

A NOVEL FOULING AND CLEANING SET-UP FOR STUDYING THE REMOVAL OF MILK DEPOSITS PRODUCED DURING UHT-TREATMENT

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ABSTRACT

The buildup of fouling during ultra-high temperature treatment (UHT, 140°C) of milk and its implication for cleaning has so far not been studied in sufficient detail to establish the cleaning mechanism. It is however clear that increases in temperature causes an increased mineral deposit, due to the decrease in calcium phosphate solubility with temperature. In this study, we present new experimental set-ups to produce fouling and to follow the subsequent cleaning process in line, where both set-ups allow the process parameters to be varied in a wide range. Our set-up allows the use of optical as well as other techniques like ultra sound methods for monitoring the cleaning process. Here we report some initial image analysis of the removal process. The long-term goal is to provide a deeper understanding of the cleaning process in order to model the process for design of tailored cleaning programs for different dairy processes.

INTRODUCTION

Heat treatment of milk is necessary, and milk and milk products for human consumption can either be pasteurized, i.e. heat-treated to about 75°C, or subject to ultra-high temperature treatment (UHT, 140°C) to prolong the shelf life and allow storage at room temperature. Some milk components, i.e. proteins and calcium phosphate, are however affected by the heat treatment, leading to e.g. aggregation and decrease of solubility

The solubility of calcium phosphate has an inverse temperature dependency and the solubility of the mineral will therefore decrease with increasing temperature. Whey proteins in milk will denature at high temperatures and precipitate onto the surface together with casein. Hence, milk processing gives a fouling containing both proteins and minerals. For temperature below 100 °C the fouling on heated surface mainly contains protein (~60 %), whereas a

change occur for temperatures above 120 °C, where the predominant constituents are inorganic compounds (~80 %). Milk fouling is consistently often only classified in a protein rich type A fouling and a type B fouling with a high proportion of mineral deposit (Burton, 1968). Since this pioneering work, other models of heat exchanger fouling have been published, e.g. describing fouling generated in tubular heat exchangers during UHT heat treatment of milk has been published (Nema and Datta, 2006).

Up to 6 hours per day is needed for sufficient cleaning of certain parts of the dairy process equipment such as sterilizers. The water consumption during cleaning is high, approximately 0.5 to 5 liter per liter milk processed (Alvarez et. al., 2010). Cleaning is often performed in a closed loop (Cleaning in place, CIP) with no other possibility to detect the result but to open the equipment. The mechanisms of both fouling and cleaning have been studied for several decades, but fundamental understanding of the mechanisms behind cleaning of milk fouling is still lacking. This is especially true for the mineral rich fouling formed during elevated temperatures.

There are a number of techniques available for studies of the cleaning process. The most used industrial techniques are primarily based on pressure drop or the use of temperature- and heat transfer- parameters. Additional techniques exist based on acoustics, which has recently been reviewed (Wallhäuser et. al., 2012).

The approaches to study the mechanisms behind the removal of protein and mineral fouling from the heat treatment of milk range from lab scale trials with whey protein based model fouling to full-scale studies in dairy plants. Whey protein isolate (WPI) and whey protein concentrate (WPC) are commonly used to generate model fouling, in particular of the protein rich type A fouling (Kroslak et al., 2007; Mercadé-Prieto et. al., 2008). The

type B fouling only occurs for temperatures above 120 °C and in the presence of a high concentration of minerals. UHT treatment of only a WPC solution will therefore mainly produce type A fouling (Christian and Fryer, 2006). The formation and properties of the type B fouling formed during UHT treatment require the use of milk and no good model system has so far been presented (Lalande et. al., 1984; Foster& Green, 1990).

The lab-scale tests allow for detailed analysis of the process, but relevance of the model fouling can be questioned. The full scale studies are expensive and the knowledge of the fouling and cleaning process relies on analyzes of the eluted solution from the system as a function of time. However, this does not give the structural and spatial information about the fouling and the fouling removal. Spatial information about the process requires

measurement of the amount of deposit and structural changes over time. Important here is to obtain knowledge on the swelling of the protein layer as well as dissolution of the mineral layer. Image analysis of the deposit can be used to gain knowledge on how the fouling is released from the surface with time.

