1 Introduction

The dairy industry has been confronted with fouling since the first commercial pasteuriser in the mid-1880s (Westhoff, 1978) and plate heat exchangers were introduced in the 1930s (Visser and Jeurnink, 1997a; Wang et al., 2007) for pasteurizing and sterilizing milk. Since then, diverse technological approaches have been proposed and applied to mitigate milk fouling, although such strategies are limited, need to be adapted to the product or are not effective and sustainable in controlling deposit formation. The control of fouling in the food industry is essential to prevent food contamination and the risk to consumers' health. Therefore, heat transfer systems are regularly cleaned, resulting in: *(i)* loss of production efficiency, due to downtime for cleaning; *(ii)* additional energy and resource consumption, to counter heat transfer inefficiencies caused by fouling, and to heat cleaning solutions; and *(iii)* waste production and the necessity to treat the effluents. While the global production of milk products is consistently increasing on average, milk fouling remains an unresolved issue at present. Owing to the insufficient knowledge about the factors and conditions affecting the incidence of fouling as well as the complexity of deposition and cleaning mechanisms, the heat transfer equipment is often over designed and most CIP systems are operated on a semi-empirical basis. This scenario gives rise to new needs, new technological developments and requirements (Wilson, 2005; Napper, 2007; Guignard et al., 2009) and thus reflects the focus of this research.

The adhesion of particles to surfaces is unavoidable in food processing facilities (Bobe et al., 2007). The attachment, adhesion, retention and removal of foulant components to the surface during the thermal processing of food products are complex processes involving interactions between the surface, the deposit and the foulant or cleaning solution. In addition, these processes are affected by diverse factors. Fig. 1.1 summarizes the influencing factors on deposition, $\dot{m}_d$, and removal, $\dot{m}_r$, of whey protein and calcium phosphate, the main components of milk deposits, during fouling.

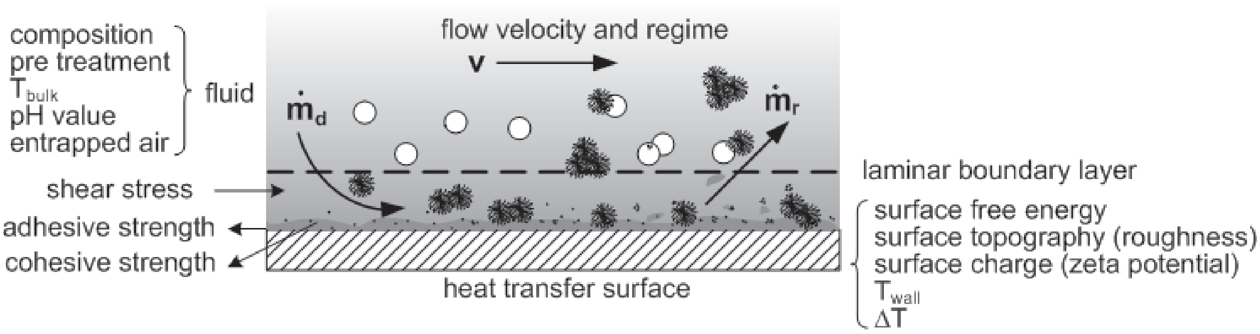


Fig. 1.1. Deposition and removal on a heat transfer surface by a calcium phosphate–rich whey protein solution. ○ native and ✺ denatured β-lactoglobulin, · calcium phosphate nanoclusters, crystals or particulates (adapted from Boxler et al., 2014b)

In order to understand the mechanism of deposit formation and removal, topographic and energetic surface properties have been modified and their effects on parameters such as heat transfer performance, pressure drop, deposit characteristics and properties, deposit adhesive and cohesive strengths and cleaning kinetics have been related. The defined surface modification offers strong potential to avoid or minimize fouling, as well as enhancing the cleanability of the surface, given that the interaction between heat transfer surface and process fluid constituents in the building of the first fouling layers can be altered/changed. The change of the interactions at the interface liquid/deposit might thereby result in longer operational times and shorter cleaning periods. However, an anti-fouling surface, approved for use in the food industry, is easy to clean, resistant in operation and remains effective over the lifetime of a plant is still a challenge (Boxler et al., 2014a).

The aim of the present work is to extend the knowledge about the fouling process occurring during the heat treatment of milk products. For this purpose, the fouling behavior of three model solutions (whey protein, SMUF – a solution that simulates the mineral composition of milk, and a SMUF–rich whey protein solution) on amorphous hydrogen containing carbon coatings, namely a-C:H, a-C:H:Si and a-C:H:Si:O, with different energetic surface properties is to be examined. These coatings show non-cytotoxicity, satisfy corrosion and mitigation standards for food contact and offer superior mechanical properties, thus probably being suitable for many applications in the food industry. The fouling experiments will be carried out under batch conditions and in a pilot scale plate heat exchanger, attempting to approach an industrial situation and permitting the comparison of both processing modes. Previously published studies (as will be discussed in Chapter 2) investigated mainly the influence of process conditions or of surface properties on the formation and composition of whey or milk deposits. However, the simultaneous influence of process and surface related variables on milk fouling is missing. Therefore, further objectives of this work are to quantify and model the relationship between process conditions, surface properties and deposition parameters as well as to find out the particular influencing variables.

