Fouling of Heat Exchangers in the Dairy Industry

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A general overview is given of the main factors in the fouling of processing equipment used for heating dairy fluids. The data collected indicate that the primary step in fouling is the adsorption of a monolayer of proteins onto the wall of the heating equipment at room temperature. Real fouling (i.e., the formation of macroscopic layers of foulants), however, is caused by particle formation in the bulk of the liquid being processed. These particles include both whey protein aggregates and calcium phosphate particles. Their formation is heat induced, and the deposition takes place through diffusion toward the heating surface. Only very high flow rates are able to prevent their deposition and subsequent sticking. To better control the process of fouling, special attention is given to the parameters affecting the formation of both types of particles and how their formation can be retarded or prohibited, including the role of calcium sequestrants, pH, preheating, and flow rate herewith. © Elsevier Science Inc., 1997

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INTRODUCTION

The dairy industry has been confronted with "fouling" of metal surfaces since plate heat exchangers (PHEs) were introduced for pasteurizing and sterilizing milk in the 1930s. For most of the heat exchangers used, cleaning of the equipment at least once per day is common practice. Recently, the fouling at relatively low temperatures of other materials, such as rubber teat cups in milking machines [1] and membranes in separation processes, also have been found to limit processing time and (intermediate) cleaning has become necessary as well [2]. The costs of cleaning are very high. In France alone, the total cost of fouling in the dairy industry in 1991 was estimated at 1000 million French francs [3]. The fact that, during cleaning, a process has to be temporarily halted makes many dairy operations rather cumbersome. A large number of investigations to better understand the process of fouling have already been performed with success by Delplace et al. [4], Fryer et al. [5], de Jong et al. [6], Jeurnink [7], Lalande et al. [8], and many others, but a real breakthrough—the complete control of fouling—has not been reached. This is mainly due to the complexity of the dairy systems under consideration and a lack of understanding of the mechanism of fouling.

The objective of this study is to review the existing knowledge in the area of fouling, to establish the basic factors involved hereby, and to present an up-to-date view on the processes taking place.

GENERAL ASPECTS OF THE FOULING OF HEAT EXCHANGERS

Fouling Hypotheses

Apart from the various factors that are known to play a role in fouling, such as the pH, the temperature, and the corresponding heat denaturation of whey proteins, only a few general hypotheses exist with regard to the overall mechanism of fouling. According to Fryer et al. [5], fouling is a bulk-controlled homogeneous reaction process rather than a mass transfer or a surface reaction process. In their view, fouling is the consequence of aggregation of milk components within the bulk of the fluid upon heating. Fouling is seen as at least a two-step process, starting with an induction period when protein adsorption takes place with only calcium ions involved [9], followed by a fouling period when protein aggregates are deposited. On the other hand, Toyoda et al. [10] have developed a fouling model in which they make the assumption that, for each protein present, mass transfer takes place between the bulk and the thermal boundary layer, but only aggregated proteins can adhere to the wall in such a way that the deposition is proportional to the concentration of aggregated protein in the thermal boundary layer. The validity of this model was demonstrated by the fit with experimental data. Experimental data of Delplace et al. [4], obtained by heating a whey protein isolate solution

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in a plate heat exchanger at 95°C, confirm Toyoda's hypothesis.

Our own results [11], however, indicate that, upon heating a whey protein solution, respectively the milk salt system, only particles formed in the bulk, both for protein and for mineral particles, lead to bulk fouling. This is illustrated by the data presented in Fig. 1. As can be seen, the deposition of calcium phosphate particles onto a chromium oxide surface starts at the temperature where the solution becomes turbid. The deposition reaches a maximum as soon as the solution becomes visually turbid—that is, when the particles have grown to such a size that they are entrained with the flow and the deposition drops to zero. For whey proteins, we found a similar effect. Although adsorption of whey proteins already occurs at room temperature, bulk fouling starts when visual protein aggregates in the solution are formed, either by heating at 80°C and pH = 6.8 (Fig. 2) or upon acidification to pH = 5.3 at the same temperature (Fig. 3). In other words, we support the hypothesis of Belmar-Beiny [9] that fouling is controlled by reactions taking place in the bulk, through the formation of particles that are subsequently deposited onto the heating surface.

