# **CRYSTALLIZATION FOULING ON MODIFIED HEAT EXCHANGER SURFACES**

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# ABSTRACT

Fouling of heat transfer surfaces is a major challenge in design and operation of the process equipment. Fouling decreases economic profitability of processes as well as increases the environmental impact of production. Significant savings could be achieved with even rather small improvements in prevention of fouling of heat transfer equipment. One of the options to prevent fouling on heat transfer surfaces is to modify the heat transfer surface.

This study investigates the effects of different surface modification methods to prevent fouling on a heat transfer surface by coating, grinding, polishing, and patterning. Fouling behavior of the surface modifications are studied in a laboratory scale fouling test set-up using supersaturated calcium carbonate solution as a test fluid.

Surface modifications are found to have a significant effect on the fouling induction time when compared to the unmodified stainless steel. The most significant increase in the induction time is obtained by the organosilicon thin films deposited on the stainless steel (AISI 316L 2B) having up to 7.5 times longer induction time of the unmodified reference material. Patterning increases the induction time up to 2.5 times and grinding up to 1.7 times. The mechanism in the fouling reduction seems to be related to chemical functionalization, hydrodynamic effects, and surface morphology.

# **INTRODUCTION**

Heat exchangers are facing severe problems due to accumulations of unwanted material, i.e. fouling, on the heat transfer surfaces. Fouling increases environmental impacts (Müller-Steinhagen et al. 2009) of processes and decreases economical profitability (Bansal et al. 2008) of production due to significant energy, material and production losses, which arise due to fouling.

Fouling is often impossible to avoid totally. Instead, many methods have been proposed for controlling fouling. These methods include e.g. mechanical methods (e.g. scraping, brushing), use of chemical additives (e.g. sequestering agents, threshold agents, crystal modifiers, dispersants or corrosion inhibitors), non-chemical treatments of the process fluid (e.g. magnetic, ultrasonic, electric, acoustic or catalytic treatment), and modifications to the flow conditions (e.g. using pulsating or reversing flow, turbulence promoters, vibration). (Cho et al. 2004a, Cho et al. 2004b, Lee et al. 2006, Föster 1999, Augustin et al. 2010) In addition, chemical (e.g. coating) and physical (e.g. polishing, patterning) surface treatments have been proposed for fouling reduction (Karabelas 2002, Dowling et al. 2010, Puhakka and Lecoq 2013, Guillot et al. 2015, Pääkkönen et al. 2013).

Surface characteristics, such as surface energy, are important parameters on fouling processes. Surface studies have had growing interest amongst researchers since mid 90's. In many studies lower surface energy has observed to reduce fouling, but also contradictory results have been reported. (Müller-Steinhagen et al. 2007, Förster and Bohnet 1999, Geddert et al. 2007) Studies on the interactive forces between deposits and surfaces have provided some insights into the adhesion mechanisms on modified surfaces (Müller-Steinhagen et al. 2011). The control or the modification of the surface energy can be achieved by the deposition of a coating to the surface in order to control and tune various parameters such as the elemental composition, the wettability, the charge state or the crystallinity of the surface.

Physical surface treatment may be of different scale ranging from nanostructured surface to sub-micron and even to millimeters scale. Grinding and polishing are examples of the surface treatments leading to micron scale surface roughness. The diffusion flux of ions to the surface is affected by real surface area increased by roughness (Föster and Bohnet 1999). The number of roughness peaks per surface area is suggested to determine a threshold and rate of nucleation (Peltonen et al. 2004). Also, roughness affects wettability and adhesive strength of the crystal at the heat transfer surface due to changed contact area (Herz et al. 2008, Keysar et al. 1994). In addition, the tenacity of the deposition is affected by the surface roughness (Keysar et al. 1994). Different roughness parameter has been developed further by availability of areal surface imaging such as AFM. The most commonly used parameters (developed 2D before AFM) may not be specific enough to describe such as precipitation of crystals and wetting (Peltonen et al. 2004). The surface morphology affects the deposition to the surface and removal from the surface also

due to hydrodynamical effects, which contributes to the mass transfer to the surface and shear stress at the surface (Förster et al. 1999, Herz et al. 2008, Pääkkönen et al. 2013). These effects are significant especially with larger surface patterns (Pääkkönen et al. 2013).