The cleaning process is affected by six parameters: temperature, chemistry, cleaning time or duration, fluid mechanical action, type and amount of deposit and surface material or properties, as described in the extended Sinner's circle (Graßhoff, 1998). Here again, many studies have shown the separate influence of process parameters and surface properties (mainly surface material and roughness) on different type of deposits, but no attention has been given on the simultaneous influence of more than one surface property (surface free energy and surface roughness) on cleaning. Thus, another focus of this work concerns the understanding of the cleaning process of milk deposits formed on surfaces with different properties. The combined influence of the surface properties on the cleaning kinetics will be be identified and quantified. For this purpose, reproducible deposits will first be generated on the amorphous hydrogen containing carbon coatings, which are then examined regarding their cleaning behavior.

2 Theoretical Background

In this chapter, aspects of fouling in general and milk fouling in particular are presented. Furthermore, the deposition mechanisms of milk constituents such as proteins and salts are brought to perspective. In this context, influencing factors and fouling mitigation strategies are outlined. Section 2.3 addresses cleaning mechanism and models. Finally, the influence of surface properties on fouling and cleaning of food deposits is discussed.

2.1 Fouling – General concepts

Fouling is the formation and accumulation of unwanted deposits on the surfaces of heat exchangers (Bott, 1995). Soiling also includes the accumulation or presence of residues, cleaning agent residues and residues from rinse water (Maxcy, 1973). The fouling layers lead to a drastic reduction of the equipment thermal efficiency and an increase of the pressure drop in heating systems. Furthermore, the deposits can contaminate the fluids with which they come in contact and promote favorable environmental conditions for the growth of microorganisms and biofilm formation (Marchand et al., 2012). Consequently, additional capital and operating costs and the loss of production opportunities due to production downtime are caused. In the food industry, fouling might also cause a reduction of food quality due to overheating or insufficient heating, resulting in the loss of product quality (Cattaneo et al., 2008) or the potential risk of microbiological contamination (Holsinger et al., 1997). Hence, regular and intensive cleaning procedures are required to remove the deposits, maintain production efficiency and meet hygienic standards and regulations.

2.1.1 Fouling mechanisms and phases

Fouling is a complex process, usually involving various physicochemical sub-processes, which on the other hand are related to the composition and physicochemical characteristics of the fluids in contact with the surface, the properties of the heating surface, design of the heat exchanger, mode of heat transfer, operating conditions (mainly temperature and flow regime) and the type/nature of the fouled layer.

The fouling process can be classified into five groups (Epstein, 1981), depending on the key physical or chemical fouling mechanisms:

1. Crystallization or scaling formation: the precipitation of soluble material from the bulk fluid onto the solid surface due to a reduction in its solubility at the wall temperature. This category also includes the freezing fouling, which is the deposition of solid material from the process fluid itself through cooling down to its freezing point (Bott, 1990);
2. Particulate sedimentation, accumulation or silting: the deposition of finely dispersed insoluble solid particles from the process stream onto a heat transfer surface;
3. Chemical reaction accompanied with product attachment: deposit formed by chemical reactions, such as the decomposition or polymerization of organic matter at the heat transfer surface, in which the surface material itself is not a reactant;

4. Corrosion of the heat transfer surface: corrosion of the substrate resulting in corrosion products, which foul the surface and can foster the attachment of other potential fouling compounds;
5. Biological fouling or biofouling: deposition and growth of microorganisms at the heat transfer surface. The transport of the cells towards a surface, their initial adhesion and the polymer production by the cells leads to the formation of biofilms. The presence of suitable nutrients in a particular environment will determine the survival of the microorganisms, the production of exo-polysaccharides and their consequent growth (Bott, 2011).

A combination of several of the above mechanisms can occur simultaneously, forming a mixed or composite fouling (Epstein, 1981; Bott, 1990; Sheikholeslami, 1999), such as deposits formed in the food industry (Fig. 2.1).

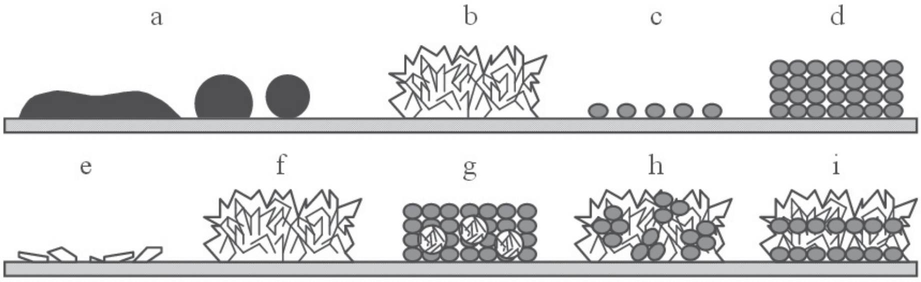


Fig. 2.1. Deposits formed by heating of food products (Kessler, 1996). a: aqueous solutions or fat; b: sugar or low molecular weight carbohydrates, crystal formation by adhesion and agglomeration; c: adsorption of a protein monolayer; d: cross-linked protein agglomerates; e: adsorption of ions or crystals; f: crystallization; g: protein deposits with salt inclusions; h: salt deposits with protein inclusions; i: mixed deposits of protein and salt layers

The overall fouling process consists of a number of sub-processes (Epstein, 1981), encompassing bulk, induction, fouling and aging reactions, as well as diffusion (Sandu and Lund, 1985). The five most important sub-processes are summarized in Fig. 2.2. Here, again an overlap of phases during fouling can occur, such as simultaneous deposition or re-entrapment of particle agglomerate or particulate and removal, or deposit aging, which starts as soon as it has been laid down on the heat transfer surfaces (Epstein, 1981; Bohnet, 1987).

