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Review

Constituent fouling during heat treatment of milk: A review

Thom Huppertz [a, b, *], Hans Nieuwenhuijse [a]

[a] FrieslandCampina, Amersfoort, the Netherlands
[b] Wageningen University & Research, Wageningen, the Netherlands

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ABSTRACT

Constituent fouling during thermal processing of milk is reviewed. Fouling occurs during continuous-flow thermal treatment, but the size and the type of fouling deposit strongly depend on both processing conditions (e.g., temperature, time, flow conditions) and product properties (e.g., composition, pH). Heat-induced destabilisation of proteins and heat-induced precipitation of calcium phosphate are the main drivers for component fouling during thermal processing. Whey proteins are included in fouling deposits at temperatures above their denaturation temperature, whereas caseins are included only at temperatures >100 °C. Calcium phosphate can be part of fouling deposits at temperatures >50 °C. Fat also contributes to fouling, but inclusion of fat is driven by interactions of proteins on the emulsion droplet surface. Component fouling of milk can be considered an extension of typical protein aggregation and salt precipitation mechanisms, where the deposit on the heating surface is considered as an additional, and often preferred, surface for interaction.

Contents

* Corresponding author. Tel.: +31 6 11187512.
E-mail address: thom.huppertz@frieslandcampina.com (T. Huppertz).

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1. Introduction

The fact that milk is a biological fluid intended for the complete nutrition of the neonate also means that it is an excellent substrate for the growth of spoilage and pathogenic microorganisms. Because of this, the shelf-life of raw milk is limited and various processing steps are applied to extend the shelf-life of milk. Most common treatments are based on thermal processing, to inactivate the bacteria, and/or the removal of water by (spray-)drying, which is often preceded by evaporation. These processing technologies are widely applied in the manufacture of milk and dairy products and dairy ingredients. Despite the efficiency of these unit operations, based on more than a century of ongoing developments, running times of the various unit operations are still limited due to the occurrence of fouling.

Fouling during processing of milk and dairy products may be physicochemical or microbial in nature. In this paper, the focus is on physicochemical fouling, i.e., fouling relating to the undesired deposition of proteins, salts and other constituents of milk and dairy products on the wall of processing equipment during heat treatment of milk and other liquid dairy products. Particular emphasis will be paid to the fouling of heat exchangers during the processing of milk, but also other liquid dairy streams, such as, e.g., whey protein concentrate (WPC) or whey protein isolate (WPI). Fouling of membranes is outside the scope of this paper. In this review, findings in scientific literature in relation to physicochemical fouling of milk and other liquid dairy streams will be discussed from the perspective of the latest insights into the (in)stability of the proteins, minerals and other constituents in milk and how they are influenced by increasing temperature and/or concentration. Because of the intricate relationships and interactions between the proteins and minerals in milk and other dairy products, it is important to consider this in a single encompassing model, rather than separately, as is the case in much literature available on the topic. In this research, we will focus primarily on fouling as observed in factory or pilot-scale heat exchangers during heat treatment of milk or other dairy products. Preferably, studies are carried out under industrially-relevant conditions, i.e., where milk is thermally processed for long durations (e.g., 10–12 h) without recirculation of the milk through the system; however, such studies are limited. Deposit formation of dairy constituents on other hot surfaces, e.g., in lab-scale setups, is considered only for additional mechanistic insights.

2. Heat-induced fouling of milk: some basic considerations

Decades of research on fouling of milk and dairy products during thermal processing, has led to a wealth, or perhaps even plethora, of information. The reported studies highlight a variety of starting materials used, processing conditions applied and methods used to determine the extent of fouling. Previous reviews on the topic were published by Bansal and Chen (2006), Burton (1994), De Jong (1997), Jeurnink, Walstra, and De Kruif (1996a), Sadeghinezhad et al. (2015) and Visser and Jeurnink (1997). Based on these reviews, and the underlying experimental studies, it appears that completely avoiding fouling during processing of milk or whey under common industrial conditions is not possible, as a monolayer of protein will always form on the wall of heat exchangers, even in the low-temperature sections, e.g., at 20 °C (De Jong, 1997; Jeurnink et al., 1996a).

However, the formation of this monolayer of several nm in thickness is not of practical concern, because it is not thick enough to be the cause of a notable reduction in heat transfer capacity or form a restriction to flow, which are undesirable effects (De Jong, 1997; Jeurnink et al., 1996a). Such undesirable effects only occur when the fouling layer grows many orders of magnitude in thickness, due to subsequent association of proteins and minerals with the initial monolayer. For example, a monolayer is a protein load of approximately 2 mg m^{-2}, a fouling layer of 1 mm at 20% protein is approximately 200 g m^{-2}. Such fouling is often monitored via the heat transfer coefficient or pressure in the system, which decrease and increase, respectively, when fouling occurs (De Jong, 1997; Jeurnink et al., 1996a).

The time period over which only a very thin (mono-)layer of deposit is formed on the surface of the heat exchangers, and heat transfer and flow are not impaired, is typically referred to as the induction time or lag time. In tubular heat exchangers, this induction time may vary from several minutes to an hour and, for the same product, depends on temperature (Jeurnink et al., 1996a; Visser & Jeurnink, 1997), flow conditions and the surface of the heat exchanger (Saget et al., 2021). In plate heat exchangers, there is typically no induction period. This has been related to the fact that plate heat exchangers contain low-shear areas in which deposition starts within minutes and builds up further after that (Indumathy, Sobana, & Panda, 2021; Schnöing, Augustin, & Scholl, 2020). Because fouling of milk constituents in heat exchangers is a surface reaction, flow conditions are very important. Increasing the Reynolds number (Re), which increases wall shear-stress, has been found to reduce fouling during whey protein processing (Belmar-Beiny, Gotham, Paterson, Fryer, & Pritchard, 1993). In plate heat exchangers, corrugation of plates is also a very important factor for controlling fouling, with both corrugation shape and corrugation orientation being key factors (Grijspeerdt, Hazarika, & Vucinic, 2003). Particularly when studying fouling of milk at lab- and pilot plant-scale, it is important to keep flow parameters in mind when interpreting results. In general, Re is low at low flow rate and/or large distance between plates (for plate heaters) and a large tube diameter, which is often a problem for lab or pilot scale heaters in which only tens to hundreds of litres per hour are processed. This requires tubes to have a diameter of ~1 mm to achieve flow conditions representative of industrial processing; however, a diameter of for example 5–10 mm is much more commonly used, which can lead to fouling behaviour at lab- and pilot plant-scale which may not be representative of fouling behaviour at industrial scale.

An overview of the composition of fouling deposits taken from heat exchangers reported for whole milk and skim milk is shown in Table 1 and Fig. 1. From these, it is clear that a notable variation in fouling deposit composition observed, which is, perhaps, not surprising given the differences in milk type, temperatures and type of heat exchanger studied (Table 1). Fig. 1 shows that protein:mineral ratio in the fouling deposits depends on the temperature of heat treatment; i.e., a high protein:mineral ratio at lower temperatures and a low protein:mineral ratio at higher temperatures. This is in line with the commonly used classification of fouling deposits from milk as so-called type A and type B or type I and type II deposits (Bansal & Chen, 2006; Burton, 1994; Jeurnink et al., 1996a; Sadeghinezhad et al., 2015):

- Type A (or type I) deposits are typically observed on treatment at temperatures <110 °C, are voluminous and consist of 50–70% protein (predominantly whey protein) and 30–50% minerals.
- Type B (or type II) deposits, in contrast, are typically observed on treatment at temperatures >110 °C, are more compact and granular, rich in minerals (70–80%), and their protein fraction (10–30%) consists primarily of caseins.

