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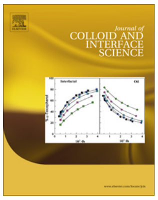

# Toward the understanding of the interfacial dairy fouling deposition and growth mechanisms at a stainless steel surface: A multiscale approach

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ABSTRACT

The microstructures of two dairy fouling deposits obtained at a stainless steel surface after different processing times in a pilot plate heat exchanger were investigated at different scales. Electron-Probe Micro Analysis, Time-of-Flight Secondary Ion Mass Spectrometry, Atomic Force Microscopy, and X-Ray Photoelectron Spectroscopy techniques were used for this purpose. The two model fouling solutions were made by rehydrating whey protein in water containing calcium or not.

Results on samples collected after 2 h processing show that the microstructure of the fouling layers is completely different depending on calcium content: the layer is thin, smooth, and homogeneous in absence of calcium and on the contrary very thick and rough in presence of calcium.

Analyses on substrates submitted to 1 min fouling reveal that fouling mechanisms are initiated by the deposit of unfolded proteins on the substrate and start immediately till the first seconds of exposure with no lag time. In presence of calcium, amorphous calcium carbonate nuclei are detected in addition to unfolded proteins at the interface, and it is shown that the protein precedes the deposit of calcium on the substrate. Moreover, it is evidenced that amorphous calcium carbonate particles are stabilized by the unfolded protein. They are thus more easily trapped in the steel roughnesses and contribute to accelerate the deposit buildup, offering due to their larger characteristic dimension more roughness and favorable conditions for the subsequent unfolded protein to depose.

## 1. Introduction

Fouling is generally defined as the unwanted formation of thermally insulating materials or deposits from process fluids onto heat transfer surfaces. Fouling in food-processing industries leads to the functional decline of thermal and hydrodynamic equipment performances, decreased product quality, and lack of sterility as well as decrease in the surface hygiene [1]. These two last points particularly induce a severe sanitary risk by favoring the development of pathogenic agents. Food contamination creates an enormous social and economic burden on communities and their health systems. These serious consequences, as well as the environmental concerns, force the food-processing industries to take drastic and expensive cleaning measures [2]: in petrochemical industries, pipe cleaning is carried out once a year, whereas in food-processing industries, it has to be done at least once a day. These frequent cleanings of food-contact surfaces result in a pronounced economic impact since (i) costs of chemical and energy required for cleaning are fairly high, (ii) time consuming is important, and (iii) cleaning generates excess effluent.

Milk is a complex biological fluid composed of several components including whey proteins, calcium, and lipids. Under 100 °C, thermal treatments in heat exchangers induce fouling of the stainless steel surfaces, which proceeds essentially from the denaturation of whey proteins. Among them, β-lactoglobulin (BLG), accounting for half of the whey proteins [3,4], is predominant in fouling ability of milk derivatives. These last twenty years, many research teams have tried to understand the mechanisms leading to dairy fouling of plate heat exchangers. The chemical composition of fouled layers has been characterized in various process conditions, and the main role of processing temperature was evidenced [5]. Indeed, two main chemical compositions of dairy fouling can be distinguished. Type A fouling is found under

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100 °C: it forms a rough and white deposit, composed of 50–60% proteins, half of which being BLG, as well as 30–35% minerals (essentially calcium and phosphate), and about 5% lipids [6]. Temperatures over 100 °C lead to the formation of type B fouling, that is, a gray and brittle deposit containing 70% minerals, 15–20% proteins, and around 5% lipids [7,8]. The present study was carried out using conditions leading to type A fouling, like in industrial heat treatments of pasteurization, where BLG is known to play the major role [6].

Mechanisms leading to fouling are nowadays intensively investigated. According to the literature, the fouling phenomenon can be separated in two phases, the first one being a thin induction layer. A number of studies have attempted to determine which milk components deposit during this induction layer [6,9–11]. However, there has been no agreement between researchers. Delsing and Hiddink [12] concluded that a conditioning film of proteinaceous material was most likely to be the first fouling layer to form. They also found that further growth of the fouling layer only appeared possible if calcium was present. Fryer [13] suggested that the presence of a layer of mineral salts adjacent to the heated surface shows that this layer was the first to be deposited. However, Foster and Green [10] argued that the proteinaceous layer was diffuse and irregular and that it seems very probable that salts could pass through it thus allowing the salts and protein layers to be built up simultaneously. Belmar-Beiny et al. [6] concluded from their surface analysis results that proteins were most likely to be the first species to adhere to the stainless steel surface [14]. “Proteins are very surface active and a clean metal surface has a large free surface energy gradient. Proteins will therefore be absorbed to the surface reducing this free surface energy” [6].