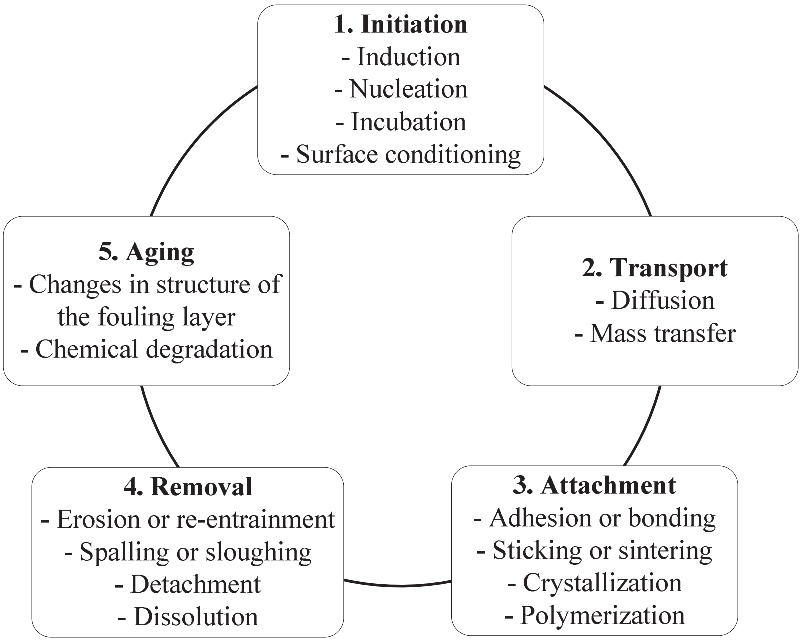


Fig. 2.2. Important phases of fouling (Epstein, 1981; Bohnet, 1987)

2.1.2 Fouling related costs

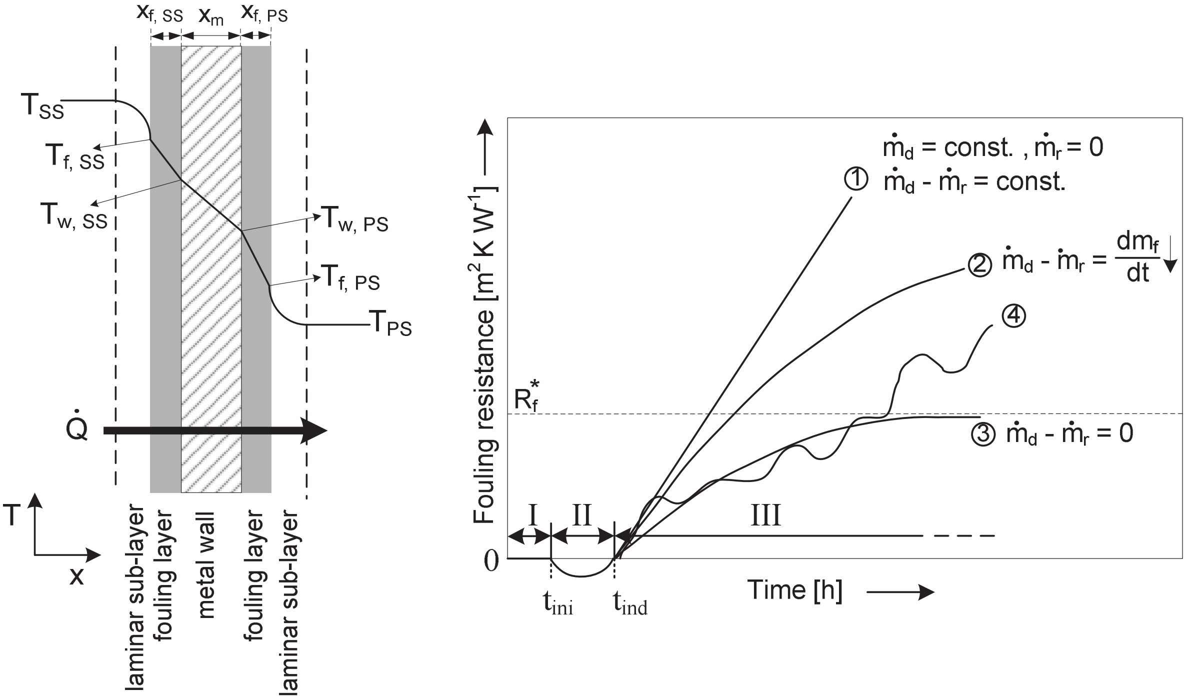
It is estimated that the worldwide costs due to fouling amount to several billion €/a. In industrial operations, the cost of fouling is in the order of 0.1 – 0.3 % of Gross National Product (GNP) (Garrett-Price et al., 1985; Bohnet, 1987; Chenoweth, 1990; Steinhagen et al., 1993; Xu et al., 2007). In the dairy industry, fouling and the resulting cleaning of the process equipment accounts for about 80 % of the total production costs (Bansal and Chen, 2006). The cost of fouling in the French dairy industry reached 150 million €/a in 1990 and 36 million €/a in the Netherlands in 1986 (Visser and Jeurnink, 1997b). The estimated product loss costs in the Netherlands are around € 3,200/ton deposit (de Jong et al., 2002). An overview of the environmental and ecological impact of the dairy sector (farming and processing) regarding the greenhouse gas emission, primary energy consumption and water use is given by Theilen and Goldbach (2000), Umweltbundesamt (2005) and Guignard et al. (2009). The cleaning of equipment plays a major role in both hygienic and economic considerations and has enormous potential for optimization. About 1.70 kg alkali and 0.60 kg of acid (Spreer, 2005) or 3 kg cleaning and disinfection agents and 1.5 m^3 water (Molkerei Weihenstephan, 2005, 2008; Guignard et al., 2009) are required per ton of processed milk. In Germany, it corresponds to an annual consumption of 70 – 90 million tons of cleaning and disinfection agents and 45 million m^3 water. For other dairy products such as cheese or yoghurt, a specific consumption up to 6 m^3 water per ton product can be estimated (mostly cleaning/rinsing water) (Guignard et al., 2009).