Here we have built a new set-up that can be placed in-line a dairy process plant and generate fouling under relevant (UHT process) conditions. The fouled substrates can then be placed in a pilot cleaning process plant, where the removal can be followed *in situ* under wide range of processing conditions. Here we report the first results based on color image analysis of the removal of the fouling layer.

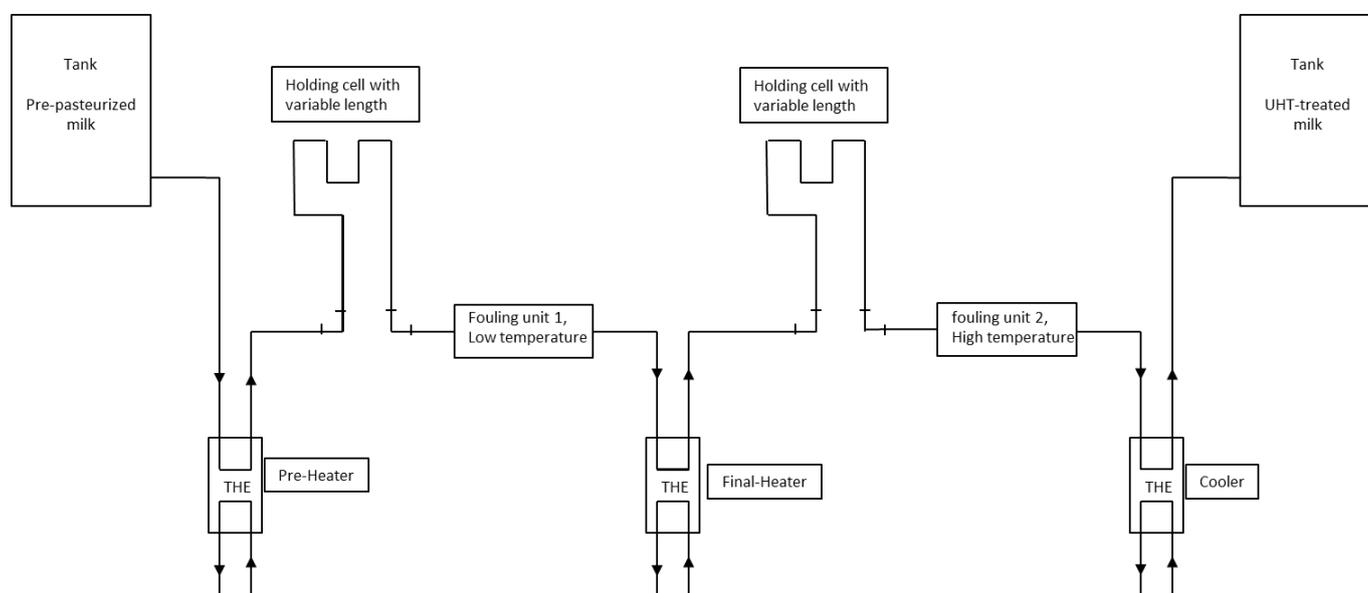


Fig. 1 Simplified schematic figure of the pilot fouling equipment. The two fouling units (1 and 2) could easily be shifted in terms of process time and temperature by changing number of tubes in the pre-heater, final heater and/or the two holding cells respectively

MATERIAL AND METHOD

Two experimental set-ups have been built. The first, (Pilot fouling equipment) which are installed in-line in a dairy plant, is used to produce fouling under real process conditions and the other (Pilot cleaning equipment) to *in situ* monitor the cleaning process under controlled environments. The fouling is transferred between the two equipment by interchangeable coupons.

Pilot fouling equipment

Milk fouling produced during UHT-processing is not directly accessible as the process is aseptic and it is also hard to generate in lab-scale. For this purpose, a pilot plant

with indirect heating was designed and constructed (Fig. 1).