Table 1
Composition of fouling layers as reported in different studies.[a]

Reference	Milk type	Temp. (°C)	Equipment	Protein (%)	Minerals (%)	Fat (%)
Lyster (1965)	Whole	85	Plate heat exchanger	60	25	12
Delsing and Hiddink (1983)	Skim	76	Tubular heat exchanger	78	17	–
Lalande et al. (1984)	Whole	65–70	Plate heat exchanger	50	40	1
Lalande et al. (1984)	Whole	120–138	Plate heat exchanger	15	75	3
Fung, McCarthy, and Tuoc (1998)	Whole	4–90	Tubular heat exchanger	32	5	50
Tissier et al. (1984)	Whole	72	Tubular heat exchanger	50	15	25
Tissier et al. (1984)	Whole	90	Tubular heat exchanger	50	40	1
Tissier et al. (1984)	Whole	138	Tubular heat exchanger	12	75	3
Skudder et al. (1986)	Whole	80–110	Plate heat exchanger	51	20	6
Skudder et al. (1986)	Whole	110–140	Plate heat exchanger	22	53	5
Grandison (1988)	Whole	110–140	Plate heat exchanger	19–44	57–20	1–28
Jeurnink, Brinkman, and Stemerdink (1989)	Whole	85	Tubular heat exchanger	64	18	15
Jeurnink et al. (1989)	Whole	120	Tubular heat exchanger	43	49	3
Yoon & Lund (1994)	Whole	88	Plate heat exchanger	43	45	ND
Yoon & Lund (1994)	Whole	120	Plate heat exchanger	45	40	ND
Calvo & de Raffael (1995)	Whole	80	Plate heat exchanger	52	9	23
Jeurnink and De Kruif (1995)	Skim	85	Plate heat exchanger	44	45	–
Ma et al. (1998)	Whole	85	Tubular heat exchanger	20	4	45
Ma et al. (1998)	Skim	85	Tubular heat exchanger	64	13	–
Truong (2001)	Whole	110	Direct steam injection	39	8	39
Truong (2001)	Whole	105	Direct steam injection	63	20	3

[a] Values are reported on a dry matter basis.

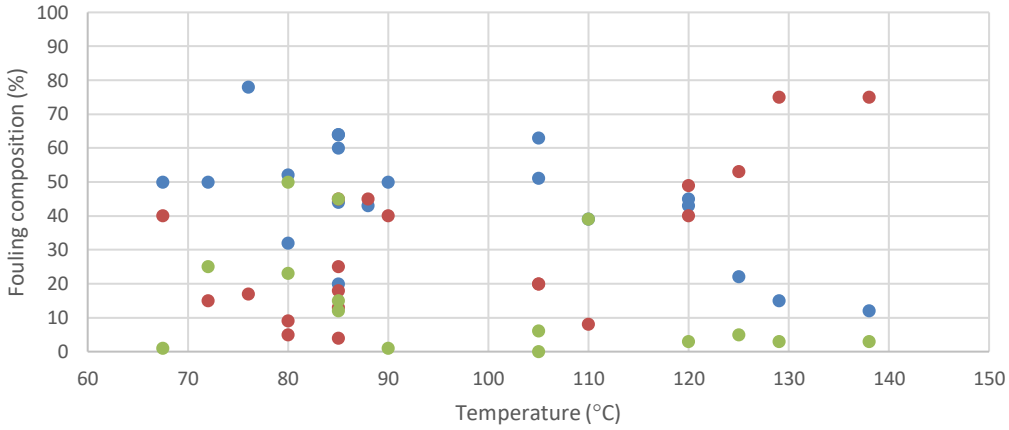

Fig. 1. Influence of temperature on the composition of fouling deposit from whole and skim milk: ●, protein; ●, fat; ●, minerals. Data from Table 1.

It is important to keep in mind that the type of deposit is not only determined by temperature, but also by other processing conditions such as heating rate, because deposition is driven by the local concentration of reactive components. De Jong, Waalewijn, and Van Der Linden (1994) observed that heating of milk by steam infusion at temperatures in the range 100–170 °C resulted in a type A rather than type B deposit, which can be explained by the fact that upon instantaneous heating, reactive serum proteins are present in the holder at UHT-temperature, which also deposit on the wall.

To understand the formation of fouling deposits during heat treatment of milk, and how fouling deposits are affected by various temperatures, it is important to not only consider changes in whey proteins, caseins and minerals individually, but also in conjunction with each other; i.e., how do changes in calcium phosphate solubility affect the denaturation of whey proteins and the stability of casein micelles, or how does whey protein denaturation affect casein micelle stability. For this purpose, heat-induced changes in milk proteins and milk salts are described in the Section 3. In subsequent sections, such changes will be put in the perspective of fouling.

3. Heat-induced changes in proteins and salts in milk

3.1. Heat-induced changes in milk salts

One of the unique features of milk is its ability to transfer the required amounts of calcium and phosphate to the neonate in a stable and bioavailable form, particularly considering the very low solubility of calcium phosphate. This is emphasised by the distribution of calcium and inorganic phosphorus (P_i) in milk. Of the ~30 mmol Ca and 20 mmol P_i per litre bovine milk, approximately two thirds of total Ca and half of total P_i is not found in solution but in the casein micelles, because the soluble (serum) phase is saturated with respect to the various calcium phosphate salts. Of the soluble calcium, more than half is complexed with citrate, and smaller quantities are associated with other anions, leaving ~2 mmol Ca L^{-1} as free Ca. Likewise, part of the 10 mmol L^{-1} inorganic phosphate in the serum phase of milk is also complexed with various cations (Holt, 1997; Nieuwenhuijse & Huppertz, 2021; Walstra, Wouters, & Geurts, 2005).

The so-called reverse solubility of calcium phosphates means that solubility decreases on increasing temperature and the concentration of Ca and P_i in the milk serum decreases (Pouliot, Boulet, & Paquin, 1989a,b). As a result, the excess Ca and P_i precipitates, but it is not fully clear in which form(s). One option is that the insolubilised Ca and Pi is stabilised in the casein micelles (Nieuwenhuijse & Huppertz, 2021; Walstra et al., 2005). A possibility for this could be the association with calcium phosphate nanoclusters present in casein micelles, but their growth would contradict the highly-defined nature and thermodynamic stability of calcium phosphate nanoclusters in casein micelles (Holt, 2004) and the nuclear magnetic resonance (NMR) results by Wahlgren, Dejmek, and Drakenberg (1990). Another option on the reduction of solubility of calcium phosphates on increasing temperature is the formation of (amorphous) precipitates of calcium phosphate, whose growth can be limited through the adsorption of caseins or SerP-containing casein-derived peptides on the surface (Holt, 2004; Holt & Van Kemenade, 1989; Nieuwenhuijse & Huppertz, 2021). In milk at room temperature, not all caseins are sequestered with the nanoclusters, and particularly the fractions of non-micellar casein could be essential in stabilisation of such precipitates. When temperature increases, more calcium phosphate precipitates (On-Nom, Grandison, & Lewis, 2010) so it is less probable that all is stabilised by the casein, which probably explains that type B deposit is mainly calcium and phosphate.