Composition of Deposits

According to Burton [12], the deposit formed between 80°C and 105°C on the surface of a heat exchanger is a white voluminous precipitate, which is predominantly proteinaceous (type A). The major protein present in the deposit is β-lactoglobulin (β-LG), and the remaining mineral part is composed of calcium and phosphate. The overall composition of a type A deposit is 50–60% protein, 30–50% minerals, and 4–8% fat. Type B, the high-temperature deposit found at temperatures exceeding 100°C, according to Burton, has a hard, granular structure and is grey in color. This deposit consists of 70–80% minerals, 15–20% protein, and 4–8% fat. The total amount of the deposit diminishes by increasing the temperature further. The proteins present in this case are mainly β-casein (50%) and α-S1 casein (27%).

A more detailed composition analysis of PHE fouling is given by Bouman et al. [13]. These authors found fouling to take place only on the raw milk side, not on the pasteurized side of the PHE. The composition of the deposit in the regenerative section of the raw milk side, where the temperature reaches a level of 57°C, was found after 12 h of processing to be (in mg/plate): 30 for P, 51 for Ca, and 52 for protein. In the heater section, where a temperature of 70°C is maintained, the values after the same time of processing are respectively 36, 95, and 133 mg/plate. In other words, the weight ratio of calcium phosphate to protein in the deposit is up to a factor of 30 larger than that in milk.

Preheating of milk at 80–85°C for 5–10 min alters the composition of the deposit totally. The amount and the nature of the deposit reduces then to a predominantly mineral one as a result of the predenaturation of the whey proteins.

What Comes First: Proteins or Minerals?

After the typical composition of fouling deposits has been established, the next question raised in the literature on the process of fouling of milk is, What comes first: protein deposition or calcium phosphate deposition? (given that both components are found in fouling deposits [Table 1]). In this connection, one can also pose the question whether the formation of insoluble calcium phosphate particles in solution is essential for the subsequent deposition of whey proteins. Or, is whey protein denaturation, and subsequent aggregation either with itself or with the casein micelles present in milk, induced by calcium ions, the cause of the deposition of whey protein, respectively, of whey protein-casein aggregates? It is clear that whey protein denaturation and aggregation, respectively, and calcium phosphate particle formation are two totally different processes that follow different kinetics. In other

![Figure 1. The rate of deposition of milk salts onto chromium oxide as a function of temperature (squares) and the corresponding change in turbidity (circles) [11].](image-url)
words, the build up of minerals and proteins in a foulant layer may proceed independently. Our own results obtained by depositing whey proteins and calcium phosphate particles upon heating a whey protein isolate dissolved in a milk salt buffer as illustrated in Fig. 4 confirm this. As can be seen from the scanning electron micrograph, the mineral particles are embedded in a proteinaceous matrix [14]. Belmar-Beiny and Fryer [9], on the other hand, have shown that, for a whey protein concentrate (WPC) solution, the initial layer of the deposit in the first seconds of processing consists mainly of protein. We have confirmed this: whey proteins from an aqueous solution of a whey protein isolate (BIPRO), pure β-LG or cheese whey, adsorb onto metal surfaces already at room temperature, limited to a monolayer on chromium oxide (Fig. 5). In other words, the first layer will always be proteinaceous. But this first layer adsorbed at room temperature will not lead to a further build up of protein layers, because bulk fouling starts only at temperatures above 72°C, provided calcium ions (25 to 40 ppm) are present (Fig. 6). In the case of stainless steel, whey protein adsorption leads to a further demetallizing of its already demetallized chromium oxide surface. This adsorbed layer may be more prone to sequential protein and calcium phosphate binding than is the original stainless steel surface, covered with chromium oxide. In general, we observe in all our deposition studies an underlying layer of individual protein molecules, seen as a colored layer of a given thickness (e.g., 150 nm for a blue layer), on top of which big aggregates with an open network structure as in a protein gel are found, both at the isoelectric point (pH = 5.13) and at pH = 6.8. At the latter pH, this layer of protein is observed only when calcium ions necessary for the protein to aggregate in the bulk are present (Figs. 2 and 7), because we could not detect by weighing a measurable quantity of deposited whey proteins in their absence.