Equipment was constructed, which is placed in-line a dairy process plant and generate fouling under relevant conditions in a range of temperatures from 80°C to 140°C. The equipment is constructed to achieve the possibility to alter the temperature and holding time at certain important sections. The time-temperature calculations for the design of the fouling set-up follow the same time-temperature dependency as for an industrial UHT plant (Fig 2). Fouling unit 1 and fouling unit 2 seen in both Fig. 1 and Fig. 2 are used to collect fouling with different time and temperature profiles.

One important aspect of the production of fouling for cleaning studies was the flexibility of the substrate or coupon that the fouling was growing on. In order to move the fouling from the fouling equipment to the cleaning equipment, stainless steel coupons were designed (Fig. 3). The interchangeable coupons have an additional benefit of making it easy to compare the fouling and cleaning on different surface material as well as surface structures, by simply produce different kind of coupon surfaces.

Here, all coupon surfaces are made from 316 stainless steel and had been subjected to chemical pickling, i.e. they were exposed to 30 w/w% nitric acid (HNO_3) and 8 w/w% hydrofluoric acid (HF) at 20°C for 45 minutes, in order to obtain the same surface finish as in the other parts of the dairy equipment. The area of contact of each coupon is 15x40mm

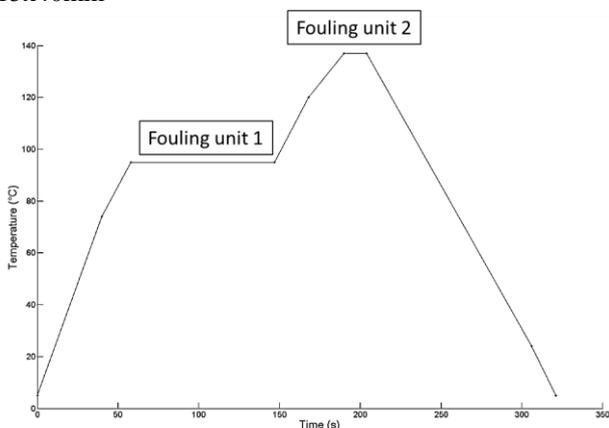


Fig. 2 The time-temperature curve was used for the design of the fouling pilot set-up to generate the type A fouling in the low temperature heating section and type B fouling the high temperature heating section. Fouling units 1 and 2 show the temperature location of the two sections, same as for Fig. 1.

The fouling is generated on the coupons in 6 channels, visible to the left in figure 3), and divided in two temperature profiles and located either after the holding cell at a lower temperature (fouling unit 1, Fig. 1), or downstream of the second holding cell (fouling unit 2, Fig. 1), keeping the temperature of the UHT-process (140 °C). The fouling equipment is constructed to be easy adaptable to a range of desired conditions. The temperature at the two fouling units can be altered as well as the time of passage through a temperature section. The residence time in each section can be altered by changing the length of the holding cell.

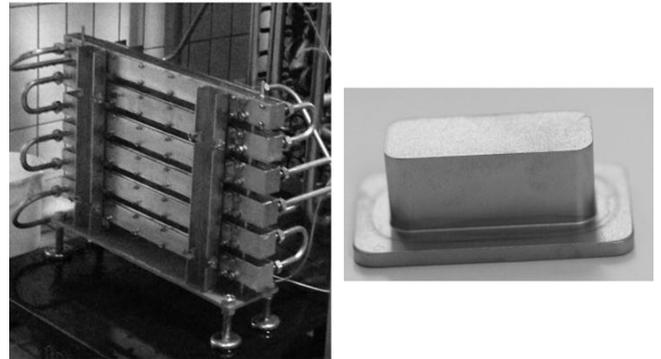


Fig. 3 A total of 120 stainless individual coupons (right) are mounted inside six rectangular units vertically assembled into a single test unit (left). The top surface of the coupons are in contact with the heated skim milk and will be covered with fouling during production.