To summarize, this induction period corresponds *presumably* to the adsorption of a whey protein monolayer onto hot surfaces [11,15], during which almost no change of heat transfer coefficient or pressure drop happens. The induction period is *assumed to* correspond to a nucleation phase which will gather the conditions for the attachment of subsequent whey protein layers [6,15].

The successive layers *would be* bound together by means of proteic thiol groups and calcium [16].

The way Ca and proteic thiol groups interacts to shape the deposit layers are not wholly elucidate in literature even if among the mineral salt, the interaction between Ca and BLG in the fouling solution has been the most studied [17,18]. It has been recognized that calcium ions affect substantially the interactions between protein molecules [19] and have a strong impact on the BLG denaturation/aggregation mechanism [20–23]. However, these mechanisms describing *calcium ion–protein* interactions are still poorly understood at a molecular level. At the present time, there has been little published information which show how the calcium ions interfere with the substrate [24] and/or how the calcium allows making bridges and provide cohesion between elements of the material.

The aim of this work was thus to set a characterization procedure to generate a type A fouling and to investigate particularly the role of calcium in the fouling growth, at the first instant of the fouling phase (when no fouling can be visually observed) and after longer fouling times.

To investigate the adhesion of foulant components on stainless steel surface, various analytical techniques were used: Scanning Electron Microscopy (SEM), Electron-Probe Micro Analysis (EPMA), Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS), Atomic Force Microscopy (AFM), and X-Ray Photo-electron Spectroscopy (XPS). Two different fouling solutions and time of processing runs (1 min and 2 h) were used to attempt to demystify fouling mechanisms and the effects of material using a multiscale approach. The paper is separated in two parts: one part presenting the main results obtained by combining these different powerful characterization tools after 1 min and 2 h fouling; and a discussion part, in which the authors detail the assumed fouling deposition and growth mechanisms when two different fouling solutions are used.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Stainless steel

The steel surface tested in this study is a 316L stainless steel provided by Aperam. The detailed chemical composition of the industrial grade (analyzed by X-ray fluorescence) is presented in Table 1.

Prior to any testing, bare stainless steel plates (1 $cm^2$) were degreased first by an acetone/ethanol (50/50) blend, then soaked for 10 min at 65 °C in a 2% (v/v) RBS 35 (Société des traitements chimiques de surface, Lambersart, France), and rinsed two times for 5 min in distilled water at 65 °C and two times for 5 min in distilled water at room temperature.

The contact angle of the cleaned stainless steel measured by a GBX Digidrop goniometer is 70 ± 5°. Surface energy of 39.5 mN/m has been calculated following Van Oss model.

#### 2.1.2. Fouling fluids

The first fouling model fluid was obtained by reconstituting 1% w/w Whey Protein Concentrate (WPC) powder (Promilk 852 FB1, 86% proteins in dry state, IDI SAS France) in water of Total Hardness zero. Calcium content was determined using an atomic absorption spectrophotometer (Philips, Pye Unicam). This analysis shows that this solution contains 30 ppm calcium, issued from the reconstituted proteins: calcium was trapped when the proteins were dehydrated.

The second fouling model fluid was obtained by reconstituting 1% w/w Whey Protein Concentrate (WPC) powder (Promilk 852 FB1, IDI SAS France) in water containing 90 ppm calcium. Absorption analysis confirms a total calcium content of 120 ppm in the rehydrated protein solution, the difference being again due to the calcium issued from the whey proteins. The water used also contains Mg (less than 10 ppm), Na (about 20 ppm), K (about 4 ppm), and Chlorides (about 40 ppm) [25].

Seven hundred liters of both solutions was prepared the day of the experiment. It was prepared carefully to ensure that its physical properties (density, specific heat, thermal conductivity, and Newtonian viscosity) remained constant for all runs. The pH of the fouling product was remained quite constant between 7.3 and 7.7.

### 2.2. Experimental fouling equipment

The pilot-plant test ring figure is displayed in the ESM (Fig. 1’).

A plate heat exchanger (PHE) was used in a counter-current configuration (Model V7 of Alfa-Laval Vicarb, France). It consists in five passes of one channel for the two sides. The length between the two frames was fixed at 47.0 mm which means that the equivalent space between two plates was equal to 3.93 mm. The WPC solution was passed through a preheater composed of V7 type plates, 10 passes, and 1 channel per pass for the two sides of the heat exchanger to ensure the required inlet temperature (62 °C) to the test section. The protein solution was not re-circulated to avoid fouling from material which had already been treated. During fouling experiments, the inlet hot water product was adjusted to ensure a constant outlet product temperature close to 92 °C, maintained in a holding zone composed of square pipes where stainless steel plates (15 × 10 × 1 $mm^3$) are inserted. The ratio of