<table>
<thead>
<tr>
<th>Component</th>
<th>Skim Milk</th>
<th>Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total protein</td>
<td>37.2</td>
<td>44.4</td>
</tr>
<tr>
<td>Whey protein</td>
<td>6.1</td>
<td>33.3</td>
</tr>
<tr>
<td>Casein</td>
<td>31.1</td>
<td>11.1</td>
</tr>
<tr>
<td>Minerals</td>
<td>7.4</td>
<td>45.0</td>
</tr>
<tr>
<td>Calcium</td>
<td>1.32</td>
<td>15.7</td>
</tr>
<tr>
<td>Phosphate</td>
<td>2.04</td>
<td>23.0</td>
</tr>
<tr>
<td>Lactose</td>
<td>52.6</td>
<td>0.02</td>
</tr>
</tbody>
</table>

to the time required for the formation of insoluble calcium phosphate complexes or whey protein aggregates in solution before further adsorption can take place. In a plate heat exchanger where an intense mixing of the fluid takes place, this time may be much shorter or almost instantaneous, so here fouling starts immediately in contrast with a tubular heat exchanger where the mixing is less intense.

Seasonal Variations

Because the degree of fouling of processing equipment, according to Burton [12] and Grandison [16], is found to be seasonal dependent, one may raise the question whether there is a link between the degree of fouling and the pH, the calcium level, the heat stability of the milk being processed. Does the number of free SH-groups play a role hereby, as it does on the heat stability?

Tissier [17] has already indicated that autumn milk systematically causes the least fouling. He was able to correlate his results with the milk quality expressed in terms of NH₃ level. Grandison [16], on the other hand, on the basis of a larger number of data collected throughout the year, could establish a correlation only between the degree of fouling and the level of Mg in milk. Addition of Mg to milk immediately before processing indeed gave rise to a vast reduction in running time, as did calcium addition. He concluded that the addition, without enough time for equilibration, may upset the delicate equilibrium between calcium and phosphate ions and the inhibitors present in milk preventing their precipitation. The added Mg should act in this case as a promoter of calcium phosphate crosslinking of casein [18], rather than as an inhibitor for precipitation. In our research [19], a correlation between heat stability of milk and the degree of fouling could be established. Hence seasonal variations in fouling are at least partly due to the changes in heat stability in the course of the year.
Figure 6. Deposition of whey proteins (0.25% BIPRO) at pH = 6.5 as a function of temperature in the presence of calcium (25 ppm).

Summary

The major components in fouling are calcium phosphate ions and whey proteins. Both components form insoluble aggregates in the bulk of the liquid as a result of their heat sensitivity. In the initial phase of fouling, however, individual whey protein molecules are adsorbed onto the stainless steel heating surface. After the metal surface has been totally covered by a protein monolayer, the deposition of aggregates formed in the bulk, both as calcium phosphate and as whey protein particles, will start. The speed of their formation determines the lag time before fouling begins. All factors affecting the instability of these aggregates, such as the pH, the level of calcium ions, and those responsible for the heat stability in milk, will promote fouling.

WHEY PROTEIN DENATURATION AND PARTICLE FORMATION

Introduction

As heretofore discussed, fouling is controlled by the formation of calcium phosphate and whey protein particles in the bulk of the fluid processed. To better understand the process of fouling, insight into the process of formation of these particles may help us to unravel the mechanism of fouling. In the next two sections, therefore, we will analyze in more detail the processes taking place in this context and how these processes can be affected so as to minimize fouling.

The Proteins of Milk

As shown in Table 1, the proteins in milk can be divided into two fractions: the caseins and the whey proteins. The difference between these two fractions is that the caseins are heat insensitive and precipitate upon acidification, whereas the whey proteins in their native form are heat sensitive and do not precipitate at their isoelectric pH. As far as the whey proteins are concerned, it is generally accepted that a direct link exists between fouling and the heat denaturation of these proteins when dairy fluids are processed at temperatures above 70°C; that is, under conditions where the whey proteins undergo irreversible changes (e.g., start to unfold, expose their free SH-groups until they become insoluble, and form aggregates or a gel). It is clear that a closer look at these proteins and...
their heat sensitivity may help us to understand the process of fouling in more depth. The role of the caseins in fouling is less clear. Their presence in a fouling deposit under pasteurization conditions is only minor (see Table 1) and may be a consequence of the heat-induced interaction with the major whey protein component, β-LG, which has an optimum at about 90°C [20]. The fraction of casein in deposits, however, increases with temperature and is particularly pronounced at temperatures above 100°C, as Burton has shown [12].