Before start of the dairy process that generates the fouling the coupons were pre-cleaned with 2.5 % alkaline solution (Ecolab P3-mip-SP, Ecolab AB, Älvsjö, Sweden) for 30 minutes at 90°C and 1% acid HNO_3 (Ecolab P3-mip-SP, Ecolab AB, Älvsjö, Sweden) for 30 minutes at 60°C and thoroughly rinsed with water before exposed to a low temperature pasteurized skimmed milk (preheated at 75°C for 16 s). Flow velocity in the pipes was 0.83 m/s, that is in the turbulent regime at Reynolds number, $Re = 40\ 500$. The corresponding value for a circular pipe with a diameter of 14.4 mm is 0.85 m/s ($Re = 46\ 300$). The coupons were exposed for the skimmed milk for up to 24 h. To simulate the real conditions of a dairy plant the milk was not recirculated, but pass the coupon surface only once.

After 24 h, the unit is rinsed with water until the temperature was lowered to below 100 °C before the test unit with coupons from the equipment was removed. The coupons were stored at 4°C and 100% relative humidity with 3mM Bronopol (Alfa Aesar GmbH & Co KG, Karlsruhe, Germany) before mounting in the cleaning pilot plant.

Pilot cleaning equipment

A dedicated pilot cleaning equipment was built to follow *in situ* the cleaning process and removal of fouling (Fig. 4). The benefit of the cleaning unit design is the possibility to assure that the desired cleaning liquid concentration, flow and temperature is established, before exposing the fouled coupon to the cleaning liquid. The cleaning solution is indirectly heated by a tubular heat exchanger and the cleaning agent concentration is controlled by conductivity measurements. In the set-up it is possible to pressurize the cleaning circuit and to control the flow and temperature in a wide range in order to mimic different industrial conditions. Valve 2 (V2) to valve 4 (V4) is opened when the cleaning liquid is under the correct conditions. The cleaning unit is also connected to a separate cold water

feed in order to rinse the system independently of the heating circuit.

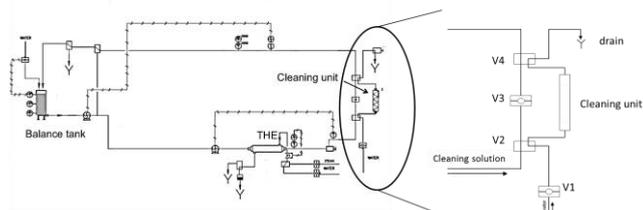


Fig. 4 Schematic figure of the pilot plant cleaning set-up used for *in situ* studies of the fouling removal. The tubular heat exchanger is marked as THE. V1 to V4 is used as signs for the valves used to control the flow through the cleaning unit.

The cleaning unit consists of a rectangular channel with the same dimensions as in the tubes in typical dairy heat exchangers. Therefore fouled coupons are only subjected to the cleaning solution when this solution has achieved the correct flow and temperature conditions (Fig. 4). A detailed side view of the cleaning unit with the coupons is shown in Fig. 6.

The cleaning solutions used in this study is 1.5% NaOH (VWR International, Fonteray-sous-bois, France) at the temperature 120 °C, at a flow rate of 1.17 m/s and the Re number 42 700 and 2% HNO₃ (Swed Handling AB, Norrköping, Sweden) at the temperature 80 °C, a flow rate of 1.17 m/s and the Re number 28 800, which are commonly used in the dairy industry.

Image analyses of cleaning process

In situ imaging was used to record the dramatic changes of the fouling layer. The fouling layer are expected to be removed either by homogenous dissolution of the layer from the top down, by selective dissolution of one or several of the components in the layer and/or by heterogeneous removal as parts of the layer. By using image analysis of the recorded images as a function of time, we can distinguish between homogeneous or heterogeneous removal of the fouling layer.

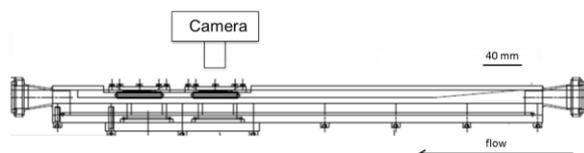


Fig. 5 A side view of rectangular channel cleaning unit is shown. The coupons are placed in the far end from inlet to obtain a well-defined turbulent flow before the cleaning solution reaches the coupon.