In general, the costs caused by fouling involve:

i. capital expenditure: overdesign of the surface area and extra pumps;
ii. provision of additional equipment to clean the process plant;
iii. loss of production as a result of downtime for cleaning;
iv. energy costs for increased heating demand, sterilization of equipments and the operation of the plant during cleaning;
v. costs with cleaning and disinfection agents and water as a solvent and detergent and steam as an energy source and for sterilization;
vi. disposal or processing for re-use of cleaning chemicals and effluent treatment;
vii. operating costs of anti-fouling devices: employment of biocides to avoid biofouling; purchase and dosing of biocides (Bott, 2011).

2.1.3 Fouling resistance

The fouling resistance, sometimes called the fouling factor, can be defined as the adverse thermal effects of the presence of a deposit on heat transfer surface (Bott, 1995). Fig. 2.3a illustrates the various resistances to heat transfer encountered as heat flows from a hot fluid to a cold fluid (e.g a food product) and the accompanying temperature drops due to the presence of fouling layers.



(a) (b)

Fig. 2.3. (a) Idealized distribution of service, product, wall and deposit temperatures across a fouled heat transfer surface of a generalized heat exchanger; (b) Characteristic fouling curves

For a constant heat transfer rate and steady state conditions and assuming the formation of a uniform fouling layer, the heat flow for parallel plates is given by:

$$\dot{Q} = h_{SS} A(T_{SS} - T_{f,SS}) = \frac{\lambda_{f,SS}}{x_{f,SS}} A\left(T_{f,SS} - T_{w,SS}\right) = \frac{\lambda_m}{x_m} A\left(T_{w,SS} - T_{w,PS}\right) = \frac{\lambda_{f,PS}}{x_{f,PS}} A\left(T_{w,PS} - T_{f,PS}\right)$$
$$= h_{PS} A\left(T_{f,PS} - T_{PS}\right) \qquad (2.1)$$

The overall temperature driving force to accomplish the heat transfer between the hot and the product fluid streams is the sum of the individual temperature differences. i.e.:

$$(T_{SS} - T_{f,SS}) + \left(T_{f,SS} - T_{w,SS}\right) + \left(T_{w,SS} - T_{w,PS}\right) + \left(T_{w,PS} - T_{f,PS}\right) + \left(T_{f,PS} - T_{PS}\right) \quad \text{or} \quad T_{SS} - T_{PS} \qquad (2.2)$$

Then the heat flux for parallel plates with identical heat transfer surface is given by:

$$\dot{q} = U_f \left(T_{SS} - T_{PS}\right) \qquad (2.3)$$

The overall heat transfer resistance ($1/U_f$) for the fouled surface is a sum of the individual resistances, namely the resistance of the outer and inner convective heat transfer, the thermal conduction through the heat exchanger and the fouling resistances on the surfaces of the hot and the product fluid streams. Since the heat transfer area remains unchanged, overall heat transfer resistance U_f for the fouled surface is:

$$\frac{1}{U_f} = \frac{1}{h_{SS}} + \frac{x_{f,SS}}{\lambda_{f,SS}} + \frac{x_m}{\lambda_m} + \frac{x_{f,PS}}{\lambda_{f,PS}} + \frac{1}{h_{PS}} \qquad (2.4)$$

The thermal impact of fouling is often expressed in terms of the fouling resistance R_f which is defined by the difference between the inverse of the fouled U_f and the clean U_{clean} overall heat transfer coefficient. Assuming no change of the film heat transfer coefficients (h_{SS} and h_{PS}, respectively), considering fouling only on the product side, i.e. $x_{f,SS} = 0$ m and $x_{f,PS} = x_f$ for simplification, the thermal fouling resistance can be written as:

$$R_f = \frac{1}{U_f} - \frac{1}{U_{clean}} = \frac{x_f}{\lambda_f} \qquad (2.5)$$

Assuming a uniform coverage of the entire heat transfer surface, the deposit coverage (mass per unit area) m_f in the fouling layer can be expressed by:

$$m_f = x_f \rho_f \approx \rho_f \lambda_f R_f \qquad (2.6)$$

At constant density and thermal conductivity of the fouling layer, m_f is directly proportional to R_f. However, it is not usually a good assumption, given that the fouling layer distribuition on the surface is seldom uniform, the values of ρ_f and λ_f are highly dependent upon the conditions existing at the time of deposition (Knudsen, 1980) and they can vary with deposit aging (Davies et al., 1997).

In most cases, the deposition is simultaneously accompanied by a removal process that is determined by the adhesion and cohesion forces between deposit/heat transfer surface or deposit/deposit and the shear strength of the fouling layer. According to Kern and Seaton (1959), the net rate of fouling or the rate of the increase of solid in the fouling layer thus results from two competing process deposit formation and removal:

$$\frac{dm_f}{dt} = \dot{m}_d - \dot{m}_r \tag{2.7}$$

The progress of a fouling process can be described by a plot of thermal fouling resistance or mass of deposit per unit heat transfer surface against time. The three most characteristic fouling curves, namely linear (1), non-asymptotic or falling rate (2) and asymptotic (3), are shown in Fig. 2.3b. The sawtooth behaviour (4) displays a net rising curve periodically interrupted by drops in the fouling resistance.