The Major Whey Proteins

The two major proteins in the whey fraction of milk are β-LG and α-lactalbumin (α-LA). Both proteins are of a globular nature and sensitive to heat. β-Lactoglobulin is the dominant protein, and so the emphasis in fouling studies is on the behavior of this protein because this protein is also more heat sensitive than is α-LA. In this review, we will therefore limit ourselves to the properties and the behavior of β-LG.

There are two major genetic variants of β-LG in western cattle, variant A and variant B, with a slight difference in amino acid composition and in thermal behavior. β-LG-B, the dominant variant used in model studies, contains 162 amino acid residues and has a molecular weight of 18,277 [21]. Of the five cysteine residues present, each having one SH-group, four are linked together and form a cystine, or S-S, bridge. At room temperature, the remaining free SH-group is buried inside the three-dimensional structure of the protein (Fig. 8) [22].

pH Effects on β-LG

Native β-LG in aqueous solution undergoes a series of associations depending on the pH, as shown in Fig. 9 [23].

At pH < 2.0 and room temperature, β-LG is monomeric owing to strong electrostatic repulsive forces [24]. Upon heating in aqueous solution, initially compact irregular particles, 0.2 μm in diameter, are formed. These particles then fuse together into aggregates 0.5–1 μm in size, linked together into chains less than 0.3 μm long [25]. No S–S bridges can be formed at this pH, because the SH-mediated SS-exchange reaction is inhibited. Fouling at this pH will be limited owing to the strong electrostatic repulsion between the molecules themselves and with regard to stainless steel, which has an isoelectric pH of about 4.0 [26].

At pH = 4.65 β-LG, close to its isoelectric point (pH = 5.13) [21], is octameric at room temperature [23]. Upon heating, the protein starts to aggregate and ultimately precipitates. Fouling will be severe at this pH because no electrostatic barrier against deposition is present (see Fig. 3).

In the pH range of 5.5–6.5, β-LG dissolved in distilled water is present as a dimer. The dimensions of the dplet are: 17.9 Å (1.79 nm) for the radius of the two composing monomers and 69.3 Å for the length of the particle (see Fig. 9). Upon heating, this dimer dissociates into a monomer at 323 K (50°C) [27]. At temperatures above 333 K (60°C), the buried SH-group is exposed to the solution by the unfolding of the protein and becomes reactive. When heating is prolonged, aggregation and particle growth sets in, according to neutron scattering initially to

Figure 8. Tertiary structure of β-lactoglobulin, according to Papiz et al. [22].
particles of a size between 8 and 10 nm (M. Verheul, personal communication, 1994) and according to light scattering at 90° in up to 20 mM of NaCl to a constant particle size of 25–30 nm. Ultimately, in 100 mM of NaCl, densely aggregated protein particles, 0.2–0.3 μm in diameter, are formed. These particles are linked together into a chainlike fibrous structure when acid precipitated or at neutral pH into a turbid gel when the concentration is sufficiently high [25]. The formation of these particles is of direct relevance for the fouling behavior of whey protein-containing systems, owing to their accumulation at the heating surface.

Above pH = 6.5, only limited coagulation occurs when β-LG is heat denatured (e.g., after 10 min at 80°C); at neutral pH and low protein concentrations, the solution even remains crystal clear. The change in thermal behavior at pH = 6.5, according to de Wit [28], is due to an increased thiol activity. At pH = 7.5, the Tanford et al. [29] or N-R transition (Dunnill and Green, Ref. 30) leads to the monomeric form upon raising the pH to 8.0, and aggregation upon heating is inhibited.

Because most dairy fluids are processed in the pH range between 6.0 and 7.0, knowledge of the temperature effect on the properties of β-LG in this range is of direct relevance for understanding the various processes taking place upon heating these fluids. In particular, this is the case for the aggregation and gelation behavior of this protein because of the accumulation of protein aggregates formed in the bulk solution at the heating surface whereby the critical (bulk) gelation concentration may be reached (see the section on gel formation).

At high pHs (8 and above), when the formation of large aggregates is prohibited, fouling of whey proteins accordingly will be substantially diminished. The same could be achieved by an alkaline shock (10 min at pH = 11), which inhibits the formation of large aggregates and enhances denaturation through irreversible exposure of two carboxyl groups [31].