The images are recorded with a Canon Eos 600D and a Canon EFS lens (EF-S60mm f/2.8 MACRO USM). Image analysis is performed by using MATLAB Image Processing Toolbox. For first step of the cleaning process,

that is the alkaline cleaning step, we made a detailed analysis of the color shift observed, by separating the color images in blue, red and green.

The cleaning unit is designed in such a way it would also allow for ultrasonic monitoring. Qualitative analysis of the images recorded during the acid cleaning step was also performed.

Thickness measurements

Laser triangulation sensor was used to monitor the thickness change during the cleaning process. The method is based on measuring the angle from which the laser beam is reflected from the surface to calculate the distance between the sensor and the surface. For this purpose the Opto NCDT ILD1700-10 sensor from Micro-epsilon (Ortenburg, Germany) was used. The measurement range is 10 mm with a resolution of 0.5 μm.

RESULTS

Pilot fouling equipment

The test unit of the pilot plant consists of 6 separate rectangular channels with 20 stainless steel coupons in each section. Rectangular channels allowed the use of flat coupons with the surfaces located horizontally in the set-up. The rectangular channels are designed to mimic the flow pattern of a circular tube with the hydrodynamic diameter of 14.4 mm. In the period of 24 hours the fouling typically grows to a thickness of 2 mm (Fig. 6).

In this study we have focused on the result from the formation and cleaning of fouling that is formed during temperature treatment at 140 °C. The initial inspection of the fouling layer formed at high temperature revealed that a rather hard layer, with relatively low water content, appears which was brownish in color.

It should be noted that the layer closest to the metal surface appears to be more compact and less hydrated than the top layer. We also note that no significant difference in the fouled layer on the coupons placed next to the inlet in fouling test unit compared to those in other places in the unit was found.

An important parameter for the subsequent cleaning is the storage of the fouled coupons and we here found that they could be store at 100% relative humidity and at 4°C with Bronopol as preservative.

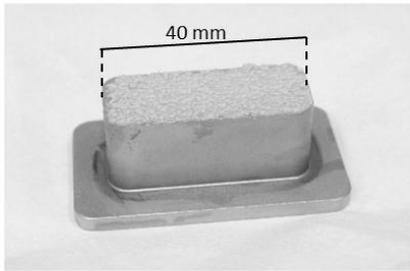


Fig. 6 On top of the coupon a hard fouling layer with a rough surface structure was formed during the UHT treatment in the pilot plant.

Pilot cleaning equipment

The removal of fouling from the coupons was successfully studied under industrially relevant conditions using the pilot plant cleaning set-up at approximately 1.17 m/s. These flow parameters were selected, although they are in the lower end of the range of flow rates used for CIP (cleaning in place) in the dairy industry.

Image analyses of cleaning process

The cleaning was satisfactorily performed, using both an alkaline and an acid step. The fouling removal could be followed *in situ* both as a change in morphology and as relative changes in color of the fouled layer.

A time-series of typical images of the coupons from a cleaning cycle, using 1.5% NaOH at 120°C ($Re = 42\,700$) are shown in Fig. 8. The most notable change is that the color changes from brown to pale beige. The fouling layer becomes out of focus during the cleaning process, revealing that the topmost layer has changed in position relative to the fixed camera position. This indicates the possibility of a swelling of the fouling layer. This is consistent with an expected swelling of the protein component during the alkaline treatment. The change in color of the fouling could indicate a rapid homogenous reaction or removal of one of several fouling compounds. Over time a more heterogeneous removal was observed, i.e. the fouling was removed in larger constructs or lumps. Image analysis was performed to further analyze the observed shift in color. This was done by dividing the image in its red, green and blue components.