The different fouling curves are described as:

(1) Linear fouling: represents a process in which the deposition proceeds at a constant rate and the deposit removal is negligible or the deposition and removal rates have a constant difference. A linear increase of deposit mass and thus also the fouling resistance with time takes place;

(2) Non-asymptotic or falling rate fouling: with increasing of the fouling layer thickness and mass the deposition slows down, without the R_f tending towards a maximum value. This behavior can also be observed when the deposition rate remains constant (and the surface temperature decreases) and the removal rate increases with time;

(3) Asymptotic fouling: a steadily decreasing difference between deposit formation and removal, in which the difference approaches zero as mass of the fouling per unit area and thus R_f approaches a finite value (m_f^* or R_f^*, respectively). Removal of deposit might begin right immediately after the deposition starts.

(4) Sawtooth fouling: a collection of increasing and rising curves, in which the fluctuations of the fouling resistance are caused by a periodically removal of relatively large chunks of deposit. Here, the removal process is determined by: *(i)* low deposit adhesive and cohesive strengths, which can be caused by changes in the deposit structure and chemical degradation; *(ii)* increased shear or thermal stresses; or *(iii)* corrosion of the substrate.

Regarding the time profiles of fouling, three different phases can be distinguished, as suggested in Fig. 2.3b:

I. Delay or initiation period: can be observed before any appreciable fouling is recorded after starting a process. This does not imply that no fouling occurs, although at this time the first fouling layer is formed, e.g. nucleation in crystallization fouling or organic monolayer formation in protein or biological fouling (conditioning of the surface). The initiation phase ends at the initiation time t_{ini};

II. Transition period: deceptively low and even negative values of R_f can be measured, whereby the deposit roughness gives rise to an increase in the convective heat transfer coefficient between the surface and the fluid, compared to that of the clean surface (Albert et al., 2011; Epstein, 1981). In this “roughness controlled phase”, variations in the initial temperature profiles, pressure drop and deposit mass can be detectable;

III. Layer growth or fouling phase: the effect of deposit roughness declines in relative importance as the fouling layer thickness increases and R_f becomes large. A compact fouling layer grows up.

Phases I and/or II do not necessarily occur (Bohnet, 1987) and both together are also called the induction phase. The induction phase ends at the induction time t_{ind}. From an industrial perspective, the physicochemical interactions that take place in the induction phase and the formation of the initial fouling layer are very important because they determine the deposit adhesion strength and the cleanability of the surface (Bobe et al., 2007; Boxler et al., 2013a).

2.2 Milk Fouling

The economic importance of the world dairy industry is highlighted in The World Dairy Situation (2010), and for Germany by Wohlfahrt (2012). The worldwide milk production was 703 million tons in 2009, of which ca. 590 million was cow milk, including 120 million tons of liquid milk for direct consumption. In Germany, approximately 30 million tons of cow milk is produced and processed annually, of which 14 million tons, or almost half, is exported. The German dairy industry generated annual sales of around 24 billion € in 2011, making it by far the largest food industry in Germany. In 2011, an average consumer consumed almost 120 kg of dairy products in the form of liquid milk and other products such as cream, butter, yoghurt and cheese. Considering the magnitude of these numbers and the costs due to fouling and cleaning, as indicated in section 2.1, it can be concluded that the understanding of fouling and cleaning mechanisms holds great importance to prevent, avoid or reduce fouling, as well as improving the cleaning efficiency in dairy.

Thermal treatment has long been used for preservation purposes in the processing of dairy products (Westhoff, 1978; Holsinger, 1997). Raw milk is subject to pasteurization for at least 15 seconds at 72 °C (Böhm et al., 2000; Regulation EU No. 605/2010**,** 2010) in order to destroy heat sensitive spoilage and pathogenic bacteria. Further processing steps (UHT treatment - at no less than 135 °C in combination with a suitable holding time (Böhm et al., 2000; Regulation EU No. 605/2010, 2010) or drying) are designed to limit the growth of the thermoduric bacteria that survive the pasteurization. Heating the milk also deactivates enzymes that could degrade the product quality and eliminates non-pathogenic microorganisms that could produce lactic acid or enzymes, leading to off-flavors, thus increasing the product shelf life. Heat treatments also confer various functionalities to dairy ingredients, such as viscosity, gelation, renneting, foaming, and emulsifying properties (Augustin and Udabage, 2007). On the other hand, excessive heating of milk can lead to undesirable alterations in the milk constituents that subsequently influence the functional properties of the dairy products. One consequence of the thermal treatment is the building up of a fouling layer on the heat transfer surface due to physicochemical changes in the product.

The first published papers on milk fouling deal with the soiling of dairy farm utensils or batch-wise pasteurizers, referred to as milk stone or milk scale, and were presented in the early 1930s (Parker and Johnson, 1930; Tuckey, 1931).

Milk stone is the product resulting from the reactions between an initial film formed on the equipment surface or remnant of deposit that was not readily removed by cleaning, and the chemical constituents of water supply and cleaning detergents with repeated cursory washing/cleaning cycles (Leeder, 1956; Gordon et al., 1968; Maxcy, 1973). The initial milk film is formed by remained phospholipids where heat processing is not involved or remained protein or milk salts due to heating of milk or milk products. The initial film or soil contributes to the accumulation of additional residual, thereby permitting the growth of microorganisms (Gordon et al., 1968; Maxcy, 1973).