**Heat Denaturation of β-LG at Neutral pH**

Heat denaturation of β-LG at pH values that are of interest for fouling (between pH 6 and pH 7) is a multistage process. When the thermal differential scanning calorimetry (DSC) data are plotted in an Arrhenius plot, the denaturation of β-LG, according to Anema and McKenna [32], can be described as a two-stage consecutive process, comprising unfolding of the molecule followed by aggregation. The first step is reversible and is considered to follow first-order reaction kinetics; the second step, the aggregation step, in the absence or at low levels of salt, is an irreversible process, following second-order kinetics. Overall, however, Anema and McKenna describe the denaturation of β-LG with a reaction order of 1.5.

According to Roefs and de Kruif [33], in analogy with a radical polymerization reaction, in the temperature range of 60–70°C, the heat denaturation of native β-LG in water in the absence of electrolytes can indeed be described by 1.5-order polymerization reaction based on an intermolecular exchange between intramolecular disulfide bonds and exposed reactive thiol groups until a polymer of finite length is obtained by a so-called termination reaction when two SH-groups are finding each other. A schematic representation of Roefs’s model is given in Fig. 10 [34]. In the initiation phase of the process after the dissociation of the dimer (BB) into the monomer (B) at 50°C, an activated form (B*) of β-LG is formed at 65°C. This activated form can react with a nonactivated monomer under the formation of an activated dimer (B’*). This dimer in the propagation phase of the denaturation process can react with a nonactivated monomer under the formation of an activated dimer (B’*). This dimer in the propagation phase of the denaturation process can react with a nonactivated monomer (B), forming a trimer (B’*), and so forth, until, in the termination phase, two activated complexes (B’ and B’*) find each other, whereby B (B_rev) is formed and the aggregation process comes to an end. The particle size attained in this way is 25 nm. When a sufficient amount of protein is available, these particles form a transparent gel. At high salt levels, secondary aggregation takes place, according to
Jeurnink et al. [35], leading to a further growth in particle size, whereby the solution becomes turbid and ultimately a gel is formed when the protein level is high enough.

A typical concentration-time profile of native (B), activated (B*), and aggregated (B_i) β-LG, calculated for a β-Lactoglobulin concentration of 0.25% at a temperature of 85°C, is given in Fig. 11. The figure illustrates that there is only a limited lifetime (e.g., of less than 3 s) for each B_i to be present in the solution.

No information is yet available on the effect of calcium ions on the heat denaturation model of Roefs and on the formation of B*. In general, one can say that, in the presence of calcium ions, the aggregation will be enhanced, as illustrated schematically in Fig. 12 [36].

**Denaturation Temperature**

The peak temperature, T_D, in a DSC plot of β-LG is greatly affected by the pH and decreases from 82.5°C (pH = 4.0) to 72.5°C (pH = 8.0) [37]. At pH = 6.75 and 8.0, T_D passes through a minimum at a concentration of 25 mg/ml; whereas, at low pH, T_D is almost concentration independent. T_D is further strongly dependent on the scanning rate; the lower the rate, the lower its magnitude. As we observed, a maximum in deposition at 78°C at pH = 6.5 (Fig. 6), a parallel between T_D and the degree of fouling, is suggested. Hence, the effect of protein concentration and scanning rate on T_D may explain the effect of native protein level and heating rate on fouling.

**Gel Formation and the Role of Sodium and Calcium Ions and pH**

Unfolding and gelation of β-LG is pH dependent. At 2 < pH < 4 and at 6.2 < pH < 8.2 when the protein concentration is sufficiently high (8%), calcium ions are absent, and the ionic strength is kept to a minimum, a fine-stranded gel is formed upon heating β-LG above
65°C. In the latter pH region, the gel is transparent and elastic, comprising particles of 20 nm in diameter. The protein polymer particles forming the gel network are aggregated through an intramolecular exchange reaction between intramolecular disulfide bonds and exposed relative thiol (SH) groups. In the region 5.8 < pH < 6.3, a flexible particle gel that spreads like a cream is formed, with particles of 0.2 μm in diameter.