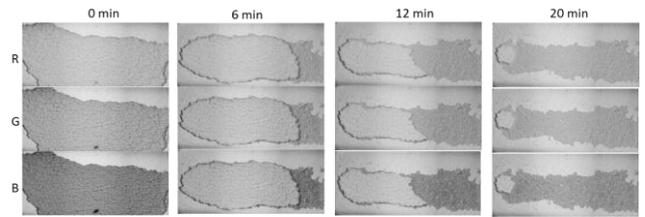


Fig. 7 The images show the fouling removal as a function of time, where the first image was recorded at time 0, and then from left to right after 6, 12 20 min. All three color components of the image are shown and indicated as R (red), G (green) and B (blue). The image size is approximately 14x30 mm. For detail analysis we selected three different spots, region of interest (ROI), each with the approximate size of 3x3 mm.

The color of the image is followed by visualizing the mean value of the pixels in a certain region of interest (ROI). The different ROI, i.e. area A-C, investigated are indicated in Fig. 8. The reason for choosing several ROI is that we wanted reveal the homogeneity of the cleaning process, i.e. removal of lumps vs. dissolution of the layer and whether the color shift, which potentially could reveal the composition in the ROI..

Area A was chosen to be in the area that still contained some of the top most layer of the fouling at the end of the alkaline cleaning step. Area B was chosen to be in the area that had been covered with fouling but had in the process lost the entire fouling layer. Area C was chosen to be in the area that had lost the topmost layer but still was covered with a fouling next to the stainless steel. The mean values of the pixel intensity, from the ROI in the red, green and blue component images, are plotted as a function of cleaning time in Fig. 8.

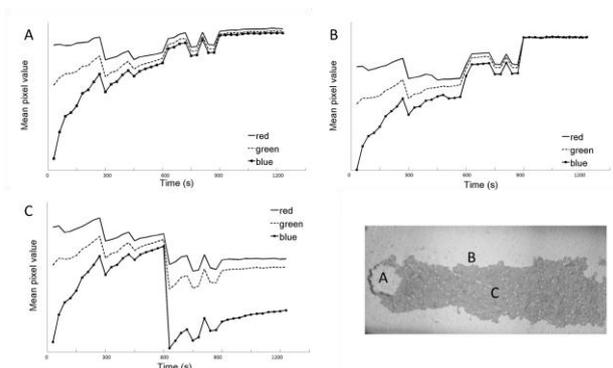


Fig. 8 The mean values of the pixel intensity, from the ROI in the red, green and blue component images, are plotted as a function of cleaning time. The ROI, indicated as A-C in the image, was chosen based on the different end results after the 20 minute alkaline cleaning. The development of the fouling layer during cleaning was shown by the color shift.

It is clear that for area A, the largest changes are observed for the blue component, which starts at a rather low intensity and increases with time. After about 20 minutes all the component images show similar mean pixel intensity value. This suggests that some component or structure absorbs light in the blue wavelength range. Here we also note that scattering of particles also contributes to the absorbance. In fact so-called Rayleigh scattering of particles (<40 nm) is strongly wavelength dependent, where the scattering intensity is proportional to the $1/\lambda^4$. This means large “effective” absorption of blue light.

The discontinuity in the intensity values for all three colors can possibly be assigned to a removal of lumps of the deposit. This can for instance be seen in Fig. 8c after about 600 s (20 images) there a considerable decrease in the pixel values in the blue channel is obtained. The decrease is interesting as it could indicate that the exposed layer now consists of less of this structure or component. It should be noted that for ROI B the exposure of the clean metal is reflected in the equal value of the three color components.

Full cleaning cycles can be visualized by combining images from alkali and acid steps together with intermediate water rinses (Fig. 9). The removal of fouling is visualized both by images of the fouling texture recorded at different stages of the cleaning as well as well as the corresponding color shift of the images.

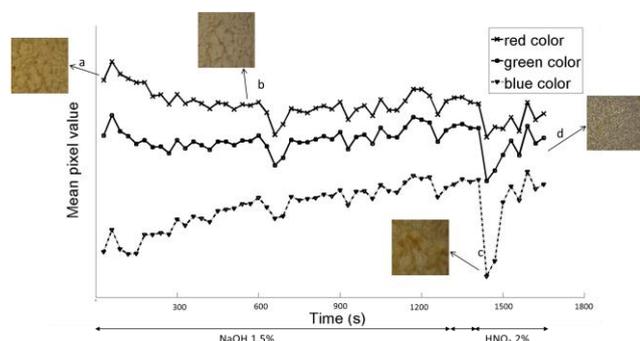


Fig. 9 The change in mean pixel value of the images of the fouling layer as function time after initiating the cleaning with both alkali and the subsequent acid cleaning step visualize. Images in the figure show the fouling layer at a, $t=0s$, b, $t=570s$ (after swelling of the fouling), c, $t=1440s$ (beginning of the acid cleaning cycle) and d, $t=1650s$ (end of a complete cleaning cycle).