Various processes occur during milk fouling, with the numerous interactions among the milk components complicating the observation, understanding and prediction of the fouling mechanism, only allowing for an approximate description. This is due to the fact that milk is a biological and complex medium, whose composition varies seasonally and with the cattle diet. Furthermore, a large number of physical and chemical factors such as the pH, age and pre-treatment of the milk influence the formation, extent and nature of fouling. A general overview of the milk fouling mechanism and the factors affecting it will be presented in the next sections.

The individual milk constituents are involved in varying degrees and phases of the fouling layers' formation and growth due to their different physicochemical properties and especially because of their different heat sensitivity. The raw milk (Table 2.1) and milk deposit (Table 2.2) compositions are significantly different. Lyster (1965) and Jeurnink et al. (1996a) showed that the milk deposit mainly constitutes whey proteins and milk salts. By contrast, the other milk constituents such as casein, lactose and fat play a minor role in the fouling processes (Jeurnink et al., 1996a) and only make a small portion of the deposits, although they together account for over 80 % of the colloidal and soluble compounds in milk. Severe fouling by casein micelles only occurs if the colloidal stability of the casein micelles is reduced, e.g. by lowering the pH or by high pressure treatment (Jeurnink et al., 1996a).

Deposits formed after the heat treatment of milk are classified as type A or type 1 and type B or type 2, depending on the heating temperature. With deposit type A, half of the protein deposit consists of whey protein (Lyster, 1965; Lalande et al., 1985). Both fouling types might also occur simultaneously during High Temperature Short-Time (HTST) pasteurization, performed in the range of 72 °C – 100 °C, or during pasteurization prior to UHT thermal treatment, resulting in a dense deposit with a foam-like structure (Barish and Goddard, 2013).

Table 2.1. Average cow milk composition and size of the major constituents (Walstra and Jenness, 1984; Kessler, 1996; Walstra et al., 1999; Michalski et al., 2004; Töpel, 2004; Lucey and Horne, 2009)

Constituents	Average concentration [% w/w]	Size [nm]	Constituents	Average concentration [% w/w]	Size [nm]
Water	87.5	~ 0.3	Lactose	4.6	1
Total solids	13	--	Minerals	0.8	0.5 (ions)
Proteins	3.4	--	Calcium	0.1 – 0.12	--
Casein micelle	2.8	10 – 600	Magnesium	0.01 – 0.015	--
α_{S1}-casein	1	--	Potassium	0.12 – 0.16	--
α_{S2}-casein	0.26	--	Sodium	0.03 – 0.06	--
β-casein	0.93	--	Carbonate (including CO_2)	~ 0.02	--
κ-casein	0.33	--			
γ-casein	0.08	--	Chloride	0.08 – 0.12	--
minerals	0.2	--	Citrate	0.13 – 0.2	--
Calcium	0.008	--	Total phosphorous (all forms)	0.09 – 0.1	--
Magnesium	0.0004	--			
Inorganic PO_4^-	0.1	--			
Citrate	0.018	--	Inorganic PO_4^-	0.17 – 0.2	--
Whey proteins	0.6	1 – 10	Sulphate	~ 0.01	--
β-lactoglobulin	0.32	1.2 – 6	Fat globule	3.9	100 – 10,000
α-lactoalbumin	0.12	3	Others (vitamins, organic acids, etc)	0.3	--
BSA	0.04	3 – 12			
IgG, IgA, IgM	0.08	--			
Other proteins	0.36	--	pH	6.7	--

PO_4^- = phosphate, BSA = bovine serum albumin, Ig = Immunoglobulin

Table 2.2. Characteristics of milk and whey protein deposits

Original fluid	Deposit type	Process parameters	Composition [% w/w dry basis]	Appearance
Whole milk	Type 1 (Lyster, 1965) or Type A (Burton, 1968)	Pasteurization T = 75 – 100 °C	Protein: 50 – 60 Minerals: 30 – 35 Fat: 4 – 8	Soft, spongy and voluminous structure, white or cream-colored
Whole milk	Type 2 (Lyster, 1965) or Type B (Burton, 1968)	Ultra-heat treatment (UHT) T = 110 – 140 °C	Protein: 15 – 20 Minerals: 70 – 75 Fat: 4 – 8	Brittle and porous, grey
Whey protein	-- (Robbins et al., 1999; Christian et al., 2002; Hooper et al., 2006)	Pasteurization or ultra-heat treatment	depends on the solution composition: WPC, WPI or whey	Soft and spongy structure, white or transparent
Residues from food processing and imperfect cleaning	Milk stone (Leeder, 1956; Kulkarni et al., 1975)	Pasteurization	Protein: 4 – 44 Minerals: 42 – 67 Fat: 4 –18; up 72 °C mainly fat and protein, above 72 °C also minerals	Yellow hard compact or grey porous soft film

