Published online www.heatexchanger-fouling.com

ON-LINE MONITORING OF DEPOSITION AND REMOVAL OF MILK SALTS ON COATED SURFACES

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ABSTRACT

Fouling of process equipment during heating is one of the major problems in the dairy industry. Deposit formation limits the desired heat transfer required for the microbiological safety of the product. Surface properties play a crucial role in the build-up and removal behavior of food foulants. The alteration of these properties is one of the promising solutions to minimize fouling.

Since milk salts are the principal component of the deposit by heating milk at temperatures above 110°C, their adsorption and removal behavior on unmodified and modified stainless steel surfaces was studied by an on-line monitoring device. The modification of the surface consisted of amorphous carbon-based (a-C:H:X) coatings, namely a-C:H, a-C:H:Si and a-C:H:Si:O, that were obtained by plasma enhanced chemical vapor deposition (PECVD).

Contrarily to other methods to detect fouling, which are either offline, not very sensitive to detect the initial deposit build up or invasive, the mechatronic surface sensor (MSS) is non-invasive and has enough resolution and accuracy to detect on-line the initial adsorption of the foulant to the surface and to differentiate the type/structure of deposit.

The results indicate that the main driving force for the attachment of ions or particles to the surface is the Lewis acid/base force.

INTRODUCTION

Fouling of heat transfer equipment is a crucial problem in the milk processing industry and appears frequently as a limiting factor in heating processes. To maintain production efficiency and keep the strict hygienic standards the processing equipments have to be cleaned regularly and effectively. The costs associated with cleaning can be significant and include those for detergents, rinse water, effluent treatment/disposal, energy and stand-by operation.

The attachment, adhesion, retention and removal of soils is influenced by the interaction between heat transfer surface and process fluid. An understanding of these effects is a crucial step forward to reduce the formation of the first layer at the solid surface and in succession the growth of fouling deposits in processing equipment.

Previous works (Andritsos et al., 2002, Rosmaninho and Melo, 2006b, Visser and Jeurnink, 1997) have given special attention to investigate the mechanism of calcium phosphate deposition, the main mineral component of milk deposits at a heating temperature up to 100°C.

During the heating of milk, part of the soluble calcium and phosphate will become insoluble and will precipitate as a calcium phosphate salt in solution or on the surface of the processing equipment, or will associate with milk proteins. Moreover the precipitate formed in bulk solution can attach to the surface as well as can be removed. As has been pointed out, the mechanism involves: (i) nucleation, (ii) precipitation due to supersaturation, (iii) adhesion and cohesion, (iv) diffusion, (v) growth and (vi) removal, which make this crystallization fouling complex.

Assuming that the surface modification can influence the deposition mechanism, this parameter can be used to study the formation of crystalline phases during the induction period in crystallization fouling (Geddert et al. 2009; Puhakka et. al., 2011) and therefore give more advice about the interaction between surface and foulant.

Andritsos et al. (2002) examined the effect of surface modification by DLC, Ni-P-PTFE and silica coating and SiF_3^+ ion implantation on scaling formation using SMUF (Simulated Milk UltraFiltrate) solutions. Deposit was characterized ex situ using different physiochemical analysis. The results suggested that surface modifications might reduce the adhesion strength of the deposits which would more easily clean-up.

Rosmaninho and Melo (2006a) investigated the fouling behavior from SMUF on stainless steel surfaces modified by Ni-P-PTFE and SiO_x coating and SiF₃⁺ and MoS₂ ion implantation. The thickness and mass of the deposit were measured ex situ and the aggregates formed were observed using scanning electron microscopy. The influence of the Lewis base surface energy component (γ) on the spread, number and size of the initial aggregates and consequently on the final structure of the deposits were reported. These works gave qualitative and quantitative information on the structure and composition of the dried deposits. However, it is very demanding to gather information during the deposition formation in real time.

This study investigates the formation and removal of calcium phosphate deposits on modified stainless steel surfaces using an on-line non-invasive monitoring device, called Mechatronic Surface Sensor (MSS) (Patent US 2008/215248 A1).

The MSS device is based on the propagation of nanovibrations along the fouled surface. An actuation and a sensor element are placed outside the surface to be examined. The actuation element makes the surface vibrate. This vibration is then captured by the sensor and the response signal is processed using Fast Fourier Transforms in: frequency, amplitude, "flight" time, peak-to-peak value, damping factor. The amplitude and the damping factor showed to be the best parameters to monitor the formation/removal and the structure of the deposits respectively (Pereira et al., 2006).