Thickness measurements

Visualization with images and the use of image analysis reveals information on the lateral structure and whether the fouling is removed as larger pieces that expose new surface structures underneath. However, these images do not allow us to unambiguously establish if the protein fouling component swells during the alkali cleaning. Neither does it allow us to quantify the gradual removal of fouling. Laser triangulation sensors is used for this purpose

and allows us to monitor the swelling behavior during the first cleaning step, but also show the rapid fouling removal during the acid cleaning step (Fig. 10). The triangulation is used to measure the gradual removal locally, i.e. an area corresponding to about 1 mm^2 , and within this area the fouled layer is not removed in lumps but is connected with a continuous decrease in thickness..

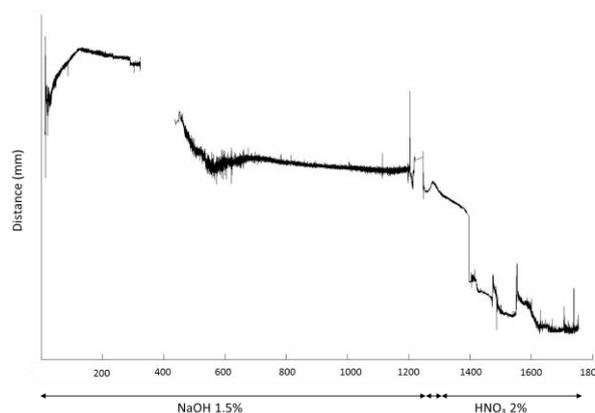


Fig. 10 Data from laser triangulation sensor that was used to measure the changes in fouling thickness during the cleaning process. The graph visualizes a filtered average of the thickness recorded during the cleaning process.

DISCUSSION

One of the great challenges with studying fouling and its removal during the cleaning process is that an industrially relevant fouling is difficult to come by. Therefore it is common to use milk protein model systems, which gives information that is difficult to correlate to the fouling and cleaning that occurs with UHT-treatment. The benefit with the set-up used here is that we have the opportunity to study the cleaning process with a fouling produced during industrial UHT flow, temperature and time settings.

In this preliminary study we have demonstrated that we with *in situ* imaging can with image analysis get insight on the cleaning mechanism and possibly also on the change in composition of the fouling layer with time during the cleaning process. In addition laser triangulation sensor measurements allow us to directly quantify these changes. The few published studies of high temperature fouling (type B) have been done on larger scale, either processing thousands of liters of milk or recirculating the liquid that affects the properties of the fouling created (Grijpsperdt, 2004; Burton, 1968). It should be noted that none of these studies includes *in situ* imaging of the fouling removal during the cleaning process, which our design allows for.

As discussed in the results section we expect a swelling of the protein component of the fouling layer. In our study we observed that as the image appears to be out of focus. This swelling behavior was quantified with the use of laser triangulation to monitor the thickness changes. Swelling of protein fouling has been observed and is taken into

account in most models that describe removal of dairy fouling.

In our study we observe signs of both dissolution of the fouling layer as well as removal of larger portions of the layer, observed as abrupt changes in pixel intensity in Fig. 9. These phenomena are not determined by the individual components but rather the properties of the fouling layer as a whole, reflecting the cohesive and adhesive strength of the layer. The adhesive and cohesive properties of the fouling have been found important, but there is not yet a straightforward answer to which one has the strongest influence in a protein fouling layer (Liu et. al. (2006). The balance between the adhesive and cohesive properties determines how the fouling layer is removed, i.e. if shredding of protein in layers and ripping lumps of protein from the surface occurs (Xin et. al. 2004).

