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Deposition from a milk mineral solution on novel heat transfer surfaces under turbulent flow conditions

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Abstract

One of the strategies to reduce fouling during heat treatment in the dairy industry is the modification of the surface properties of the stainless steel used in heat exchangers, in order to decrease its appetence for milk deposits. To evaluate the importance of such properties on the formation of mineral deposits, the calcium phosphate fouling process was studied using stainless steel surfaces modified by TiN sputtering. The present experiments were performed in the turbulent flow regime in a heat flow cell where the fouling thermal resistance was monitored. The deposition and removal parameters were compared in terms of the influence of surface energy components on the type of deposit formed. The dependence of the fouling phenomenon on the electron-donor component of the surface energy in the turbulent flow regime was found to be similar to the one determined by the authors for the laminar regime in previous work. The present work also showed the usefulness of such modified surfaces as part of an anti-fouling strategy since all of them, independently of their surface energy properties, retained less deposit than the normal stainless steel surfaces (316 2R) after cleaning with water.

Keywords: Modified stainless steel surfaces; Calcium phosphate; Fouling; Surface energy

1. Introduction

It is common knowledge that fouling layers caused by milk on heat transfer surfaces are essentially composed by whey proteins and calcium minerals (Visser & Jeurnink, 1997). However, most of the milk fouling studies until now were primarily focused on the protein fouling mechanisms, hardly including fouling caused by mineral precipitation probably due to the higher impact of the voluminous protein deposits on pressure drop, as well as to the complexity of the calcium phosphate deposition phenomena (Jun & Puri, 2005). This reflects on the fact that there is still no modelling work linking the overall fouling kinetics to the role of minerals such as calcium phosphate. Such models are needed to improve fouling prediction and optimize dairy equipment design and operation (Jun & Puri, 2005). Even when a significant part of the milk deposit is composed of proteins, a mineral layer usually predominates next to the deposition surface (Changani, BelmarBeiny, & Fryer, 1997). This emphasized the importance of the interactions between mineral deposits and metal surfaces in milk processing.

When in solution, calcium phosphate precipitates in several Ca–P phases, including mainly dicalcium phosphate ($CaHPO_4 \cdot 2H_2O$, DCPD), octacalcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$, OCP) and hydroxyapatite ($Ca_5(PO_4)_3OH$, HAP). HAP is considered more thermodynamically stable in physiological environments than OCP and DCPD. Because the Ca–P system equilibrium in milk is quite complex, a mixture of the various calcium phosphate phases is normally encountered in the deposits formed during its heat treatment, depending on the bulk temperature, level of supersaturation, pH or overall ionic environment (Andritsos, Yiantsios, & Karabelas, 2002). For milk with a pH around 6.7 and a heating temperature

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Notation

γ^{TOT}	surface energy (mJ/m^2)
γ^{LW}	Lifshitz–van der Waals component (mJ/m^2)
γ^{AB}	acid–base component (mJ/m^2)
γ^-	electron-donor component (mJ/m^2)
γ^+	electron acceptor component (mJ/m^2)
k_m	mass transfer coefficient (m/s)
k_a	particle adhesion coefficient (kg/m^2 s)
D	diffusion coefficient (m^2/s)
Re	Reynolds number
Sc	Schmidt number
V	fluid velocity (m/s)
v	kinematic viscosity (m^2/s)
C_b	bulk concentration (kg/m^3)
C_i	interface solid–liquid concentration (kg/m^3)
C_s	saturation concentration (kg/m^3)
$\dot{m}$	mass flux (kg/m^2 s)

which is sufficiently high, the prevailing phase is the thermodynamically stable microcrystalline HAP, preceded by the formation by OCP, which is spherulitic in nature (Visser & Jeurnink, 1997).

In a heat transfer fouling process, deposit formation also depends on the interfacial free energy between the deposit and the heat transfer surface. The magnitude of the interfacial energy between the heat transfer surface and the fouling compound is a measure of the ability for heterogeneous nucleation of calcium phosphates (Wu & Nancollas, 1999), higher nucleation rates occurring on surfaces with higher values of Lewis acid–base components of the surface energy (Liu, Wu, Sethuraman, & Nancollas, 1997; Wu, Zhuang, & Nancollas, 1997). This is in accordance with classical nucleation theories (Mullin, 1993) which state that the higher tendency of a surface for heterogeneous nucleation, as compared to homogeneous nucleation, can be directly related to differences in the activation energies needed for each type of nucleation, represented by the so-called "shape function" (Φ) which can be defined as

$$\Phi = \Delta G_{HET}/\Delta G_{HOM}. \tag{1}$$

ΔG_{HET} is the free excess energy variation for the heterogeneous process, while ΔG_{HOM} represents its value for the homogeneous one. The "shape function" can be considered as a measure of the interfacial energy between the surface and the forming nucleus. It can be related to the contact angle (θ) between the two and indicates the predominance of the heterogeneous nucleation whenever Φ has a value below 1, opposing to what happens for values higher than 1. This happens for smaller contact angles, i.e., for higher surface energy values

$$\Phi = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}. \tag{2}$$

Nucleation on titanium-based surfaces has been evaluated with respect to several calcium phosphate phases. It has been shown that titanium oxide (TiO_2) surfaces are able to induce nucleation of dicalcium phosphate dehydrate (DCPD) (Combes, Freche, Rey, & Biscans, 1999), octacalcium phosphate (OCP) (Szekeres et al., 2005; Wu & Nancollas, 1997a) and hydroxyapatite (HAP) (Wu & Nancollas, 1997b) through a surface controlled reaction, when in contact with solutions that are supersaturated with respect to the corresponding phase.

In many industrial applications, the only possible way to influence the interfacial free energy is to modify the surface energy characteristics of the heat transfer surface (e.g., surface free energy) to a condition which is less appealing to fouling (Föster, Augustin, & Bohnet, 1999). The more recent anti-fouling strategies seek to decrease the adhesive strength between deposit and heat transfer surface as a way to increase the induction period of fouling or to build up layers which can be more easily cleaned. Forster and Bohnet (2000), Zettler, Weiss, Zhao, and Müller-Steinhagen (2005) and Zhao, Liu, Müller-Steinhagen, and Liu (2002) studied the role of the Lewis acid–base interactions on scale formation and/or deposit removal, as well as the effects of different surface modifications techniques on fouling, and demonstrated that low surface energy materials have the potential to reduce scale and biological fouling. Previous work by the authors (Rosmaninho & Melo, 2006a) on the deposition of calcium phosphate on stainless steel-based modified surfaces, in laminar flow, showed that fouling could be reduced by using low energy surfaces as deposition substrates. However, the surfaces used in that work were prepared by quite distinct modification techniques and each one presented a totally different chemical composition.

The present work was focused on the fouling behaviour of calcium phosphate from a milk mineral solution (simulated milk ultrafiltrate, SMUF) and its interaction with the surface properties by evaluating the effect of the different surface energy values on the type of deposition as well as on the easiness to clean. Although the system tested here is a synthetic one, the use of the SMUF solution has two significant advantages: (i) it allows separating the build-up of mineral deposits from the protein deposition and (ii) the system chemistry mimics the mineral part of milk, i.e., SMUF is not equal to a simple calcium phosphate aqueous solution. In order to eliminate the differences in materials chemistry and to focus on modified surfaces with qualitatively similar chemical composition and surface roughness but different surface energies, the materials deployed in this work are all based on stainless steel surfaces modified by TiN sputtering (Rosmaninho, Rocha,