Even the surface modifications have shown to provide improvement to the fouling behavior, the modifications having different morphologies and length scales have not been compared earlier. This study aims to prolong the induction time of fouling by surface modifications and to compare the potential of chemical (siloxane coatings) and physical (grinding, polishing and patterning) surface treatments for fouling mitigation in calcium carbonate crystallization fouling on a heat exchanger surface.

## METHODS

## **Experimental**

Fouling experiments are done in a fouling test set-up shown in Fig. 1 and described in detail in Pääkkönen et al. (2012) and Riihimäki et al. (2009). The set-up is a closed loop system containing a 100 dm<sup>3</sup> tank (1) (see Fig. 1 for numbers), from which the solution is circulated by a pump (2) through filters (3) and a double pipe heat exchangers (4) to a test area (5) in which fouling takes place. The system has a controlled flow rate (v = 0.17 m/s – 0.4 m/s; D<sub>h</sub> = 0.037 m, Re = 5 800 – 12 300), bulk fluid temperature (T<sub>b</sub> = 30 °C) and conductivity (6) as well as heat flux from the heated test surface (q =  $50 - 78 \text{ kW/m}^2$ ).



Fig. 1 Fouling test set-up (modified from Riihimäki et al. 2009).

The fouling behavior of different surface modifications is studied using supersaturated aqueous CaCO<sub>3</sub> solution, from which inversely soluble CaCO<sub>3</sub> precipitates to the heated test surface. The solution is prepared by mixing dissolved NaHCO<sub>3</sub> and CaCl<sub>2</sub>  $\cdot$  2H<sub>2</sub>O salts (0.5 – 0.75 g/l) with deionized water. (Pääkkönen et al. 2012) The precipitation of CaCO<sub>3</sub> on the heated surface increases the heat transfer resistance, which increases the measured wall temperature. The fouling resistance  $(R_f)$  can be calculated from the wall temperature as

$$R_f = \frac{T_W^t - T_W^0}{q} \tag{1}$$

where  $T_w$  is the wall temperature, q the heat flux, and t denote the time.

The fouling of different modified surfaces are measured in slightly different operating conditions, but a reference experiment on an unmodified surface is always done at the same conditions. This allows comparison of different surface modifications to the unmodified stainless steel surface using relative fouling rates and induction times.

### Surface modifications

Fouling behavior of three different surface modifications (i.e. coating, roughening/polishing, and patterning) is studied by comparing the fouling of each modification on a flat reference surface. The test surfaces are stainless steel surfaces (AISI 316L 2B or 304L 2B).

Coating Organosilicon thin films (SiOC) are chosen for fouling studies due to the possibility for chemical and morphological modification. The coatings are obtained via copolymerization of metacrylic acid (MA) and vinyltrimethoxysilane (VTMOS) in argon discharge (Manakhov et al. 2012). Coatings are deposited by Atomospheric Pressure - Plasma Assisted Chemical Vapour Deposition (AP-PACVD) using DBD Lux 600 reactor developed in the Fraunhofer Institute (Thomas et al. 2007). With these materials morphology and concentration of negatively charged functional groups is varied using different power and duty cycles during coating. More detailed description of the coating chemistry and the deposition process is described in Lecoq and Puhakka (2013).

The coated samples are characterized by X-ray photoelectron spectroscopy (XPS) in order to quantify the chemical groups like –COOH and –CO coexisting at the surface of the layer. The surface free energy (SFE) of the coatings is calculated from the contact angle measurements (water, diiodomethane and ethylene glycol) using the sessile drop method. Dispersive and polar components of the surface energy are calculated using the Owens-Wendt approach.

The reference stainless steel sample is prepared prior to coating and characterization by washing it with an alkaline detergent solution followed by rinsing with distilled water, acetone and ethanol.

Ten different organosilicon thin films (coatings) deposited on unmodified stainless steel are studied in this work. The coatings are listed in Table 1 with their surface morphology classification and roughness values. Fig. 2 shows the scanning electron microscopy (SEM) and the confocal microscopy images of studied smooth, rough and granular coating. Confocal microscopy is used to determine roughness values, and together with SEM to confirm homogeneity of morphology and to identify possible coating defects. Mean roughness depth (Rz) is the averaged

vertical distance from the highest peak to the lowest valley within five sampling lengths. It means that the extremes have a great influence on the final value as Rz averages only the fives highest peaks and the five deepest valleys.

Table 1. Studied coatings with their morphology and roughness (Rz).