Contrarily to acoustic techniques based on frequencies higher than 20 kHz (ultrasound range), the MSS actuates the surface with a low-frequency excitation, that make the equipment cheaper, less complex and feasible for industrial applications.

MATERIAL AND METHODS

1. Surface modification

Stainless steel (AISI 304) was coated with amorphous carbon hydrogen layers by plasma enhanced chemical vapor deposition (PECVD) in a high-vacuum chamber. Amorphous hydrogen containing carbon coating (a-C:H:X) was modified by build-in of oxygen and silicon inside the carbon matrix. Namely DLC (a-C:H), SICAN (a-C:H:Si) and SICON[®] (a-C:H:Si:O) were generated for this work. Due to the high wear and thermal stability, as well as hardness and chemical inertness of a-C:H:X coatings (Charitidis, 2010; Hieke, 2001; Robertson, 2002), their use in the food processing industry is promising.

Before deposition experiments as well as before surface characterization, the stainless steel and the coated surfaces are cleaned with 0.5 wt% NaOH, 0.5 wt% HNO₃ and a commercial detergent (10 g/l RBS35, RBS Chemical Products, Belgium) at 50°C for 1 h.

2. Surface characterization

Roughness

Roughness measurements were carried out by means of the tactile stylus method using the Perthometer Concept 5.0 (Mahr GmbH) according to DIN EN ISO 3274. For the evaluation of surface contour the R-profile (roughness profile) is deployed by filtering the original P-profile (primary profile).

Surface free energy

In order to calculate the surface free energy, the contact angle was measured using the Drop Shape Analysis System DSA G10 (Krüss GmbH, Hamburg, Germany). The principle is based on the measurement of the shape of droplets of different defined liquids. Through contact angle measurements the total interfacial surface energy between a solid and a liquid γ_{12} can be expressed by the use of the Young's equation:

$$\gamma_{12} = \gamma_{23} - \gamma_{13} \cos\left(\theta\right) \tag{1}$$

where subscripts 1, 2 and 3 mean liquid, solid and gas, respectively.

The approach of van Oss et al. (1988) considers the total surface tension of a solid or a liquid as the sum of a nonpolar Lifshitz-van der Waals component (γ^{LW}) and a Lewis acid-base polar component (γ^{AB}). The component (γ^{AB}) can be subdivided in two non-additive parameters, one for the electron donor (γ) and one for the electron acceptor

 (γ^+) contribution: $\gamma^{AB}=2\sqrt{\gamma^-\gamma^+}$. The total interfacial tension between phases solid and liquid can be expressed as:

$$\gamma_{12} = \left(\sqrt{\gamma_{13}^{LW}} + \sqrt{\gamma_{23}^{LW}}\right)^2 + 2\left(\sqrt{\gamma_{13}^{-}}\gamma_{13}^{-} + \sqrt{\gamma_{23}^{+}}\gamma_{23}^{-} - \sqrt{\gamma_{13}^{+}}\gamma_{23}^{-} - \sqrt{\gamma_{13}^{-}}\gamma_{23}^{+}\right) (2)$$

The liquids used were water, ethylenglycol, formamide, 1-bromonaphtalene and diiodmethane.

3. MSS Measuring System

The MSS (mechatronic surface sensor) is attached to the outer surface of a stainless steel plate (225 x 41 x 0.6 mm³) that replaces the flat base of a semi-circular flow cell made of Perspex[®] (internal diameter = 30 mm, equivalent diameter = 18.3 mm) (see Figure 1). The flow cell is described in detail in Patent US 2008/215248 A1.

Only the inner site of the plate, which is in contact with the foulant solution, was coated. The actuation and the sensing elements are glued to the outer surface of the plate. The excitation voltage is generated via a data acquisition board (National Instruments, NIDAQ-card PCI-6221) and directly applied to the piezo actuator (BM 70/25/200 M, Piezomechanik GmbH). The vibration waves are captured periodically during the experiments by an accelerometer (ADXL-103, Analog Devices, Inc.) and mathematically processed on a computer.