In casein-free systems, such as WPC, the absence of caseins for stabilisation of mineral deposits renders whey proteins the only stabilising constituents, thus increasing the chance of formation of calcium phosphate precipitates. Previous work by Schmidt, Both, Visser, Slangen, and Van Rooijen (1987) suggests that the whey proteins have little or no ability to stabilise calcium phosphate precipitates, but the casein-derived proteose peptone (PP) fractions PP5 and PP8fast, which consist of phosphorylated peptides and can also be present in whey, are potent stabilisers of calcium phosphate precipitates. PP content of whey depends on the plasmin activity in the milk before and during cheesemaking, typical concentration is 5–10% of total serum proteins; at neutral pH, a considerable part is present in the casein micelles, but at pH < 5 all is in the whey, so cheese whey contains less PP5 and -8-fast than acid whey (Walstra et al., 2005). In addition to calcium and phosphate, some magnesium and citrate may also be observed in these structures. Amorphous precipitates of calcium phosphate usually contain magnesium and citrate if these are in the salts solution, but upon ageing precipitates crystallise into pure calcium phosphates and the magnesium and/or citrate is lost (Panova, 2001). Mineral fouling is described further in section 4.2.

3.2. Heat-induced changes in whey proteins

As outlined previously, the whey proteins in milk are susceptible to heat-induced denaturation and subsequent aggregation. β-Lactoglobulin (β-LG) is crucial in this process because (i) it is the most abundant whey protein in bovine milk and most other mammalian milk types, and (ii) it contains a free thiol-group, which can interact with other proteins through −SH oxidation or −SH/−S−S− interchange reactions. At (near-)neutral pH values and moderate ionic strength, such as in milk, β-LG exists primarily in the form of dimers (Anema, 2014; Mulvihill & Donovan, 1987). When temperature is raised, the equilibrium shifts to monomers and further increases in temperature to >65 °C result in the unfolding of the β-LG molecules, thereby exposing the free −SH group at Cys^{121} (Mulvihill & Donovan, 1987). This is followed by an intramolecular −SH/−S−S− interchange reaction between Cys^{121} and Cys^{106}–Cys^{119}, leading to a Cys^{106}–Cys^{121} disulphide bridge and Cys^{119} as the free −SH group (Creamer et al., 2004; Lowe et al., 2004). This non-native monomer is typically referred to as the reactive monomer of β-LG and the basis of subsequent aggregation reactions of β-LG, including those involved in fouling. Aggregation reactions for the reactive monomer of β-LG, at conditions where weak ionic and hydrophobic forces allow sufficiently long contact between molecules and aggregates, include (Anema, 2014; Mulvihill & Donovan, 1987):

- Interactions with other β-LG molecules though −SH oxidation reactions (leading to a non-reactive dimer or multimer) or −SH/−S−S− interchange reactions (leading to a reactive dimer or multimer).
- Interactions with other whey proteins, e.g., α-lactalbumin) through −SH/−S−S−interchange reactions (leading to a reactive aggregate).
- Interactions with Cys-containing caseins (κ-casein or α_{S2}-casein) through −SH/−S−S−interchange reactions (leading to a reactive heterodimer or multimer).
- Interactions with Cys-containing proteins on the milk fat globule membrane (MFGM) through −SH/−S−S− interchange reactions.

As a result, at elevated temperature (e.g., >70 °C), milk will contain a mixture of (1) native whey proteins, (2) unfolded monomeric whey proteins, (3) whey protein aggregates, (4) casein/whey protein complexes, which may occur on the casein micelles, in the serum phase or on the surface of homogenised milk fat globules, and (5) aggregates of whey proteins and MFGM proteins.

In addition to temperature, the extent to which the different aggregation reactions occur depends on many factors, most notably protein composition, pH, ionic strength and composition (Anema, 2014; Mulvihill & Donovan, 1987). This is related to fact that aggregation reactions of the reactive β-LG monomer or reactive whey protein aggregates cannot be simply considered as chemical reactions in which a −S−S− bond is formed. Non-covalent interactions, i.e., hydrophobic and electrostatic interactions and hydrogen bonds, also play important roles in the aggregation process of whey proteins (Anema, 2014). Particularly the electrostatic interactions, which can be either attractive or repulsive, are strongly influenced by factors such as pH, ionic strength and mineral composition of the serum phase. A change in pH can affect the degree of protonation of amino acids with side groups capable of carrying charges. In the neutral pH range, particularly the protonation of the imidazole side chain of His (pKa ~6.0) is strongly affected by small changes in pH.

3.3. Heat-induced changes in caseins and casein micelles

In contrast to the whey proteins, caseins do not show significant reduction in secondary and tertiary structure on increasing temperature. Casein solutions, in general, are very heat-stable, with, e.g., sodium caseinate solutions requiring extremely long heating times at high temperature before coagulation occurs (Guo, Fox, Flynn, & Mahammad, 1989). However, caseins in milk are mainly in the form of casein micelles, which can become unstable during heat treatment at > 120 °C (Dumpler, Huppertz, & Kulozik, 2020; Huppertz, 2016).

Casein micelles can be described as association colloids stabilised sterically by the κ-casein-rich brush on the surface of the particles, with colloidal stability governed by brush height and brush density (De Kruif, 1999). Reducing brush density, e.g., by (partial) removal of the brush on renneting, destabilises the casein micelles, making them more susceptible to coagulation, with other micelles or with the wall of a heating unit. Collapse of the brush occurs on acidification, as a result of charge neutralisation, and also

makes the casein micelles susceptible to aggregation (De Kruif, 1999). Both removal and collapse of the κ-casein brush can occur during heating of milk and can result in the heat-induced destabilisation of casein micelles (Huppertz, 2016). Heat-induced reductions in milk pH are strong contributors to loss of solvency of the κ-casein brush, and it has been estimated that the pH of milk may decrease from 6.6 to 6.7 to as low as 5.5 on increasing temperature (no holding time) to 140 °C (Fox, 1981). This decrease in pH occurs because of heat-induced reductions in water pH and the formation of insoluble calcium phosphates, with the concomitant release of H^+ ions (Huppertz, 2016).

Partial brush removal during heating of milk can occur as a result of heat-induced dissociation of κ-casein at temperatures >60 °C, which leaves a (partially) depleted surface and can reduce the stability of casein micelles (Anema, 2021). pH is a major contributor to heat-induced κ-casein dissociation: the extent of heat-induced dissociation of κ-casein from casein micelles increases with increasing pH. Heat-induced dissociation of κ-casein is also more extensive in milk concentrated by evaporation, but not in milk concentrated by ultrafiltration (Anema, 1998, 2021; Anema & Klostermeyer, 1997; Anema, Creamer, & Singh, 1993). Addition of $CaCl_2$ to milk has been found to reduce heat-induced dissociation of κ-casein, whereas addition of phosphate salts has been found to increase heat-induced dissociation (Singh & Fox, 1987). In contrast to changes in the mineral composition of the serum phase, (moderate) changes in the calcium phosphate content of casein micelles do not influence heat-induced dissociation of κ-casein (Singh & Fox, 1987). In the absence of whey proteins, heat-induced dissociation of κ-casein still occurs (Anema & Li, 2000). The extent of heat-induced dissociation of κ-casein has been found to be the main determinant for the distribution of κ-casein/whey protein aggregates between the micellar and serum phases of milk (Anema, 2021).

