Applied Thermal Engineering 106 (2016) 427–431

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research Paper

Use of a sol-gel hybrid coating composed by a fluoropolymer and silica for the mitigation of mineral fouling in heat exchangers

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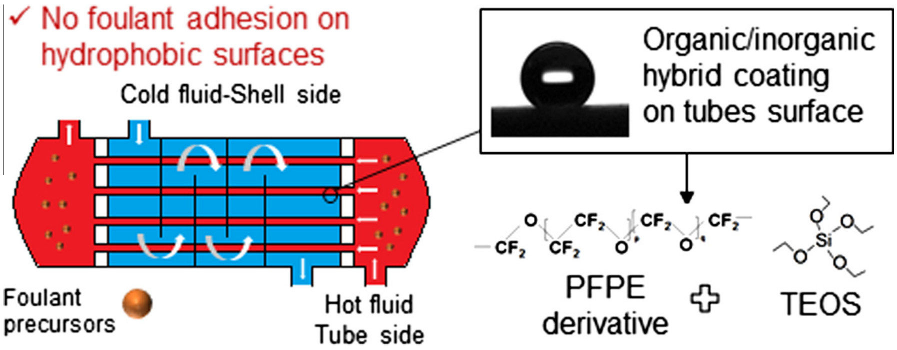
HIGHLIGHTS

- A hybrid coating containing a perfluoropolyether and a silica network was prepared.
- The coating was hydrophobic and showed high mechanical and thermal stability.
- The coating was applied on the heat transfer surfaces of a pilot plant.
- The heat transfer performances in presence of crystallization fouling were checked.
- The fouling induction period increased of 200 h by the presence of the coating.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 February 2016
Revised 25 April 2016
Accepted 2 June 2016
Available online 3 June 2016

Keywords:
Fouling
Heat exchangers
Hybrid coatings
Hydrophobicity

ABSTRACT

The technology of the organic/inorganic hybrid coating was employed in the preparation of a hydrophobic coating (contact angle higher than 140°) for fouling mitigation on stainless steel heat transfer surfaces. A commercial triethoxysilane perfluoropolyethers was combined with a sol-gel silica network with the aim to increase the mechanical and thermal resistance of the films when exposed to aggressive liquid environments as the heat exchanging fluids. The experimentation on a shell and tube heat exchanger pilot plant confirmed the ability of the hybrid coating to prolong the crystallization fouling induction period of 200 h in respect to an uncoated heat exchanger, operating in the same conditions. Moreover, the fouling particles deposited on the coated heat transfer surfaces had only slight adhesion strength toward the coated surfaces and were easily removed by inducing higher wall shear stresses inside the tubes of the plant.

1. Introduction

Heat exchangers provide the perfect conditions for fouling; the heat exchanging fluids often contain dispersed or dissolved particles, which can adhere on the heat transfer surfaces, and the working temperatures are in general favourable for microorganism proliferation. The main effects of fouling in heat exchangers can be summarized as the increase of the overall heat transfer resistance and the increase of the pressure drop due to the reduction of the cross-sectional flow area, which means losses in the heat transfer efficiency [1,2]. Among all the possible techniques available for fouling control in heat exchangers, the use of metal surfaces, which do not suffer from deposition phenomena, would be certainly one of the best options [3]. To achieve this goal, an anti-fouling coating can be applied on the heat transfer surfaces. Many researches attest in particular the effectiveness of hydrophobic coatings on

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http://dx.doi.org/10.1016/j.applthermaleng.2016.06.014
1359-4311/

mitigation of crystallization fouling in heat exchangers [4–7]. Crystallization fouling is one of the most common types of fouling involving heat exchangers and consists in the precipitation and deposition of dissolved salts, after the supersaturation [8].

The preparation of anti-fouling coatings for application on heat transfer surfaces, however, is not trivial [9]. Beside the typical properties of mechanical, chemical and thermal stability, anti-fouling coatings for heat exchangers should not represent a further heat transfer resistance, hence their thickness have to be maintained lower than 5 μm to ensure no insulator effects [3]. Moreover, the effect of the coatings on the average surface roughness should be controlled; the average roughness of the heat transfer surface can in fact greatly influence the flow regime of the fluid in contact with the heat surface as well as the extent of the fouling phenomenon [10,11].

The organic/inorganic hybrid coating technology can contribute to the obtainment of an anti-fouling coating with the properties just discussed. The careful combination of an organic compound with an inorganic one permits in fact the obtainment of a composite material possessing both the typical properties of the two components [12].

Several reviews [13–15] attest the efficiency of the hybrid coating technology in the mitigation of bio-fouling. Even so, only few researches report the effects of the use of hybrid coatings in the mitigation of other types of fouling phenomena, such as mineral fouling, corrosion fouling or crude oil fouling, especially in heat transfer equipment. Cai et al. [16] studied a composite coating composed by titanium dioxide nanoparticles and fluoroalkylsilane, observing a lower fouling resistance in pool boiling saturated by $CaCO_3$ in presence of the coating. Holberg and Bischoff [17] reported the application of hybrid coatings composed by an urea-siloxane systems. By the optimization of the synthesis, the authors obtained a mechanical robust hybrid coating with proven ability to repel crude-oil derived foulants on heat transfer surfaces.