Coating #	Morphology	Rz [nm]
1	smooth	
2	smooth	< 50
3	smooth	< 30
4	smooth	
5	rough	
6	rough	50 - 200
7	rough	
8	granular	200 700
9	granular	200 - 700



Fig. 2 SEM and confocal microscopy images of a smooth (#3), rough (#7), and granular (#9) coating.

*Grinding/polishing* Stainless steel samples are polished and ground with Struers ApS consumables using a LaboPol-6 grinding and polishing machine. For polishing a woven acetate cloth MD-Dac and DiaPro Dac 3  $\mu$ m diamond suspension are used. Grinding is done with 80 and 220 grit MD-Piano resin bonded diamond discs with hand grinding wetted with water. The ground and polished samples are listed in Table 2 with their surface morphology and roughness. Roughness average (Ra) is the arithmetical average value of all absolute distances of the roughness profile from the center line within the measuring length.

Table 2. Ground and polished samples with their roughness (Ra) properties.

Sample	Morphology	Ra [nm]
Reference, 2B	untreated	290
DiaPro Dac 3 µm	smooth	< 50
220 grit	rough	50 - 200
80 grit	coarsely rough	200 - 700

**Patterning** The surface patterns studied in this work are presented in Fig. 3 The height of the patterns varies between 20 - 50 mm and width between 7 - 8.5 mm, and they are pressed on stainless steel 304L 2B.



Fig. 3 Patterned surfaces used in the fouling studies with a sketch of the profile of the pattern #3.

# **RESULTS AND DISCUSSION**

#### Fouling on unmodified surface

Fig. 4 presents the fouling resistance curves for the repeated experiments done with unmodified stainless steel samples. The fouling resistance starts to decrease right after the beginning of the experiment. This indicates the formation of the first nuclei on the surface, which increases the surface roughness and the heat and mass transfer coefficients. This leads to decrease in the wall temperature and the fouling resistance. This period is defined as induction period (Bansal and Müller-Steinhagen 1993, Föster et al. 1999) induction time is used as a measure for comparison of the surface modifications in this paper. As the crystals grow further, a resistive fouling layer is formed, which overcomes the effect of the enhanced heat transfer due to the (hydrodynamic) roughness effect, and the more steady growth of the fouling resistance begins, defined as fouling period.

Fouling curves in Fig. 4, show the repeated tests giving corresponding behavior in terms of both the induction time and the fouling rate. Based on the repeated tests with unmodified stainless steel and modified surfaces, the standard deviation is less than  $\pm 20\%$  for the fouling resistance and the induction time.



Fig. 4 Repeated fouling resistance curves for unmodified stainless steel samples used as the reference surface.

#### Fouling on coated surfaces

In one fouling experiment four samples are tested simultaneously, including a reference stainless steel sample with three coated steels in the test section. The induction time is calculated relative to this parallel reference sample. Fig. 5 presents the fouling curves for selected coatings with a parallel stainless steel reference. Relative induction times for all the tested coatings are presented in Fig. 6 in the order of the increasing roughness. The induction times of the coatings are increased by a factor of 2 to 7.5 compared to the reference. As can be seen in Fig. 6, roughness of the coated samples does not correlate clearly with the induction time. Therefore, the chemical composition or morphology may affect more on the induction time.



Fig. 5 Fouling resistance curves for selected organosilicon thin films deposited on stainless steel.



Fig. 6 Relative induction times of the tested coatings.

XPS analysis of the surface chemical composition shows the differences in the amounts of chemical groups of the functionalized thin films used in the fouling experiments. Figs. 7-9 show the correlation between -COOH, -CO, and the sum of -COOH and -CO groups with the induction time, respectively. The different morphologies are labeled separately (smooth, rough, and granular). Thus, one can note that all the organosilicon coatings improve the surface against fouling.

For the smooth coatings the induction time increased with the decreasing –COOH (Fig. 7) and increasing –CO contents (Fig. 8). For the granular and rough coatings, the –COOH content correlated with the increasing induction time (Fig. 7). With –CO, the induction time varied despite of the relatively constant –CO content (Fig. 8). Taking into account only one of these functionalities present at the surface does not allow to explain the increase of the relative induction time. However, considering the sum of –COOH and –CO functionalities show reasonable correlation with increasing induction time (Fig. 9). From these observation we can conclude that the chemical composition of the surface has more effect on the fouling process than the nanometer scale morphology and that the richer the surfaces in –CO and -COOH the longer the induction time.