The interactions between κ-casein and whey proteins on the casein micelle surface also affect the stability of casein micelles. In the pH region where acid-induced coagulation dominates, the interaction with whey proteins may make the micelles more susceptible to acid-induced coagulation, analogous to effects observed on acid-induced gelation in yoghurt manufacture (Huppertz, 2016). However, the interactions with whey proteins also provide increased brush height/density, as a result of which additional stability is gained. The stability of casein micelles to heat-induced coagulation is thus determined by a balance between the stability to acid-induced coagulation and κ-casein dissociation. In the pH range 6.0–7.0, the heat stability of milk to heat-induced coagulation is typically highest at its original pH. Below this pH, acid-induced coagulation is the predominant mechanism of destabilisation, whereas at higher pH, heat-induced dissociation of κ-casein from the micelle surface is the predominant mechanism of destabilisation (Dumpler et al., 2020; Huppertz, 2016).

4. Protein and mineral fouling during heat treatment of milk: a perspective based on heat-induced changes in proteins and salts

4.1. Protein fouling

4.1.1. Protein fouling at low temperature

From the previous sections, it is clear that fouling during dairy processing, particularly in heat exchangers, is strongly related to heat-induced changes in the minerals and proteins in milk and other liquid dairy streams. However, the first step of the fouling process, i.e., the interaction of proteins with the heating surface, occurs even at room temperature, although adhesion forces between the surface and whey proteins increase with increasing temperature (Goode, Bowen, Akhtar, Robbins, & Fryer, 2013). Adhesion of β-LG to the surface does not necessarily require (pre-) denaturation of the proteins; in fact, globular proteins, e.g., β-LG, unfold at the fluid-heat exchanger interface, creating a reactive surface layer. κ-Casein was also shown to adhere to the surface, but does not displace β-LG (Roscoe & Fuller, 1993). Adhesion to the surface occurs rapidly (typically time scale <1 min), but is influenced by the type of surface and coating (Karlsson, Wahlgren, & Trägårdh, 1996, 1998). In-short: fouling never starts on a clean metal surface.

4.1.2. Protein fouling at temperatures >50 °C

However, as outlined in Section 2, it is not the formation of the monolayer of proteins, but the further deposition of materials that can lead to reduced heat transfer or impaired flow that causes issues in processing. For milk processing, proteins play an important role in this process and are a main constituent in the deposits (Table 1 and Fig. 1). The protein composition of the deposits is related to the thermal stability of the proteins. At temperatures <110 °C, casein micelles in milk are stable to heat-induced destabilisation, so their absence in fouling deposits at these temperatures is not surprising. Whey proteins, however, are highly susceptible to heat-induced denaturation and aggregation in this temperature range, and their presence as the predominant protein fraction in the fouling deposit at temperatures <110 °C can be explained based here on in. The dominance of caseins as proteins in the fouling deposits of milk at higher temperatures is in line with (i) the casein:whey protein ratio in milk (80:20) and (ii) the fact this casein micelles become prone to instability on heating at these temperatures. However, a further factor to be considered here is whether by the time the sample reaches such high temperatures, much of the whey protein has already 'reacted' and is thus found in form of aggregates. This latter point is clearly highlighted by the results of Lalande, Tissier, and Corrieu (1984), who identified characterised fouling in 5 different sections of a heat exchanger for UHT treatment of milk:

- Section 1 (<70 °C): no fouling notable
- Section 2 (70–110 °C): type A fouling, the extent of which increased with temperature
- Section 3 (110–120 °C): decrease in fouling, minimum at 120 °C
- Section 4 (120–138 °C): type B fouling
- Section 5: (138–80 °C): limited amount of fouling

Similar effects with respect to fouling of milk during the different stages of UHT processing were observed by Robbins, Elliott, Fryer, Belmar, and Hasting (1999). These authors also investigated fouling of a 1% WPC35 solution, where they observed that protein fouling continued up to UHT temperatures, despite a ~2–3-fold lower whey protein content than in milk.

From the results of Lalande et al. (1984) it is apparent that the typical whey protein-dominated type A fouling occurs in section 2 (70–110 °C). The reduction in fouling in section 3 (110–120 °C) is indicative of the lack of reactive β-LG or other reactive particles because most of this material was either 'lost' in the fouling in section 2, or has reacted with other proteins/particles to form non-reactive aggregates. In cases where heating is very rapid, type A fouling may also be observed at higher temperatures. This was e.g., the case in heating experiments with steam injection, where type A fouling was observed at temperatures up to 170 °C (De Jong et al., 1994). The protein component of the type-B fouling in section 4 (120–138 °C) observed by Lalande et al. (1984) is based on the fact that caseins become unstable at this point and thus become subject to fouling.

Casein analysis in high-heat section fouling deposits typically suggest a (partial) depletion of κ-casein compared with the casein composition in milk (Tissier, Lalande, & Corrieu, 1984), thus suggesting the fouling of κ-casein-depleted micelles, which are indeed less stable to heat-induced coagulation. In contrast, elevated levels of κ-casein in the fouling deposit have been observed at lower temperature (e.g., 90–100 °C; Jeurnink & De Kruif, 1995). At these conditions, the (κ-casein-depleted) casein micelles remain stable but κ-casein-whey protein complexes in the serum phase can get included in the fouling layer.

4.1.3. Factors affecting protein fouling from milk and whey protein solutions

Of course, other factors which reduce the stability of casein micelles can also result in casein-dominant fouling at lower temperatures; e.g., a reduction in pH (Skudder, Brooker, Bonsey, & Alvarez-Guerrero, 1986), increase in concentration or the addition of salts with a destabilising effect, such as calcium chloride (Jeurnink & De Kruif, 1995). The same applies to the whey proteins, e.g., for WPI solutions, addition of calcium-binding salts was found to reduce fouling (Hebishy, Joubran, Murphy, & O'Mahony, 2019). Hence, given the different dependences of the stability of casein micelles and whey proteins on such factors, the rather clear distinction in fouling types for the different protein classes in milk observed on heat treatment of regular milk may not be observed in the case of modified milk types. Calcium removal, by treatment with a cation exchange resin, can also somewhat increase casein fouling in milk at 85 °C (Jeurnink & De Kruif, 1995); this can probably be related to more extensive heat-induced dissociation of κ-casein in Ca-depleted milk, thereby destabilising the micelles. This is in agreement with the lower proportion of κ-casein as a function of total casein in the fouling layer in the Ca-reduced milk (Jeurnink & De Kruif, 1995).

A further potential destabilising factor is the action of indigenous or bacterial proteases in milk. Bacterial proteases can hydrolyse κ-casein and hence reduce the stability of the micelle to heat-induced coagulation and increase fouling. Such reductions in stability are for instance observed when milk is (cold-)stored for several days prior to thermal processing, where the growth of psychrotrophic bacteria and activity of the concomitantly-produced proteases can result in notable reductions in stability of milk to thermal processing (De Jong, Waalewijn, & Van Der Linden, 1993; Jeurnink, 1991). The action of the indigenous milk proteinase plasmin can reduce the heat stability of casein micelles (Crudden, Afoufa-Bastien, Fox, Brisson, & Kelly, 2005), and hence increase the susceptibility to fouling, because of hydrolysis of caseins, to which κ-casein is 'anchored' on the casein micelles surface and hence result in the release of κ-casein from the micelle into the serum.