In this research, we implemented an easy to handle procedure for the preparation of the coating, employing the well-known sol-gel synthetic technique. The procedure includes the co-condensation of tetraethyl orthosilicate, the precursor for silica coating preparation, with a triethoxysilane α,ω-substituted perfluoropolyether. This synthetic approach permits to intersperse homogeneously the inorganic phase (SiO_2) in the organic one, without compromising the typical properties of the polymer [18]. Hence, we obtained a stable hydrophobic coating based on the fluoropolymer [19] with enhanced thermal and mechanical stability conferred by the presence of the metal oxide, which possesses superior mechanical properties in respect to polymers [20]. The mechanical and chemical stability of the hybrid coating prepared in this work were investigated in liquid media, using chemically aggressive solutions and high temperatures to simulate the exposition to heat exchanging fluids. The anti-fouling properties, instead, were evaluated in a heat exchanger pilot plant, operating with water rich in carbonate salts responsible of crystallization fouling phenomena.

2. Material and methods

2.1. Coatings synthesis and preparation

The hybrid coating (briefly named $S10/SiO_2$) was prepared by combining a sol-gel silica coating and a perfluoropolyether derivative. The silica coating was prepared by classical sol-gel synthesis starting from the alkoxide precursor (TEOS), as reported by Kermadi et al. [21]. The commercial perfluoropolyether (named Fluorolink®S10, provided by Solvay Specialty Polymers) was mixed with TEOS, maintaining a weight ratio of 80/20 respectively, before the initiation of the hydrolysis and condensation reaction. iso-propanol was used as solvent in the sol-gel synthesis, the amount of solvent was maintained in large excess in order to reduce the viscosity of the sol-gel. The amount of S10 in respect to the solvent was 2.7 wt%. Water was added in the molar ratio of 4.0/1.0 in respect to TEOS, and pH was regulated at a value of 2 using nitric acid. The sol-gel synthesis was performed at room temperature, maintaining the solution under stirring for 24 h. The coatings were deposited on stainless steel substrates (plain samples of dimensions 30 × 20 mm or tubes samples with internal diameter of 8 mm and length 100 mm) via dip-coating. Namely, the substrates were kept immersed in the coating solution for 3 h and heat treated for 3 h at 383 K and for 1 h at 473 K in a static oven. Before the coating deposition, the stainless steel substrates were rinsed with water and acetone. Similarly, the tube bundle of the heat exchanger pilot plant was carefully washed with water and acetone and consequently dipped in the coating formulation (using a tank of 8 L volume) for 3 h. The heat treatment was performed as previously described.

2.2. Resistance and fouling tests

The hybrid coating prepared was preliminary studied to assess its resistance when exposed to liquids simulating the heat exchanging fluids. Plain stainless steel substrates where used as samples for the resistance tests. The chemical stability was investigated by immersing the samples in a hydrochloric acid solution (HCl, pH = 2), a disinfectant solution containing chloramines (pH = 7), and a synthetic seawater solution. During the tests, all the solutions were thermostated at a temperature of 323 K. The thermal resistance was assessed by exposing the samples to water heated at 343 K. The mechanical resistance was instead investigated by exposing the samples to a water flow, at a temperature of 323 K, and velocity of 0.17 m/s. A similar test was performed using a solution of $CaSO_4$, 4 g/L concentrated, instead of water. In that case, the $CaSO_4$ solution, pre-heated at a temperature of 313 K, was pumped (flowrate: 0.15 m/s) in a tubular stainless steel sample characterized by the presence of the coating on its internal surface. In such a way it was possible to assess the wear resistance of the coatings in presence of a solution rich in suspended particles. The apparatus used for the latter tests are described elsewhere [22]. All the resistance tests lasted for 30 days, apart from the test performed in presence of the $CaSO_4$ solution, which lasted for 43 days. The testing liquids where replaced periodically every 2/3 days, in order to maintain unaltered the environmental conditions to which the samples where exposed. The same resistance test was repeated at least two times, using different coated samples. The deterioration of the coatings was monitored by measuring the water contact angle value of the coated substrates (Kruss Easydrop instrument). For each sample, at least 5 droplets where deposited on different position of the surface, and the CA value was calculated as the average of these measurements. A decrease in the CA value was representive of a deterioration of the coating.

The anti-fouling ability of the hybrid coating $S10/SiO_2$ was investigated on real heat transfer surfaces, by the aim of a heat exchanger pilot plant. The schematic of the plant is reported in Fig. 1.

The pilot plant is composed by two shell and tube heat exchangers (STHX), TEMA type NEW, working in parallel and designed identically. During the experimentation, only the tube bundle of STHX A was coated. Each heat exchanger is equipped with control devices (Table 1), which permitted the recording of the temperatures of the inlet and outlet fluids, in both shell side and tube side. The flowrates of the inlet fluids in shells and tubes were regulated using float flowmeters (see Table 1).