The conditions for gel formation upon heating a whey protein solution under static conditions are highly relevant for the processes taking place at the surface of a heat exchanger, where, owing to the accumulation of material with time, the gelation concentration may be reached, not attainable for the solution itself. This is illustrated in the scanning electron micrograph (Fig. 7) of a whey protein deposit formed upon heating in the absence of calcium ions. At a solution concentration of 4%—that is, approximately half the concentration required for the bulk gelation of whey proteins—a surface gel is formed, its structure resembling the structure of a typical fine-stranded whey protein gel. This is a result of the accumulation of proteins at the interface until the gelation concentration is reached. The same effect is observed in the presence of calcium ions (Fig. 2), albeit that the gel structure is no longer that of a fine-stranded gel but, in this situation, resembles a particle gel. Because a gel structure resembling the structure of a whey protein gel attained under static conditions is observed in both cases, the gelation of

Figure 11. Typical concentration-time curves of native (B), unfolded (B*), and aggregated (Bn) β-LG based on computer calculations, using the Roefs–Kruif model for the denaturation of β-lactoglobulin.

Figure 12. Schematic representation of the dissociation, unfolding, and aggregation of β-LG and the consequences for deposition in the absence of calcium phosphate.
the protein at the interface is apparently not affected by the shear forces operating in the bulk solution.

**Binding of Small Molecules**

β-LG can interact independently of pH with small molecules, such as retinol and fatty acids, at a hydrophobic pocket around Trp19. When β-LG is isolated from whey without denaturing, it contains one molecule of bound fatty acid per molecule of its dimeric form [38]. The presence of these substances has a marked effect on the thermal properties of this protein: the increase in the maximum peak temperature of β-LG A in a DSC diagram increases by 7 °C for palmitic acid and by 2 °C for retinol [39]. The denaturation of β-LG at 85°C is further strongly affected by sugars: the thermal turnover is remarkably inhibited by increasing the lactose concentration, and the thermal stability is enhanced in their presence [40]. WPCs (10% protein) with a high lactose content already give high viscosities at a low degree of denaturation of β-LG. In other words, fouling results obtained with a model solution of β-LG (e.g., when delipidated and free of lactose) may not be directly translated into practical systems, as a result of the interference with the other components present in cheese whey, as shown, for example, in Fig. 5.

**Interaction with Other Proteins**

β-LG isoelectric point (IEP) = 5.2 and lactoferrin, LF (IEP = 8) strongly interact upon heating at neutral pH through their opposite charge. A 100% binding occurs at a ratio of 1:1. The interaction is weaker in salt solutions [41].

β-LG interacts with κ-casein, through S–S bridging, either at the surface of a casein micelle (at pH < 6.5) or in solution at pH > 6.8 [20]. In the latter case, κ-casein surface-depleted casein micelles are formed, lacking the stabilizing activity of the protein in question and hence prone to aggregation (e.g., by calcium ions). Above pH = 7.0, the increased pH leads to an enhanced stability and, because the free calcium activity has been decreased, the depleted micelles become stable again.

Maximum gel strength for WPC-casein mixtures is obtained at a 10% protein level when the casein content is 30%, indicating the ability of casein to interact as an active agent in the heat-induced whey protein gel structure. Hence, the deposition and fouling of whey proteins in complex dairy fluids may be affected by the other components present, which makes an understanding of the process of fouling rather complicated (Fig. 13).

**Summary**

β-LG, the major whey protein, plays a dominating role in fouling through its heat sensitivity. Its thermal properties and behavior are strongly dependent on pH and the presence of other components such as calcium ions, lactose, and casein. Upon heating at neutral pH, the molecule initially unfolds and exposes its free thiol group. This free thiol group makes the molecule reactive toward other β-LG molecules, both in the nonreactive and in the reactive state. As a result of this reactivity, the protein will form complexes in the form of aggregates, ultimately leading to gelation at the heating surface, provided the protein concentration is sufficiently high, as a result of accumulation of proteinaceous material upon adsorption.

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**WHEY PROTEIN ADSORPTION AND FOULING**

**Introduction**

With the various changes that β-LG can undergo upon heating having been established, it is interesting to see what the consequences of these changes are for adsorption and fouling of a metal heating surface. We have already indicated that the pH of the solution, the presence of calcium ions, and the heat denaturation temperature, $T_D$, have an effect on the deposition of β-LG and the subsequent possibility of surface gelation at the heating surface. The deposition of β-LG on a metal surface is a complex process involving several steps, such as adsorption, desorption, and aggregation. The stability of the adsorbed layer and the subsequent fouling of the heating surface are influenced by the presence of other components, such as calcium ions and lactose, which can affect the thermal properties and behavior of β-LG.