4.1.4. Whey protein fouling: mechanistic considerations

Mechanistically, protein fouling during heating of milk and whey protein products, such as WPC, has been described as a two-stage process, i.e., the formation of an initial (mono-)layer of proteins on the surface and the subsequent aggregation of additional protein onto this initial protein layer. As such, a scheme for protein fouling of milk and related products can be seen as an extension of common schemes for heat-induced protein interactions, which only considers the bulk of the product matrix. The extension to include is the protein layer on the surface as a further option for interaction for reactive protein particles, i.e., reactive β-LG monomers, reactive whey protein aggregates or unstable casein micelles. As such, the extent of fouling becomes a function of the number of reactive particles and their propensity to associate with the (initial or advanced) fouling layer already present on the surface.

Most mechanistic models for fouling of milk and related products describe it primarily in relation to denaturation of β-LG; i.e., the rate-limiting step is in the bulk, not at the surface (Blainpain-Avet et al., 2016; De Jong, Bouman, & Van Der Linden, 1992; De Jong et al., 1992, 1993; Lalande, Tissier, & Corrieu, 1985). In these models, the amount of reactive particles increases as a result of unfolding of whey proteins and due to the destabilisation of casein micelles as a result of κ-casein dissociation or acidification. The reactive β-LG monomers can subsequently undergo a number of interactions, resulting either in reactive aggregates that can participate in further interactions, or resulting in the formation of non-reactive aggregates. For instance, the addition of the –SH-oxidising agent KIO_3 reduces the amount of reactive β-LG molecules through oxidation of the free thiol groups, and thereby also reduces fouling (Skudder, Thomas, Pavey, & Perkin, 1981). Likewise, for camel whey proteins, where β-LG lacks a free thiol group, much lower fouling was also observed (Felfoul, Lopez, Gaucheron, Attia, & Ayadi, 2015a,b). In contrast, the addition of Cys to milk increases the amount of reactive β-LG molecules and also increases fouling (Skudder et al., 1981). Thiol reactivity is lower at lower pH, as a result of which the reactive β-LG may become 'less reactive'. However, this effect is countered by the effect of pH on protein charge.

Comparing the amount of denatured β-LG in the fouling layer with that in the milk after pasteurisation, Jeurnink et al. (1996a) suggested that (only) ~0.14% of total denatured β-LG had ended up in the fouling layer. Despite this seemingly low amount of denatured β-LG ending up in the fouling layer, Jeurnink et al. (1996a) considered there to be a highly preferential interaction of reactive β-LG with the fouling layer on the surface rather than with casein micelles or other particles in the bulk. At any moment during this heat treatment, 1 L of milk was in contact with 0.5 m^2 of stainless-steel surface, but 4000 m^2 of casein micelle surface; this suggests that the available surface for activated whey protein interacting with a casein micelle is ~4 orders of magnitude higher than the probability of an activated whey protein interacting with the protein layer on the stainless-steel surface (Jeurnink et al., 1996a). Hence, the fact that 0.14% of denatured β-LG interacts with the casein micelles suggests a preferential interaction with the fouling layer over interaction with the casein micelles. Despite the preferential interaction of β-LG with the fouling layer over interaction with casein micelles, it is important to keep in mind that only a fraction of collisions of activated monomers/aggregates results in interactions. For interaction of activated β-LG with the fouling layer, Jeurnink, Verheul, Stuart, and De Kruif (1996b) estimated a sticking probability of ~1:300; i.e., for every 300 collisions, 1 resulted in interaction. The overwhelming majority of β-LG does not get included in the fouling layer, probably because it is rendered unreactive before can interact with the fouling layer, e.g., through interactions with other proteins; after all, only a minor part of the proteins is ever close to the wall during heat-treatment.

Interactions of whey proteins with the fouling layer are influenced strongly by pH and mineral balance. The addition of calcium to WPC solutions has been repeatedly shown to increase fouling (Blanpain-Avet et al., 2012; Khaldi et al., 2015a,b). Likewise, at the same protein content and pH, WPI and pure β-LG show less fouling than whey (Visser & Jeurnink, 1997), which can again be attributed to the higher mineral content of the latter. In contrast, Christian, Changani, and Fryer (2002) reported that the addition of a combination of calcium chloride and sodium dihydrogen phosphate to a WPC solution reduced fouling. However, this could be related to the fact that pH, which is likely to change strongly on addition of these minerals, was not corrected and a pH change was thus the dominant factor. For a WPI solution, Visser and Jeurnink (1997) reported fouling rate to be at a maximum at pH ~6.5, and was ~2-fold lower

at pH 6.2 or pH 6.7. This clearly shows that even small changes in pH can already have a very large effect on fouling. It further indicates that fouling cannot be considered solely an effect of whey protein denaturation, since this maximum in fouling at pH 6.5 does not coincide with a maximum in denaturation at this pH. While the extent of fouling was strongly influenced by calcium, protein conformation in the fouling layer was not influenced by calcium content (Blanpain-Avet et al., 2016).

As is clear from the aforementioned calculations by Jeurnink et al. (1996a), the ratio of heating surface to the surface of other molecules/particles available for interaction is an important parameter. When the surface-to-volume ratio of the heat exchanger is high, chances of interaction of a reactive β-LG molecule with the fouling layer on the surface are higher. In many cases, the use of a holding tube in the pre-heating sections of heat exchangers in, e.g., UHT processing of milk is applied. Using this holding tube, also referred to as a stabilising tube, preferably with a low surface-to-volume ratio, controlled aggregation of reactive molecules/particles can be carried out to ensure that the number of reactive particles remaining in the subsequent sections is reduced. The interaction of whey proteins with casein micelles in this section can also benefit the stability of the casein micelles at later sections at higher temperatures, as is, e.g., apparent from the results of Prakash, Kravchuk, and Deeth (2015). Control of whey protein fouling essentially involves directing the process in such a way that the chance of interaction of reactive molecules/aggregates with the fouling layer is minimal. One key parameter in this respect is the number of reactive molecules/aggregates that are present.

4.1.5. Casein fouling: mechanistic considerations

As outlined earlier, inclusion of caseins in fouling deposits can also occur. At temperatures <100 °C, this appears to be predominantly κ-casein, and it is likely that this is in the form of complexes of κ-casein with denatured whey protein. In the high-heat section of UHT's, however, the casein fraction found in the deposit appear to be κ-casein depleted. This is in line with κ-casein-depleted casein micelles being less heat-stable (Huppertz, 2016). However, the causality of this link remains to be established. Heat coagulation time of milk at 140 °C typically far exceeds the times of UHT processing, particularly for milk at the natural pH of milk (i.e., >10 min versus <10 s). Even considering that the temperature near the wall will be several degrees higher than in the bulk, the typically reported ~3-fold increase in reaction rate for heat-induced coagulation of milk when increasing temperature by 10 °C does not bring the time-scale of this process within range of the holding times during UHT treatment. It could be argued, however, that the extent of instability considered in the heat coagulation time is too extensive, and would lead to near-instantaneous blockage of UHT systems rather than fouling. A less extreme form of destabilisation, i.e., the conditions at which 2% of total protein became sedimentable, was considered by Dumpler et al. (2018). For a slightly concentrated skim milk (12%, w/w, total solids), they estimated times of ~50, 30 and 10 s at 140, 145 and 150 °C for 2% of the protein to become sedimentable. Although these times are notably lower than the heat coagulation time, they are still be in excess of what would be considered representative for UHT processing of milk. Hence, a direct causal relation between heat-induced coagulation of casein micelles and fouling remains questionable, although extrapolating the results of Dumpler et al. (2018) to, e.g., 0.2% of sedimentable protein, which is still sufficient to form a fouling layer, but is not measurable experimentally, may provide sufficient argumentation.