The initial image analysis presented here show the potential of this techniques and more advanced image analysis algorithms are developed at the moment. Together with the image analysis we have to our knowledge for the first time presented the use of laser triangulation system to follow the homogenous swelling and removal of dairy fouling. In addition we have done some initial tests with ultrasonic methods to quantify the removal rate, but here still more work is need before we can present those data.

Future studies will exploit the possibility change the cleaning process parameters over wide range of settings. This will allow us to develop models of the influence of such parameters on the removal rate and efficiency.

CONCLUSIONS

This study has shown:

1. We can generate fouling that can mimic the industrial fouling. However, the main point is that fouling can be created under different temperature profiles, residence time and flow conditions in order to determine these parameters influence on the fouling composition and morphology. The fouling created is hence suitable for determine the cleaning process as a function of fouling layer properties.
2. We can *in situ* follow the cleaning process by imaging and based on analysis of these images we can obtain information about the cleaning mechanisms, such as capturing morphological changes and continuous removal of the fouling layer versus detachments of lumps from the layer.
3. We can *in situ* monitor the thickness changes during swelling and homogenous removal of fouling with the use of laser triangulation sensors.

Future work will include quantification of the removal as well as analysis of the composition and structure of the layer.

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NOMENCLATURE

CIP Cleaning in Place
 Re Reynolds number
 ROI Region of Interest
 THE Tubular Heat Exchanger
 UHT Ultra High Temperature

REFERENCES

- Alvarez, N., G. Daufin, and Gesan-Guiziou, G. (2010) Recommendations for rationalizing cleaning-in-place in the dairy industry: case study of an ultra-high temperature heat exchanger. *Journal of dairy science*, Vol. 93, pp. 808-21
- Burton, H., (1968) Deposits from Milk in Heat Treatment Plants – a Review and Discussion. *Journal of Dairy Research*. Vol. 35, pp. 317-330.
- Christian, G.K. and Fryer P.J. (2006) The Effect of Pulsing Cleaning Chemicals on the Cleaning of Whey Protein Deposits. *Food and Bioproducts Processing*, Vol. 84, pp. 320-328.
- Grijpspeerdt, K. (2004) Applications of modelling to optimise ultra high temperature milk heat exchangers with respect to fouling. *Food Control*, Vol.. 15, pp. 117-130.
- Foster, C.L. and Green M.L.(1990) A model heat exchange apparatus for the investigation of fouling of stainless steel surfaces by milk II. Deposition of fouling material at 140 °C, its adhesion and depth profiling. *Journal of Dairy Research*, Vol. 57, pp. 339-348.
- Krosiak, M., Sefcik J., and Morbidelli M.,(2007) Effects of Temperature, pH, and Salt Concentration on β -Lactoglobulin Deposition Kinetics Studied by Optical Waveguide Lightmode Spectroscopy. *Biomacromolecules*, Vol. 8, pp. 963-970.
- Lalande, M., Tissier J.P., and Corrieu G. (1984) Fouling of a plate heat exchanger used in ultra-high-temperature sterilization of milk. *Journal of Dairy Research*, Vol. 51, pp. 557-568.

Mercadé-Prieto, R., Wilson D.I., and Paterson W.R., (2008) Effect of the NaOH Concentration and Temperature on the Dissolution Mechanisms of β -Lactoglobulin Gels in Alkali. *International Journal of Food Engineering*, Vol. 4 pp.

Nema, P.K., Datta A.K., (2006) Improved milk fouling simulation in a helical triple tube heat exchanger.

International Journal of Heat and Mass Transfer. Vol. 49 pp. 3360-3370

Wallhäuser, E., Hussein M.A., Becker T., (2012) Detection methods of fouling in heat exchangers in the food industry. *Food Control*, Vol. 27 pp. 1-10

Xin, H., Chen X.D., and Özkan N., (2004) Removal of a model protein foulant from metal surfaces. *AIChE Journal*, Vol 50 pp. 1961-1973.