The induction time in Fig. 10 increases with decreasing total free surface energy. Granular surfaces have high surface energy due to the roughness effect compared with smoother surfaces (Wenzel 1936 in Peltonen et al. 2004).



Fig. 7 Carboxyl content of organosilicon thin films with induction time.



Fig. 8 Carbonyl groups correlated with induction time for organosilicon thin films.



Fig. 9 Correlation between the induction time and the total concentration of negatively charged groups.



Fig. 10 Total free surface energy of the coatings correlated with the induction time.

The zeta potential measurements are carried out using organosilicon thin films deposited on polyester (PEN) film because measurement method needed electrically resistive substrate. The pH of the solution being above 7, the ionization of the acidic groups leads to a negatively charged surface. Contrary to expectations, the highest negative zeta potential values are not obtained for samples with the highest concentration in carboxyl and hydroxyl functions. As the variations in zeta potential for the various surfaces are mostly insignificant  $-31 \pm 5$  mV, the general trend between zeta potential and induction time is not able to be correlated.

#### Fouling on ground/polished surfaces

Fouling curves for the ground and polished stainless steel samples (Fig. 11) shows that the ground sample with the grit 80 and the reference sample have the shortest and nearly equal induction times. The samples ground with the girt 220 and the polished (DiaPro  $3\mu$ m) have increased induction time. Fig. 12 shows that increasing the roughness by grinding does not affect markedly the induction period. However, decreasing the roughness increases significantly the induction period.



Fig. 11 Fouling resistance curves for the ground and polished surfaces.



Fig. 12 Induction time as the function of the roughness of the ground and polished surfaces.

#### Fouling on patterned surface

The fouling resistance curves for the patterned surfaces are presented in Fig. 13 with comparison to the flat surface. All the test surfaces show relatively deep decrease in the fouling resistance at the beginning of the fouling test. Thereafter, the fouling resistances increase linearly with variable slopes, i.e. fouling rates. The fouling rate of the flat reference surface is the highest, whereas the fouling rate of the Pattern #3 is the lowest. The fouling rates of the patterns relative to the reference surface are 0.75, 0.74, and 0.6 for the patterns #1, #2, and #3, respectively.

The relative induction times for the patterned surfaces in comparison to the flat reference surface are presented in Fig. 14. It can be seen that the induction time of the pattern #3 is about 2.5 times longer than the induction time of the flat surface. Also induction times of the patterns #1 and #2 give clearly longer induction times (about 1.7 times longer) compared to the reference.

The lowest fouling rate and the longest induction time of the pattern #3 indicate its strongest potential to reduce fouling. The curved pattern has a hydrodynamically rough surface, which causes disturbances to the boundary layer at the surface by creating vortices in the concaves between the patterns as shown by CFD modelling in Pääkkönen et al. (2013). This enhances heat and mass transfer, lowers the surface temperature, and increases the shear stress. These effects are well known to reduce crystallization fouling of calcium carbonate (Bansal et al. 2008). On the other hand, the vortices may result in areas with low velocity and low heat and mass transfer coefficients, which cause the surface temperature to increase and shear stress to decrease and fouling to increase. However, the total effect of these areas seems to be small compared to areas with reduced fouling. The curved shape of the pattern #3 also increases slightly the surface area, which could provide more nucleation sites for crystals. Since the height of the pattern is only 20 - 50m, the increase in the surface area is very low, and the effect seems to be insignificant.

The patterns #1 and #2 reduce fouling as well compared to the flat surface. The fouling reduction may be explained by hydrodynamic and thermal conditions also in the case of these patterns. However, patterns #1 and #2 have larger and sharper shapes compared to pattern #3. These may cause more severe "stagnant corners" where conditions are favorable for crystallization fouling, which would explain their lower potential for fouling reductions compared to the pattern #3.



Fig. 13 Fouling resistance curves for the tested patterns and the flat reference surface. (Modified from Pääkkönen et al. 2013)



Fig. 14 Relative induction times of different surface patterns compared to the reference (flat) surface.

# Discussion about the factors affecting on the induction time by surface modifications

The relative induction time was increased by coatings up to 7.5 times, by patterning up to 2.5 times, and by polishing up to 1.7 times compared to the plain stainless steel surface.