An alternative consideration for the inclusion of caseins in fouling deposits could be due to their association of calcium phosphate precipitates. Considering, e.g., the fouling deposit found by Hagsten et al. (2016) on UHT treatment of skim milk at 137 °C for 8 s, with a ratio of (Ca + PO_4):protein of ~6.5:1.0. Tercinier, Ye, Anema, Singh, and Singh (2013) studied the absorption of sodium caseinate on hydroxyapatite particles and estimated a surface protein load of ~2.5 mg m^{-2} if sufficient protein was present. At the aforementioned (Ca + PO_4)/protein ratio of 6.5, this would entail 1 g of dry fouling deposit to contain ~130 mg of protein and 870 mg of Ca + PO_4, and thus with aforementioned surface load a surface area of ~60 m^2 g^{-1} Ca + PO_4; assuming spherical particles, thus would suggest particles sizes in the range of ~10 nm, which is notably smaller than what was observed microscopically by Hagsten et al. (2016). Assuming larger particles than sodium caseinate, e.g., micellar fragments, to absorb on to calcium phosphate precipitates would of course increase estimated particle size. However, for particles of, e.g., 1 μm, this would entail surface loads of ~250 mg m^{-2}, which would be close to entire casein micelles. Further research in the area of casein inclusion in fouling deposits is clearly warranted.

A final factor in this respect is that proteins that end up in the fouling layer in the beginning of UHT run are likely to be strongly degraded at the end, e.g., after 10 h. Howat and Wright (1936) observed almost complete dephosphorylation and significant hydrolysis of milk proteins after 5 h heating at 120 °C. This is in line with studies on later studies on heating caseinate solutions (Belec & Jenness, 1962a; Van Boekel, 1999) and skim milk (Belec & Jenness, 1962b) for prolonged times at temperatures >100 °C. Furthermore, extensive heat-induced hydrolysis of casein also occurs during prolonged heating at such temperatures (Hustinx, Singh, & Fox, 1997; Van Boekel, 1999). Thus, the material harvested from a UHT at the end of the run is only partially representative for the material that deposited.

4.2. Mineral fouling

Salts are the other main constituent of fouling deposits. For type A deposits, the protein:salt ratio of the deposits is ~2:1, whereas for type B deposits, it can exceed ~1:2. In both cases, calcium and phosphate are the main constituents of the mineral part of the fouling deposit, with smaller quantities of most other salt constituents present in the original liquid also found. Some salt constituents may be present as counterions of the charged side groups of amino acids in the proteins in the fouling material. However, even for the extremely highly mineralised casein micelles, calcium phosphate constitutes only ~5% of dry matter, the vast majority of which is not in the form of counterions but as calcium phosphate nanoclusters. This indicates that a considerable part of salt material in fouling deposits is in the form of actual salt deposits and not co-precipitates with proteins.

As outlined in Section 3.1, solubility of calcium phosphates decreases with increasing temperature and the insoluble calcium phosphates may subsequently form amorphous precipitates that may be stabilised by caseins or casein peptides. As with the proteins, for the minerals only a small proportion of the amount of minerals becoming insoluble ends up finding its way into to the fouling layer. Jeurnink et al. (1996a) estimated that on heating milk to 85 °C, ~950 mg of salts per L of milk would have become insoluble, whereas the amount of deposited salts at this temperature was ~2.3 mg per L of milk; hence this suggests that only ~0.2% of the insoluble minerals becomes part of the fouling deposit. This probably is only to be expected, given that only a small fraction of the salts is present in the laminar boundary layer, and that only part of this the salts present in the boundary layer deposit on the wall. Fouling of protein-free solutions, e.g., milk or whey permeate, gives an initial thin layer of less than 1 μm thickness and little structure

and particles formed in the bulk deposit on top of this initial thin layer (Andritsos, Yiantsios, & Karabelas, 2002).

However, as with the whey proteins described in section 4.1, considering the very fact that the total casein micelle surface area in milk is ~4 orders of magnitude higher than that of stainless steel, this still suggests a high preference of the insoluble minerals to the fouling layer. Part of this could be explained by the temperature difference between the bulk and the surface (ΔT), resulting in more extensive insolubilisation of minerals at the higher temperature closer to the wall. Obviously, this strongly depends on the ΔT, which may be as large as 20 °C or as small as 5 °C, and at the latter value the temperature difference is likely to be of little relevance. Observations that more mineral deposits are found in the heating section than in the holding section were taken by Jeurnink et al. (1996a) as an indication to support the influence of ΔT, as this would be high in the heating section and low in the holding section and are in agreement with the reports of Daufin et al. (1987). However, it is probably more important that at the final point of the heating section, when the maximum temperature is reached, minimum solubility is also reached and inclusion of minerals in the fouling layer becomes purely driven by the kinetics of transport of precipitated material to the surface, with no further driver to increase the amount of insoluble material. The surface properties also play a role in mineral fouling, as described later.

4.2.1. Mineral fouling in protein-free systems

Calcium phosphate deposits are found for both protein-free (e.g., milk- or whey permeate or simulated milk ultrafiltrate [SMUF]) and protein-containing systems (e.g., milk, whey or WPC). In protein-free systems, fouling was highest at relatively low temperature, about 50 °C, and less at higher temperatures (Andritsos et al., 2002). This is in-line with the continuous decrease in solubility with increasing temperature, starting from about 5 °C, and the decreasing fouling at higher temperature was explained by the more extensive bulk precipitation at these conditions. Also, calcium phosphate deposition has been found to be strongly pH dependent; however, this does not correlate directly with solubility. With increasing pH, the solubility of calcium phosphate decreases, as also observed by, e.g., increases in turbidity of the solutions. However, the amount of fouling deposit formed from these suspensions does not increase with pH, but rather shows a maximum around pH ~6.3–6.5, above which fouling again decreases (Andritsos et al., 2002; Morison & Tie, 2002). This has been attributed to bulk precipitation of calcium phosphates already occurring before heat treatment. For example, in the experiments by Andritsos at al. (2002) the salts solution was cold-stored at pH 6.1 and pH was increased by adding KOH shortly before heating, which results in supersaturation and bulk precipitation already before heating, and thus a reduced amount of calcium phosphate available for insolubilisation on heating. Hence, the amount of mineral fouling deposit formed cannot be directly correlated to solubility. Instead, it should probably be related to the loss in solubility on heating. Typically, milk and whey permeate and SMUF are only kinetically but not thermodynamically with respect to calcium phosphate at their natural pH and room temperature. When temperature is increased, solubility decreases, and the rate of formation of precipitates becomes faster. When the pH is reduced, the solubility of calcium phosphates increases so the system becomes unsaturated and the temperature to which the sample can be heated before saturation, and concomitant deposit formation occurs, increases. Hence, if pH of a dairy liquid is decreased to below the original pH, mineral fouling at a given temperature will decrease. However, if pH is increased to values above the natural pH, mineral fouling increases if pH increase is small, but decreases if pH increase is large, due to predominance of bulk precipitation. Additionally, the form of precipitates depends on pH (Schmidt et al., 1987), which may affect the adherence of particles to the wall, or to/in a membrane surface. The exact occurrence of the pH at which maximum mineral fouling occurs in e.g., whey or milk permeates is dependent on the mineral composition.