A sinusoidal wave with a frequency of 5 - 5.4 kHz and excitation voltage of 2 - 3 V is used to generate the actuation. This frequency matches one of the resonant frequencies of the system, i.e. the maximum output signal is achieved. The resonant frequency of the system was determined by activating the system with energy simultaneously in a given wide range of frequencies (0 - 10 kHz). The spectral magnitude for all the frequencies is obtained (white noise). The generated and the response signal are then mathematically processed (FFT) and the better defined resonant peak is selected. At the chosen frequency the system is now vibrated in the range of 2 to 5 V. The analysis of the output wave gives then the best excitation voltage.

The amplitude of the response signal and the damping factor provide information about the amount and type/nature of the deposit. The amplitude is inversely proportional to the amount of deposit attached to the surface. Pereira et al. (2006) found a good correlation between the data obtained with the MSS and the data obtained using heat transfer monitoring methods as well as mass deposit monitoring. More viscoelastic deposits, like biofilms or proteins, showed higher damping factors than inorganic deposits (Pereira et al., 2006). Different calcium phosphate deposits have not yet been compared using the MSS.

The normalized amplitude can be obtained by subtracting the A^{FFT} values collected during the experiment from the initial value (corresponding to the clean plate):

Norm. Amplitude (t) =
$$A^{FFT}_{o} - A^{FFT}(t)$$
 (3)

where A^{FFT} (t) is the amplitude at time t after Fast Fourier Transform and A^{FFT}_{o} is the initial amplitude (clean surface).

The damping factor was calculated from the output wave using the Logarithmic Decrement Method (Shabana, 1991):

$$\zeta = \left(\sqrt{1 + \left(\frac{2\pi}{\frac{1}{n} \ln \frac{x_i}{x_{i+1}}}\right)^2} \right)^{-1}$$
(4)

where n is the number of peaks and $\frac{x_i}{x_{i+1}}$ is the ratio of two non or consecutive amplitudes.

4. Fouling and cleaning procedures

Model fluid

Fouling experiments were carried out with SMUF (Simulated Milk UltraFiltrate) as foulant. SMUF is an aqueous solution that simulates the mineral composition of milk. It was prepared according Jennes and Koops (1962). The final composition is summarized in Table 1. pH value was adjusted to 6.7 using dilute NaOH before the experiment started. pH value was adjusted to 6.7 using diluted NaOH before the experiment started.

Table 1. Composition of the SMUF solution

Reagents	Concentration (mmol/l)
KH ₂ PO ₄	11.61
C ₆ H ₅ K ₃ O ₇ .H ₂ O	3.70
C ₆ H ₅ Na ₃ O ₇ .2 H ₂ O	6.09
K ₂ SO ₄	1.03
K ₂ CO ₃	2.17
KCl	8.05
CaCl ₂ .2 H ₂ O	8.98
MgCl ₂ .6 H ₂ O	3.21

Fouling runs

The model fluid was recirculated at constant conditions (see Table 2). The experimental conditions chosen depend on the limitations of the experimental set up (the flow cell is made actually from Perspex[®], that permit a visual control of the surface) and considering the following comments. At a temperature of 44°C the turbidity increases in the SMUF-solution which was related to the maximum deposit formation (Andritsos et al., 2002; Visser, 1998). Kessler

(2002) recommends a minimal velocity for the pasteurization of milk of 0.25 m/s.

The bulk temperature was measured with a thermocouple and controlled using an electrical heating element. The studied surface was not heated. Fouling takes place due to supersaturation in the bulk and nucleation or adhesion of calcium phosphate ions or particulates. The experiments were repeated at least three times and data are presented as mean values.

In order to eliminate bubbles from the system, to determine the error associated with a given measurement of a surface as well as to compare the sensor response on the different surfaces, water was set to recirculate in the flow cell at the same flow and temperature conditions for the fouling runs. After 1 h of steady-state operation, concentrated SMUF was added.



Fig. 1. Experimental setup

Table 2. Summary of experimental conditions

Parameter	Value		
Foulant fluid	SMUF		
Bulk fluid temperature	$52 \pm 1^{\circ}C$		
Surface temperature	$50 \pm 1^{\circ}C$		
Fluid velocity	0.25 m/s		
Reynolds number	8600		

Cleaning runs

The foulant solution was replaced by a 0.5 wt.% HNO₃ solution at the same flow and temperature conditions as for the fouling runs (Table 2) in order to clean the surface and monitor the cleaning process.

RESULTS AND DISCUSSION

1. Surface characterization

The mean roughness depth (Rz) and the mean roughness (Ra) for the different surfaces are presented in Figure 2.