A review of the variability on the composition of fouling layers formed from whole and skim milk heated in tubular or plate heat exchangers by diverse studies is summarized by Sadeghinezhad et al. (2013). In general, the protein content of the deposits formed at temperatures to 90 °C matches the classification for deposit type A of Table 2.2, while a lower mineral content (varying from 5 % w/w to 25 % w/w) and a higher fat content (varying to 50 % w/w) in the deposits of different studies was measured. Deposits obtained at temperatures of 110 °C – 140 °C presented a lower mineral composition (varying from normally 20 % w/w to maximal 75 % w/w) than deposit type B (Table 2.2). Milk pretreatment such as heating, homogenization or drying (in the case of reconstituted/recombined milk as model fluid), different processing conditions or equipments' types, geometries or design (including different heating sections of a heat exchanger) mainly influenced the deposit composition (Visser et al., 1997a) of the diverse works (see also Table 2.4) due to changes in chemical and physical or structural properties of the milk components (Davies, 1936; Jeurnink et al., 1996a; Visser and Jeurnink, 1997a; Lee, 2002). The deposit removal from the fouled surface and/or its dissolution procedures and different analytical methods can also result in variability of the deposit composition. Due to the difficulty of storage and avoiding the natural variations of raw milk or whey, whey protein concentrate (WPC) or whey protein isolate (WPI) have been used to obtain reproducible fouling behavior (Lalande et al., 1985; Delplace et al., 1997). However, as highlighted by Robbins et al. (1999), WPC deposits were predominantly proteinaceous at both pasteurization and UHT temperatures (Table 2.2). Given that WPI or WPC pure does not produce a mineral scale at UHT temperatures (Bird and Fryer, 1991; Delplace et al., 1994; Christian et al., 2002), synthetic milk ultrafiltrate or calcium and phosphate solutions have been added to WPI or WPC and thus used as a milk model fluid (Daufin et al., 1987; Christian et al., 2002; Rosmaninho and Melo, 2007).

Deposits formed at low temperature, e.g. by cooling of milk, show different structure, composition and mechanism (Kane and Middlemiss, 1985) and will not be discussed in detail within this work.

2.2.1 Mechanisms of milk fouling

The exact mechanism of milk fouling has not yet been fully understood (Bansal and Chen, 2006). Despite a wide range of works on the literature (Burton, 1968; Jeurnink et al., 1996a; Changani et al., 1997; Visser and Jeurnink, 1997a; Visser et al., 1997; Petit et al., 2013), it is unclear whether mineral or protein fouling form first in the induction phase and whether fouling is primarily caused by the deposition of denatured or aggregated proteins on the heat transfer surface.

Table 2.3 provides an overview of the basic and contradictory postulates of milk fouling mechanism.

Table 2.3. Basic postulates regarding milk fouling mechanisms (adapted from Bansal and Chen, 2006)

Topic	Observation	References
governing bulk reaction	protein denaturation	Lalande et al. (1985), Kessler et al. (1986), Arnebrant et al. (1987), Kessler and Beyer (1991), de Jong et al. (1992), de Jong (1997), Petit et al. (2013)
	protein aggregation	Gotham et al. (1992), Delplace et al. (1997)
first fouling layer	mostly proteinaceous	Delsing and Hiddink (1983), Belmar-Beiny and Fryer (1993), Visser and Jeurnink (1997a), Jimenez et al. (2013)
	mostly mineral	Tissier and Lalande (1986), Daufin et al. (1987), Britten et al. (1988), Foster et al. (1989), Fryer and Belmar-Beiny (1991)
	protein and minerals simultaneously	Daufin et al. (1987), Foster and Green (1990), Boxler et al. (2013b)
	proportion of minerals in deposit increases after long contact times (10 – 60 min)	Daufin et al. (1987), Hege (1984)
fouling mitigation through milk constituents	formation of protein aggregates	de Jong et al. (1992), Delplace et al. (1997)
	absence of precipitable calcium and phosphate ions	Daufin et al. (1987)
controlling step	protein aggregates are not involved in fouling/are absent in the fouling layer	Blanpain-Avet et al. (2012), Jimenez et al. (2013)
	fouling is caused only by protein aggregates	Visser et al. (1997), Mahdi et al. (2009), Jun and Puri (2007)
	fouling depends on protein reactions (in bulk) only	Kessler et al. (1986), de Jong et al. (1992), de Jong and van der Linden (1992), Belmar -Beiny et al. (1993), Delplace et al. (1994, 1997), Schreier and Fryer (1995), Grijspeerdt et al. (2004)
	fouling depends on mass transfer as well as bulk and surface reactions	Georgiadis and Macchietto (2000), Chen et al. (2002), Bansal and Chen (2006)
	fouling depends on bulk as well as surface reactions	Paterson and Fryer (1988), Fryer and Belmar-Beiny (1991), Jeurnink et al. (1996a), Boxler et al. (2013b)

The most accepted deposition stages governing milk fouling are (Belmar-Beiny and Fryer, 1993; Jeurnink et al., 1996a; de Jong, 1997; Bansal and Chen, 2006):

(i) protein denaturation and the formation of insoluble material (aggregated protein) in bulk;

(ii) transport/mass transfer of denatured and aggregated proteins or calcium and phosphate ions to the heat transfer surface;

(iii) adhesion of this material to the surface, initiating the fouling or causing the deposit to grow by further incorporation of proteins and/or calcium ions and calcium phosphate particulates, as well as the entrapment of other milk constituents (such as fat globules) into the fouling layer; and

(iv) possible transfer of proteins or crystals/particulates back to the bulk (re-entrainment).