One key parameter in this respect is the citrate content. The Ca-chelating capacity of citrate ensures that the supersaturation of calcium phosphates is reduced. In SMUF to which no citrate was added, the pH at which maximum deposition occurs at considerably lower pH and more extensive deposition occurred, despite the fact that pH of the solution without citrate was considerably lower (5.7 rather than 6.3) (Andritsos et al., 2002; Rosmaninho & Melo, 2006a; Rosmaninho, Rocha, Rizzo, Müller-Steinhagen, & Melo, 2007a; Rosmaninho et al., 2007b). In addition to aforementioned reductions in pH, also with increasing pH above the pH at which maximum deposition was observed, considerable reductions in deposition can be achieved (Andritsos et al., 2002), because of bulk precipitation in solution. Hence, to minimise mineral fouling during heat treatment in protein-free systems, reducing the saturation levels of calcium phosphate can be applied. Likewise, actually increasing saturation levels and ensuring bulk precipitation of calcium phosphate before thermal processing can be applied.

Like protein fouling, mineral fouling is also affected by the surface properties of the stainless steel surface; surfaces with a lower electron donor capacity were found to have lower concentration of mineral deposits in protein-free systems (Rosmaninho & Melo, 2006b, 2007, 2008; Rosmaninho et al., 2007a,b).

4.2.2. Mineral fouling in protein-containing systems

Another important factor in mineral fouling is the presence of proteins; in fact, the role of proteins may be considered dominant in mineral fouling in, e.g., milk or whey. Different kinetics of protein fouling and mineral fouling (Foster, Britten, & Green, 1989; Foster & Green, 1990) suggest different drivers, but they cannot be considered as entirely separate entities, since proteins can both enhance and reduce mineral fouling. As outlined in Section 3.1, proteins may reduce the amount of calcium and phosphate that can foul as mineral deposits due to association of (part of) the calcium and phosphate with the casein micelles on heating. Likewise, the presence of caseins and whey proteins in the serum phase of milk can stabilise calcium phosphate precipitates that form on heating of milk and thus limit their growth and keep them in suspension, rather than allow their interaction with the fouling layer. Results from Daufin et al. (1987) show that deposition of calcium and phosphate start at low heating temperature, and earlier during heating at pasteurisation temperature for protein-free solutions of calcium phosphate than in the presence of cheese whey proteins and that calcium and phosphate co-precipitate with the whey proteins.

However, proteins can also enhance mineral fouling. Jeurnink (1995) observed that in serum protein-depleted skim milk, both total fouling and mineral fouling were considerably lower compared with in normal skim milk, whereas the ratio of Ca:protein increased slightly. This suggests that, in milk, the presence of whey proteins in the fouling layer is important for subsequent inclusion of minerals in the fouling layer. This was also confirmed by the results published by Morison and Tie (2002). With the very rapid coverage of the stainless-steel surface by proteins, it is apparent that inclusion of minerals in the fouling layer may be through either precipitation of minerals onto the proteins in the fouling layer, followed by subsequent growth of the precipitates, or through the interaction of protein-stabilised mineral precipitates with the proteins in the fouling layer. These mechanisms are line with microstructural observations showing the presence of particulate mineral precipitates in the protein layer

on the surface, but not directly on the surface, on heating of WPC (Jimenez et al., 2013). It appears that in WPC during heating at temperatures below the denaturation temperature of the whey proteins, native proteins and calcium phosphate particles form a mixed layer that may grow in time by deposition of additional proteins and calcium phosphate particles. Above the denaturation temperature aggregation of whey proteins becomes more important, and the composition of the fouling layer is more protein-dominant, with included calcium phosphate particles.

The type B fouling in the high-temperature section of UHT's is build-up from calcium phosphate granules of at least a few μm, largely surrounded by a protein network, but also partly sintered to each other (Hagsten et al., 2016). In this study, which characterised fouling after an industrially-relevant long running time of 15 h, Ca/P was found to be 1.5, and the material was crystalline β-$Ca_3(PO_4)_2$. This indicates that at these temperatures, stabilisation by casein micelles of the calcium phosphate that becomes insoluble upon increasing temperature is less effective, as discussed in section 3.1, and maybe also that part of the native micellar calcium phosphate is not stabilised anymore, possibly because casein that adheres in the fouling layer will be largely dephosphorylated after 15 h of processing. The finding that fouling was limited in the lower temperature part of the heater at 126 °C and extensive at 144 °C (Srichantra, Newstead, Paterson, & McCarthy, 2018) indicates that especially at high temperature the calcium phosphate is less stabilised by casein micelles.

4.3. Fat and lactose in heat-induced fouling deposits of milk

4.3.1. Lactose

Compared with proteins and minerals, the other main constituents of milk and whey, fat and lactose, have only a minor contribution to fouling. Lactose typically only occurs in fouling layer as a solute of the aqueous phase entrapped in the fouling matrix, or conjugated to proteins as a result of the Maillard reaction. Published studies do not demonstrate an effect of lactose on fouling of milk or whey (Morison & Tie, 2002), but two aspects are worthwhile considering:

- With increasing lactose content, the denaturation temperature of whey proteins also increases; this increase, which was found to be ~0.2 °C per % (m m^{-1}) for another disaccharide, sucrose, will ensure a reduced extent of fouling with increasing lactose content, but only if the time–temperature profile of the heater is such that only part of the whey proteins denature. Hence, on 2-fold concentration of milk, the denaturation temperature of whey proteins can increase by ~1 °C. In highly concentrated systems, it has been shown that whey protein denaturation during pasteurisation can be completely prevented if carbohydrate content is sufficiently high. Zhang, Lu, and Huang (2019) recently showed that adding 10% glucose, fructose or sucrose to a WPI solution notably reduced deposit formation on a fouling disk at 95 °C.
- In milk and whey, a lactose derivative called lactose-phosphate occurs naturally and may be produced by lactic acid bacteria (Lifran, 2007). This compound is well-known to be a potent inhibitor of the growth of lactose crystals as a growth terminator on the surface of the lactose crystals. However, the phosphate moiety of lactose phosphate also has the ability to interact with calcium or calcium phosphate deposits and could thus act as a growth inhibitor of calcium phosphate deposits forming in the bulk (Noeparvar & Morison, 2018) or in the fouling layer.

4.3.2. Fat

While lactose is only present in fouling layers at trace levels, fat can occur at considerably higher levels in fouling deposits from whole milk (up to 10% of dry matter in normal cases, but up to 50% in extreme cases; see Table 1). This suggests that inclusion of fat in fouling matrices is more than random entrapment and involves some specific interactions. The surface layer of the milk fat globules plays an important role here, just like in heat-induced coagulation of milk. Milk fat globules surrounded by the natural MFGM are in general quite stable to heat-induced coagulation, but will interact with serum proteins upon heating and thus also end-up in the fouling layer if the membrane proteins interact with serum proteins in the fouling layer.

