, Modified stainless steel surfaces targeted to reduce fouling – Evaluation of fouling by milk components, *J. of Food Engineering*, Vol. 80, pp. 1176-1187.
- Tonelli C., Gavezotti P., Strepparola E., 1999, Linear perfluoropolyethers difunctional oligomers: chemistry, properties and applications, *Journal of fluorine chemistry*, Vol. 95, pp.51-70.
- Zhang H., Lamb R., Lewis J., 2005, Engineering nanoscale roughness on hydrophobic surface-preliminary assessment of fouling behavior, *Science and Technology of advanced materials*, Vol. 6, pp. 236-239.
- Zhao Q., Liu Y., Wang C., Wang S. and Müller-Steinhagen H., 2005, Effect of surface free energy on the adhesion of biofouling and crystalline fouling, *Chemical Engineering Science*, Vol. 60, pp. 4858-4865.