The coating by PECVD generates a 3 μ m thick second layer on the stainless steel. The original topography of the substrate by a-C:H:X coating is nearly reproduced (Geddert et al., 2009). Nevertheless, the sharp edges and narrow grooves of the stainless steel were smoothed and a slightly decreased mean roughness depth of the surface can be observed. The difference is not significant, so the effect of different roughnesses on the fouling is negligible.



Fig. 2. Surface roughness

Figure 3 shows the surface free energy of the unmodified and coated stainless steel. Comparison of the different surfaces suggests that the nonpolar Lifshitz-van der Waals component (γ^{LW}) is approximately the same for all surfaces (34 - 38 mN m⁻¹), whereas the electron donor component (γ^{-}) differs.



Fig. 3. Surface energy properties of the modified and original surfaces

2. Sensor signal on the different surfaces

The initial vibration of the system (before fouling) is affected by temperature and flow velocity and can be characterized by the amplitude $A^{FFT}{}_{o}$ and the damping factor. To evaluate the MSS response on the different surfaces, the amplitude $A^{FFT}{}_{o}$ and the damping factor with circulating water in the flow cell were measured (Table 3).

l'able 3.	Output responses	of stainless	steel	and	a-C:H:X
	coated surfaces				

Surface	A ^{FFT} ₀ (V)	Damping factor (%)
Stainless steel	0.214 ± 0.004	0.22 ± 0.01
a-C:H	0.304 ± 0.003	0.53 ± 0.02
a-C:H:Si	0.290 ± 0.003	0.36 ± 0.01
a-C:H:Si:O	0.160 ± 0.005	

3. Deposit formation

Deposit formation on the flow cell wall as well as bulk precipitation was observed. pH value achieved 6.4 ± 0.2 after 15 h of experiment for all surfaces, indicating the precipitation of insoluble calcium phosphate: $Ca^{2+} + H_2PO_4^- \rightarrow CaHPO_4 (s) + H^+$.

The adhesion curves of calcium phosphate on the unmodified as well as on coated stainless steel, monitored with the A^{FFT}, are shown in Figure 4. The uncertainty bars associated with the MSS response correspond to measurement uncertainty associated to the system. The A^{FFT} is inversely related to the amount of calcium phosphate deposit (Pereira et al., 2006). This means that the normalized amplitude curve in Figure 4 increases with increasing amount of deposit.

An increase of the normalized amplitude over time was measured for the stainless steel and for the a-C:H coating and stayed constant after 4 to 6 h, indicating that no further significant growth as well as detachment of deposit takes place. For the a-C:H:Si as well as for the a-C:H:Si:O coating an initial attachment from calcium phosphate on the surface can been observed, but the deposit has been removed due to wall shear stress. Subsequent adhesion and removal could be detected. After 8 h the amplitude A^{FFT} on the a-C:H:Si coating increases and negative values for the normalized amplitude can be observed. The a-C:H:Si:O coating shows the same behavior, however starting after 5 h fouling time. Possible explanations for this behavior could be:

- (i) The coating and/or substrate was/were damaged (although the pH value decreased by 0.3 and no HNO₃ was yet used).
- (ii) The diffusion and formation of crystals on pinholes and nanopores of the coating could additionally change the elastic properties of the film and affect the vibration's propagation.



Fig. 4. Calcium phosphate fouling curve on the surfaces assessed by MSS

Once no protein in the foulant solution is present, the build-up of a calcium phosphate deposit is governed by two driving forces due to the supersaturation: (i) bulk precipitation and (ii) crystallization on the surface. The mass transport of particulates and aggregates to the surface or to the deposit layers is lower than the transport of individual ions because of their dimensions. Moreover the particulate deposits or aggregates adhere less strongly on the substrate than the formed crystals (Andritsos et al., 2002). It implicates that the modification of the surface will alter/influence the crystallization. Rosmaninho and Melo (2006a) showed that surfaces with lower γ^{-} values promote the formation of fewer nucleation points as well as bigger and looser crystal aggregates. Contrarily, surfaces with high γ promote the formation of more crystallization sites, but smaller crystals and a more compact and homogenous structure/first layer. Zhao et al. (2005) also reported an influence of the surface free energy of Ni-Cu-P-PTFE coated surfaces on crystalline fouling. Surfaces with lower surface free energy (γ_{12}) exhibit a loose and porous structure of CaSO₄ crystals without a defined orientation.