More importantly, however, protein-stabilised milk fat globules in, e.g., homogenised milk are far less stable to heat-induced coagulation and are thus also likely to contribute to fouling (Srichantra, Newstead, McCarthy, & Paterson, 2006). In general, homogenisation reduces the heat stability of milk considerably. While this is often attributed to the increased milk protein surface area, the observed extent of the reduction in heat stability appears over-proportional to increase in surface area, when considering that the casein micelles are an order of magnitude smaller than the milk fat globules and even the extensive increase in fat globule surface on homogenisation thus only presents a small increase in total surface area. It is more reasonable to assume that the surface of the protein-covered milk fat globules is more prone to heat-induced coagulation. Casein micelles are known to spread over the fat globule interface, thereby reducing surface coverage by κ-casein; furthermore, β-LG which absorbs on the emulsion droplet interface unfolds and exposes its reactive −SH group. This makes the emulsion droplet interface more reactive and thus more prone to interaction with and incorporation in the fouling layer. Preheating homogenised milk prior to UHT treatment was found to increase fouling, regardless of whether this was fresh milk, reconstituted whole milk powder or recombined milk prepared from skim milk powder and anhydrous milk fat (Srichantra et al., 2006). Probably, this is due to (additional) dissociation of κ-casein during preheating, giving a further reduced coverage.

In addition to the influence of milk fat globules on fouling, the effect of free fatty acids (FFAs) on fouling has also been investigated. Al-Roubaie and Burton (1979) added different fatty acids to milk and observed that the addition of capric acid (C10:0) to milk, which was found to associate primarily with the casein micelles, reduced fouling considerably. This can be related to the association of capric acid with casein micelles resulting in improved stability to heat-coagulation. In contrast, addition of shorter chain fatty acids, i.e., butyric (C4:0), caproic (C6:0) and caprylic (C8:0) acids did not influence the amount of deposit formation. Likewise, lauric (C12:0), myristic (C14:0) and palmitic (C16:0) acid addition slightly increased deposit formation. Addition of stearic acid (C18:0) caused a notable increase in fouling (Al-Roubaie & Burton, 1979).

4.4. Influence of air on milk fouling

Very relevant for fouling at industrial conditions, the presence of air bubbles can also be a large destabilising factor, resulting in increased fouling. De-aeration of milk was found to reduce the extent of fouling considerably, i.e., by a factor ~20, during heating of skim milk in a lab-scale tubular heat exchanger at 85 °C (Jeurnink, 1995). It was suggested that during heating of milk, air bubbles may arise as a result of dissolved air and if these bubbles form on the heating surface, they can act as nuclei for deposit formation. The formation of air bubbles leads to the heating surface becoming dry,

with a concomitant increase in ΔT, resulting in evaporation of water from the air-liquid interface. Such evaporation can result in aggregation of protein as result of the combination of high temperature and high concentration, leading to deposit formation on the heating surface (Jeurnink et al., 1996a). Dissolved air content and ΔT can thus be major contributors to fouling. In addition to de-aeration, increased operating pressures limit the growth of air bubbles and thus reduce the propensity to fouling. Bennett (2007) studied the effect of pressure on fouling of whole milk at 90 °C and noted a decrease in fouling in a tubular heat exchanger with increasing pressure (30–80 kPa). Combinations of high dissolved oxygen and low operating pressure were also observed to increase fouling during UHT treatment, with decreasing the former or increasing the latter identified as suitable remedies (Lorin, 2018). A further factor influencing the effect of dissolved air on protein fouling is the wall shear stress; at low wall shear stress, air bubbles formed on the wall are not rapidly removed and thus increase fouling, whereas at high wall shear stress, air bubbles are rapidly removed (Jeurnink, 1995). From an industrial perspective, air inclusion should be limited under normal operating conditions but can occur with, e.g., improperly functioning pumps. In addition, risks are typically somewhat higher for when processes include a powder reconstitution step. However, de-aeration steps in the process and sufficiently high pressure are typically sufficient to counter effects of included air. In lab- and pilot plant-scale operations; however, risks of air inclusion affecting are notably larger.

5. Heat-induced fouling of milk and liquid dairy products: from mechanistic understanding to predictive models?

From the previous sections, it is clear that there is a broad basis of information reported on fouling of milk and other dairy fluids. Both the extent of fouling and the composition of the fouling layer are influenced by a wide variety of factors, both relating to product characteristics and processing parameters. In addition to studying these factors, attempts have been made to develop predictive models for fouling of milk, e.g., on how the fouling is distributed over the heat-exchanger, or on the temperature, or ΔT, dependency of fouling.

The reaction kinetics part of most of these models uses the denaturation and aggregation of β-LG only, and not the reactivity of other relevant components, which limits their use to pasteurisers. For pasteurisers, modern CFD methods allow quite correct predictions for fouling and heat transfer in the various heating sections (Sharma & Macchietto, 2021). Older models, e.g., the model reported by De Jong et al. (1992, 1993) are useful for tubular heaters, but less so for plate heat exchangers. These models can be applied for the pasteurisation of liquid milk products and but application to other products is more challenging and requires further expansion of models. For example, recombined milk products, infant formula products or high protein beverages in practice can show higher propensity to fouling, than would be predicted by aforementioned models.

For infant formula products, for instance, casein:whey protein ratio differs from that of milk and whey protein composition may also differ, when, e.g., α-La-enriched whey protein ingredients are used (Fenelon, Hickey, Buggy, McCarthy, & Murphy, 2019). These have notable effects on whey protein denaturation in these products (Buggy, McManus, Brodkorb, Hogan, & Fenelon, 2018; Halabi et al., 2020) and will also likely impact fouling. Likewise, salt composition in infant formula products also differs notably from milk. A further consideration is the presence of pre-denatured material in samples when powdered ingredients are used, where quite some whey protein may already be denatured, some still in reactive form (Fenelon et al., 2019). This provides an additional interaction point for native whey proteins on their denaturation and hence can be a strong contributor to the extent of fouling. In addition to infant formula, this also applies to recombined milk products and other dairy beverages (Srichantra et al., 2006, 2018). Also, prediction of fouling of products poorly correlates with reality when casein fouling or fouling of milk fat globules are the main contributors to product fouling. This may, e.g., be the case for calcium-fortified or reduced-pH milk products, where casein fouling can be extensive even at temperatures <100 °C, or high fat products, where fouling of milk fat globules can be extensive.

A further limitation of existing models for fouling is that they typically only consider temperatures up to ~100 °C. At higher temperatures, the contribution of whey proteins to fouling strongly diminishes and a deposit consisting primarily of minerals and caseins is found. The mineral fraction in this deposit again is predominantly the result of calcium phosphate precipitation. The inclusion of casein in this precipitate is primarily the result of heat-induced destabilisation of casein micelles due to a loss of stability, and, as such, strongly influenced by temperature, pH, minerals, solids content and pre-treatment to milk, as commonly established when studying heat coagulation time or temperature. Milk quality and seasonal effects could also be incorporated in such models. Furthermore, milk fat globules, which can represent a significant proportion of fouling are not included in fouling models and should be included.

6. Conclusions

This paper reviewed the state-of-the-art in relation to fouling of milk and other dairy products during thermal treatment. From this, it is clear that while single-constituent approaches may be interesting for fundamental studies, product-based approaches are required to understand fouling during commercial manufacture. This is because it is particularly the interactions between the constituents of milk and dairy products that determines the rate at which fouling occurs. This requires understanding of the physico-chemical properties and interactions in the starting product and how these are affected by heating. Particularly for heating processes which consist of multiple heating stages, as applied, e.g., during UHT processing dynamic approaches are required where changes during each step of the process step should be considered sequentially. Qualitative predictors for fouling behaviour of products can also be highly beneficial, but require further experimental exploration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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