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Modified stainless steel surfaces targeted to reduce fouling – Evaluation of fouling by milk components

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Abstract

Several stainless steel based surfaces with different properties were evaluated according to their fouling behaviour for different dairy products under different conditions. Surface properties were obtained by the following modification techniques: SiF_3^+, MoS_2^{2+} and TiC ion implantation; diamond-like carbon (DLC) sputtering; DLC, DLC–Si–O and SiO_x, plasma enhanced chemical vapor Deposition (PECVD); autocatalytic Ni–P–PTFE and silica coating. Aqueous solutions that simulate milk (SMUF – simulated milk ultrafiltrate for the mineral components, β-lactoglobulin for the protein components and FMF – fouling model fluid for complex milk systems) were used to study the fouling behaviour during pasteurisation. Bacteriological deposition studies were also performed with two heat resistant strains of *Bacillus*. The experiments were carried out at laboratory scale for the evaluation of calcium phosphate and protein deposition, and at pilot scale for adhesion of bacteria and deposits from complex milk systems.

In all cases, the fouling behaviour was affected by the surface material, although in different ways for the deposition or the cleaning phases. For the non-microbiological deposits (calcium phosphate, whey protein and FMF milk-based product), the Ni–P–PTFE surface was the most promising one, since it generally promoted less deposit build up and, in all cases, was the easiest to clean. On the other hand, for bacterial adhesion, the most suitable surface was the ion implanted (TiC) surface, which also showed less spores after the cleaning process.

Keywords: Modified stainless steel; Fouling; Calcium phosphate; β-Lactoglobulin; *Bacillus subtilis*; *Bacillus cereus*

1. Introduction

The formation of unwanted deposits on the surfaces of heat exchangers, known as fouling, is an inherent problem in most industrial processes. Environmental and energy conservation demands have reinforced its socio-economic relevance in the last 10–15 years, but the underlying phenomena are in many instances not yet well understood and tools for mitigating its effects are not yet satisfactory. Well established chemical and mechanical fouling mitigation strategies are available for some industrial cases. Most of them necessitate stopping the heat transfer process for cleaning and the cost is often high in terms of production losses and labour. Modification of the fluid composition by introducing chemical additives can be effective but this is not possible in many industrial applications such as in the dairy industry (Müller-Steinhagen, 1998). For these

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cases, attention must be paid to other factors known to affect milk fouling. There are many significant physicochemical factors related to both the composition of milk and the properties of the heat exchanger surface that should be considered (Changani, Belmar-Beiny, & Fryer, 1997). As has been suggested in recent years (Forster & Bohnet, 1999), a deeper knowledge on the relation between fouling material and the properties of the fouled surfaces is essential in order to delay or minimize fouling as well as to determine optimal cleaning conditions for a given process. The aim of the present work is, therefore, to investigate the fouling behaviour of several milk components, milk related microorganisms and dairy products on different stainless steel surfaces previously characterized according to their surface properties (Santos et al., 2004).

Milk is a complex biological fluid composed of several components including whey proteins and calcium phosphate, which are involved in the fouling process through interacting mechanisms. The whey proteins, particularly β-lactoglobulin, foul after denaturation and aggregation, while calcium phosphate fouls as a result of local supersaturation (Changani et al., 1997). Fouling starts as soon as a dairy product is brought into contact with a stainless steel surface albeit at a molecular level and invisible to the naked eye. It is believed that fouling starts with whey protein adhesion at room temperature. Upon heating, the whey proteins start to unfold and expose a free S–OH group, changing into an activated state which allows attachment to the protein layer initially formed (Visser & Jeurnink, 1997). This first protein layer, however, is affected by the deposition surface since protein adsorption onto solid surfaces is the result of several interactions occurring between the protein, the surface and the solvent with other solutes present in the system (Haynes & Norde, 1994). These interactions are significantly influenced by the surface properties, more precisely its surface energy. In previous studies on the adsorption of protein on surfaces with different surface energies, no clear quantitative relationship was found between the amount of protein deposit and the surface energy (Addesso & Lund, 1997; Janocha et al., 2001; Yoon & Lund, 1994). Another major contribution to fouling in milk processing is the presence of calcium and phosphate ions. Upon heating of milk, part of these ions will tend to precipitate as a calcium phosphate salt (owing to the inverse solubility of calcium phosphate with temperature) which ultimately will form a mineral deposit on the stainless steel surface in a typical crystallization fouling process (Bott, 1995; Krause, 1993). Even when the deposits were predominantly proteinaceous, a calcium phosphate layer was found next to the surface due to migration of mineral ions (Changani et al., 1997). Analysis of deposits formed on heat exchangers after heat processing showed them to be a mixture of several calcium phosphate forms like dicalcium phosphate dihydrate (DCPD) and octacalcium phosphate (OCP) which at prolonged heating are eventually transferred to the least soluble and more stable calcium phosphate complex hydroxyapatite (HAP) (Visser & Jeurnink, 1997). The crystallization process of calcium phosphate is, therefore, a very complex problem since several forms can be formed at the same time depending on ambient conditions like the pH of solution, the temperature and the presence of other milk components. To control the last type of interference, a simplified milk system is normally used in fouling experiments. The most widely used mineral fouling solution, also used in the present work, is called simulated milk ultrafiltrate (SMUF) which was first described by Jenness and Koops (1962). This solution has been used on a variety of fouling studies, from calcium phosphate crystallization (Andritsos, Yiantsios, & Karabelas, 2002) to the fouling caused by whey permeates (Morison & Tie, 2002) with results comparable to reality. In addition to the above-mentioned bulk properties, crystallization fouling is also known to be dependent on the deposition surface characteristics (Bott, 1995). Consequently some studies were made on the effect of surface energy on the type and amount of crystallization deposit formed. Forster and Bohnet (1999) found a relation between surface energy and the induction period of calcium sulphate fouling, indicating the advantage of using low energy surfaces on heating equipments. Later on, these authors (Forster & Bohnet, 1999) proved that the analysis of the interfacial energy between surface and calcium sulphate deposit can be used as a tool to predict the optimum surface energy to mitigate fouling. The effect of surface energy on the nucleation and deposit development of calcium phosphate was also studied by Liu, Wu, Sethuraman, and Nancollas (1997) and by Wu, Zhuang, and Nancollas (1997). In both cases, it was found that nucleation and deposit development was higher for surfaces having high values of surface energy. A different opinion was however presented by Zhao and Müller-Steinhagen (2001) based on a theoretical approach on the adhesion forces of calcium sulphate on modified heat transfer surfaces.

Whey protein and calcium phosphate fouling are two different processes that follow different kinetics. Although they may interact in real milk processes, there is still a need to know more about the surface effect on each one of theses processes. Consequently, the build up of minerals and proteins in a fouling layer may be studied independently.

An additional approach to dairy heat exchanger equipment fouling, which has also been the subject of several studies (e.g. Boulangé-Petermann, 1996; Melo & Bott, 1997), is to focus on bacterial adhesion on stainless steel because of its high importance related to food safety reasons. The species studied in the present work were *Bacillus cereus* and *Bacillus subtilis* which are known to develop in foods during storage and have often been responsible for food borne diseases (Luby, Jones, Dowda, Kramer, & Horan, 1993). They have also been chosen for their ability to adhere to various materials (Faille, Lebret, Gavini, & Maingonnat, 1997), for their resistance to heat and chemicals in poultry meat (Faille et al., 1997) and in milk product processing lines (Faille, Fontaine, & Bénézech, 2001) since they are able to survive heat treatment and a cleaning-in-