Based on scanning and transmission electron microscopy and X-ray microanalysis studies by other authors, as well as her mathematical model simulation, Sandu (1989) proposed a three steps mechanism or defects-growth model for milk deposit formation, also reviewed by Grant et al. (1996). In this model (Fig. 2.4), a compact and dense sublayer forms in a relatively short period of time (< 1 min) at metal surface. The sublayer contains mostly calcium phosphate and protein as a binding material. At a given stage, granules (probably of protein) build up randomly at active sites on the sublayer surface. The granules extend into the bulk phase, providing anchors for protein aggregates and leading to the growth of a porous, spongy deposit with low density and high moisture content. With increasing deposit thickness and density, proteins will crosslink and polymerize. Hence, the porous matrix of the deposit consists of proteins, with minerals agglomerated in certain regions. Fat globules and microorganisms are also entrapped inside this matrix. The compact layer continues to grow underneath the spongy deposit (Sandu, 1989) due to deposit aging by thermal reactions and diffusion of species (whey proteins, α- and β-caseins or mineral salts or ions) through the protein matrix to the deposit-metal interface (Sandu, 1989; Changani et al., 1997). Foster et al. (1989), Jeurnink et al. (1996a) and Changani et al. (1997) also describe an upper soft layer. Additionally, Foster and Green (1990), Belmar-Beiny and Fryer (1993) and Blanpain-Avet et al. (2012) demonstrate that the distribution, structure and content of deposit components in the fouling layer changes with depth.

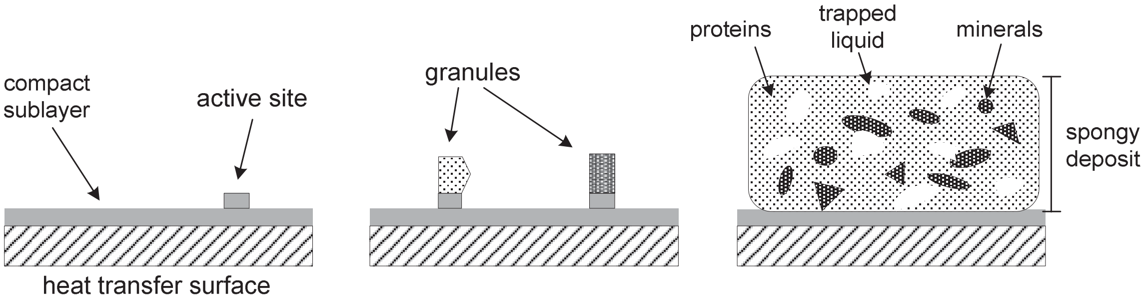


Fig. 2.4. Three stages deposit formation: compact sublayer, granule and spongy deposit (Grant et al., 1996)

Some studies have suggested that protein adsorbs first on the heat exchanger surface due to its high surface activity (Fryer and Belmar-Beiny, 1991), whereas other works have reported that the first layer is largely mineral (see Table 2.3). Maubois (1984) proposed two possible mechanisms: either denatured protein might act as nuclei for crystal growth; or denatured protein becomes adsorbed on the surface of mineral crystals. Through ToF-SIMS[1] analysis, AFM, X-ray microanalysis, X-ray photo-electron spectroscopy and SEM of fouled surfaces, Jimenez et al. (2013) proposed that the protein would be the first deposited during fouling of WPC and WPC plus $CaCl_2$.

Mass balance for denatured protein between the inlet and outlet of a heat exchanger is confusing regarding interaction of different protein stages (unfolded or aggregated) with the surface, as well as their role played on fouling growth (Blanpain-Avet et al., 2012). Recently,

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[1] Time-of-Flight Secondary Ion Mass Spectrometry

Blanpain-Avet et al. (2012) and Petit et al. (2013) have shown through Raman spectroscopy and HPLC analysis, respectively, that protein aggregates are not present in the deposit of WPI and WPI plus $CaCl_2$ generated at wall temperature of 85 °C.

The deposit growth is essentially linked to the presence of calcium and phosphate, which provide a link with denatured proteins: β-lactoglobulin alone or aggregated to κ-casein of casein micelles (Daufin et al., 1987). Besides, Daufin et al. (1987) emphasize the role played by calcium complexing substances in the broad sense (phosphates, citrates, soluble proteins, caseins) in influencing the fouling capacity of the fluid. Such a capacity decreases from ultrafiltrate to whey and milk (Daufin et al., 1987), due to the increase of bound calcium, e.g. to the casein micelles.

2.2.2 Fouling modelling/Modelling of milk fouling

Jun and Puri (2005) provide a review of fouling models in dairy processing, which correlate deposit mass or fouling progress with temperature and time of processing, fluiddynamic conditions or whey protein denaturation kinetics. The effects of pH, crystallization fouling (calcium phosphate deposition) and adhesion of further fouling components, as casein or fat, to the surface have been neglected in the developed models (Jun and Puri, 2005). Furthermore, no existing model is able to estimate milk fouling parameters based on energetic and topographic surface properties, which is the focus of this work.

McGuire (1989) and McGuire and Swartzel (1989) proposed a model for protein deposition, considering the influence of the surface free energy:

$$\frac{\partial m}{\partial t} = a\exp\left(-\frac{E_{a,T_s}}{RT_s} - \frac{E_{a,\gamma_s}}{\left|\gamma_s^{TOT} - \gamma_{s,\min}^{TOT}\right|}\right) \tag{2.8}$$

where a is a constant, $\gamma_{s,\min}^{TOT}$ the optimum surface free energy for minimal adhesion of milk protein, E_{a,T_s} and E_{a,γ_s} are the apparent activation energies required for transformation of an adsorbed specie to a irreversibly adsorbed specie on the surface, where E_{a,T_s} represents the bulk component and E_{a,γ_s} represents the surface component. E_{a,T_s} and E_{a,γ_s} can be expressed as:

$$E_{a,T_s} = b_1 + b_2 T \tag{2.9}$$

and

$$E_{a,\gamma_s} = \gamma_{s,\min}^{*} \tag{2.10}$$

where b_1 and b_2 are constants and $\gamma_{s,\min}^{*}$ ist the component of the surface free energy required for the surface reaction.