Coating had the most significant effect on the induction time. A strong dependence between the morphology and the chemical composition is found: the smooth surfaces are rich in –COOH functional groups whereas the granular shaped surfaces contain more –CO groups. Overall, the functionalization increased the induction time. The most promising were Coating #8, a bilayer coating composed of a 100 nm thick granular shaped coating capped with a smooth and COOH-rich layer, and Coating #4, a VTMOS film (no copolymerization with MA) presenting a smooth surface and a high –CO concentration. It seems that even longer induction time could be obtained by a bilayer thin film where the sub layer is granular and the top layer high in – CO + –COOH.

The coatings with lower surface energy had longer induction time, except the Coating #8, which had the

highest induction time despite of the highest surface energy. Granular morphology seems to result in high surface energy regardless of the functionalization chemistry, which is consistent with previous studies (Herz et al. 2008, Wenzel 1949).

Patterned surfaces are hydrodynamically rough affecting the boundary layer conditions. The pattern #3 gives the longest induction time, which seems to lead hydrodynamic conditions less favorable to fouling, as was also indicated by Pääkkönen et al. (2013) by CFD modelling. The fouling could be further reduced by smoothing the lower corners of the patterns to minimize the stagnant areas, which may be prone to fouling.

Grinding and coating lead to hydrodynamically smooth surfaces. Unmodified steel surface (in Fig. 15a) has high number of peaks and valleys (in Fig. 16, Ra  $0.29\mu$ m and Rz 1.3  $\mu$ m), which increases nucleation density especially on the roughness peaks. Consequently, crystals grow more preferably at peaks and eventually crystal nucleation spreads to the valleys, filling them rapidly (Keysar et al. 1994), which increases adhesion and favors crystals to grow further to form thermally resistive fouling layer.



Fig. 15 SEM image a) before and b) after fouling experiment where CaCO<sub>3</sub> is nucleated on unmodified steel (AISI 316L 2B).



confocal microscopy for the unmodified stainless steel.

Coarse grinding (grit 80) of unmodified steel slightly shortened the induction when average roughness (Ra) increased markedly. Small effect of increased Ra with coarse grinding may be due to morphology related as grinding may produce more homogeneous roughness than unmodified steel in terms of mean roughness depth Rz, when deep valleys diminish. Fine grinding (grit 220) and further polishing (DiaPro 3µm) increased the induction time markedly and gave linear correlation (unmodified steel excluded) to decreased roughness with increasing induction time. Decreased fouling by having less roughness peaks and smaller effective surface area for crystal nucleation has been observed also in other studies (Keysar et al. 1994, Peltonen 2004, Herz et al. 2008). Polishing after grinding leads to less favorable surface for adhesion due to lower valleys especially on grain boundaries, as shown in Fig. 15 b), are favored sites for crystals to adhere and grow further on unmodified stainless steel surface finish 2B.

Combination of different surface modifications, e.g. polishing before coating and patterning, or coating the patterned surface for heat exchanger plates, seems to be promising to reduce fouling. However, in further studies economic aspects and technical feasibility should also be evaluated.

# CONCLUSIONS

In this study, effect of surface modification by coating, grinding/polishing and surface patterning on to fouling process of  $CaCO_3$  on stainless steel was examined. Coating was the most promising surface modification technique, that increased the induction time by factor 7.5 compared to unmodified stainless steel AISI 316L 2B surface, patterning by factor 2.5 and polishing 1.7. The mechanism in the fouling reduction seemed to be related to chemical functionalization, hydrodynamic effects, and morphology.

The phenomena behind the different surface modifications is not fully understood and all the modification techniques, such as roughness, patterning and chemical modification, have needs to be studied more thoroughly and separately to make more precise estimates *a priori* for a certain application. It seems promising to combine different surface modifications to reduce fouling in heat exchangers.

## **APPREVIATIONS**

2D	Two Dimensional
AFM	Atomic Force Microscopy
AP-PACVD	Atomospheric Pressure - Plasma Assisted
	Chemical Vapour Deposition
DBD	Dielectric Barrier Discharge
SiOC	Organosilicon thin films
MA	Metacrylic Acid
PEN	Polyethylene naphthalate
Ra	Roughness average, nm
Rz	Mean rouhgness depth, nm
SEM	Scanning Electron Microscopy
SFE	Surface Free Energy
VTMOS	Vinyltrimethoxysilane
XPS	X-ray Photoelectron Spectroscopy

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