Dry deposit formed on stainless steel and on a-C:H surface are presented in Figure 5. The a-C:H coating has the highest γ value and hence shows smaller crystal aggregates. It agrees with the observations of Rosmaninho and Melo (2006a).



Fig. 5. Dry deposit on (a) stainless steel and on (b) a-C:H coating (optical microscopy with EDIC)

Rosmaninho et al. (2007) proposed that surfaces with higher values of electron donor component are less susceptible to crystallization fouling, caused by direct deposition of ions, and more prone to particulate fouling, caused by adhesion of suspended particles or aggregates from the bulk. Rosmaninho and Melo (2006a) observed also that the resistance of the deposit to removal by water increases with the γ^- value. These results contradict the observations of Andritsos et al. (2002) which argument that particulate deposits adhere less strongly on the substrate than the formed crystals. The normalized amplitude curves in Figure. 4 show good adhesion of the deposit on stainless steel and on the a-C:H coating. The deposits on a-C:H:Si and on a-C:H:Si:O have in contrast a lower adhesion to the surface and are probably formed from particulates or bigger and looser crystals. High normalized amplitudes are initially detected on the a-C:H:Si coating that indicates that more deposit is initially formed. This result is consistent with those of Al-Janabi et al. (2010) who showed that higher electron donor component corresponds to lower fouling. They investigated the crystallization fouling of CaSO₄ on heated surfaces without recirculation of particulates. Whereas Rosmaninho et al. (2007) have reported more initial deposition (on the first 240 min) on surfaces having higher γ^{-} .

4. Cleaning

The cleaning curves are presented in Figure 6. The system reached its clean state rapidly. The amount of deposit decreases and thus the amplitude A^{FFT} increases, i.e. the normalized amplitude decreases. MSS signals corresponded well with optical assessment of the cleaned surface.

Localized cracks in the coating could be observed (see Figure 7) which are likely to be responsible for a amplitude deviation of the clean surface from the original value as well as for the negative values. DLC itself can not corrode. But due to the amorphous nature of DLC the formation of microscale features, such as grain boundaries, pinholes or nanopores (ca. 0.5 nm), is unavoidable. Usually the corrosion initiated at these microscopic features that lead to the exposure of the metals to the environment and subsequently to a deterioration in interface adhesion (Maguire et al., 2005; Zeng et al. 2002). This finding would allow the additional use of this measuring technique for the detection of failures of the coating or changes of the surface structure during operation. This application was shown in principle by Nakra (1998) and Panteliou et al. (2001).



Fig. 6. Cleaning curves of calcium phosphate assessed by MSS by actuation of 5.4 kHz and 2 - 3V



Fig. 7. Micrographs (magnification x 1000) of surface defects on (a) a-C:H:Si and (b) a-C:H:Si:O coating

CONCLUSIONS

The MSS output signal can be used to monitor the online build-up and removal of calcium phosphate deposits on unmodified and coated stainless steel. Moreover the sensor can be used to detect defects on coatings due to aging.

The modification of the stainless steel by coating alters the damping factor of the surface since the coating is an additional source of energy dissipation.

The temporal change of the normalized amplitude, which corresponds to the fouling curve, indicates that different adhesion forces resulting in crystallization or particulate fouling occur on the diverse surfaces.

An important parameter to reduce calcium phosphate fouling and improve cleaning is the reduction of the electron-donor character of the surface. The higher γ is, the stronger is the adhesion of the deposit on the surface.

Further work should contribute to the development of a MSS device to monitor build up and removal at high temperatures. The temperature profile near the wall influences thermodynamics and kinetics of crystallization and consequently affects the scaling. Besides a systematic investigation of the behavior of a-C:H:X coatings under vibration conditions of the MSS is required.

ACKNOWLEDGEMENT

The preparation of the a-C:H:X coatings at Fraunhofer Institute for Surface Engineering and Thin Films, Braunschweig, is gratefully acknowledged. The international collaboration was funded by the Acções Integradas Luso-Alemãs/GRICES and Deutscher Akademischer Austausch Dienst (DAAD).

NOMENCLATURE

- a-C:H:X amorphous carbon-based coating
- A^{FFT} maximum amplitude after Fast Fourier Transform
- FFT Fast Fourier Transform
- MSS Mechatronic Surface Sensor
- PECVD plasma enhanced chemical vapor deposition
- SMUF simulated milk ultrafiltrate
- ζ damping factor

Subscript

o initial

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