**Figure 13.** Schematic representation of the deposition of whey proteins in presence of calcium phosphate and casein micelles; MCP, micellar calcium phosphate.
interface due to the accumulation of proteinaceous material, but the precise mechanisms behind these parameters still have to be presented and discussed.

Adsorption of β-LG at Room Temperature

At pH = 7.0 and 26°C, β-LG adsorbs onto a metal surface (Pt) as a monolayer through binding of its carboxyl groups [35] to a platinum-surface OH-group under decarboxylation. According to Liedberg et al. [43], the binding of the carboxyl groups of β-LG to a gold surface proceeds under the formation of an ester bond. Both studies indicate that the initial binding of β-LG to a metal is through a chemical linkage. The amount adsorbed onto the platinum surface equals 1.8 mg/m², which is similar to the value for stainless steel (1.5–1.6 mg/m²) [44] but lower than that for monomeric hexagonally closely packed hard spheres (2.8 mg/m²) and end-on adsorption (3.3 mg/m²) [45].

As shown in Fig. 5, we also found monolayer adsorption of whey proteins onto chromium oxide [35], albeit to a lesser extent for the pure component and its large-scale isolated equivalent (BIPRO). Probably, under the conditions measured, the adsorbed β-LG molecules repel each other owing to their negative charge, which is shielded by the calcium ions present in cheese whey, leading to a much larger packing density.

Elofsson et al. [46] have shown that indeed no S–S bridges take part in the initial adsorption of β-LG onto chromium oxide, because the addition of an SH-group blocking agent N-ethylmaleimide (NEM) has no effect on the formation of the first monolayer.

Arnebrant et al. [47] further demonstrated that, at 25°C in a phosphate buffer, bilayer formation of β-LG on a chromium surface occurs, the first layer being irreversibly adsorbed onto the metal surface and the second layer desorbing upon rinsing. This bilayer is regarded as a two-dimensional gel phase.

About the structural changes taking place upon adsorption at a solid interface not much is known. β-LG at an oil–water interface undergoes limited structural changes compared with the changes taking place when the protein is heated in solution. Our scanning electron micrographs of the initially adsorbed β-LG layers (Fig. 7) show a very regular structure of identical, closely packed spheres, suggesting that the protein is not really altered when adsorbed.

The consequences of these results are clear. Native β-LG adsors onto metal surfaces already at room temperature as a homogeneous layer of individual molecules, resembling a two-dimensional gel. This implies that any (metal) surface in contact with whey proteins will be covered with a (monolayer of β-LG). In other words, proteins will always come first, because calcium phosphate particles are formed only at elevated temperatures. The formation of this initial protein layer may also be related to the observed lag time in fouling. Only when the heating surface is covered with a monolayer of protein may further protein adsorption take place, as illustrated schematically in the bottom half of Fig. 12.

Multilayer Adsorption of β-LG

Multilayer adsorption starts as soon as the temperature of the solution reaches 65°C and initial particle aggregation in the bulk solution begins. The free SH-groups, which become exposed at this temperature and which are responsible for bulk aggregation, do seem to play a role in this secondary surface binding, because blocking of the only free SH-group of β-LG by NEM, according to Elofsson et al. [46], prevents further adsorption onto the already at-room-temperature present monolayer of β-LG on the chromium oxide surface. In the absence of calcium ions, the initial aggregation of β-LG in solution is limited, with no bulk fouling and the formation of only a limited number of protein layers visible through their interference colors, as we have noticed on stainless steel. The interference colors, ranging from blue to green/yellow, point to a layer thickness of the order of a few hundred nanometers. Scanning electron micrographs (Fig. 7) show that these color layers, the deposit of whey proteins upon heating (in the absence of calcium ions), mainly consist of spherical aggregates of 40–60 nm in diameter [14], nicely packed in a homogeneous layer. If the temperature is raised to 80°C, a systematic buildup of individual layers of spherical protein aggregates on top of one another takes place. At higher temperatures, when the aggregation of whey proteins proceeds to such an extent that very large aggregates of 0.5 μm in diameter are formed, as in the case in which calcium ions are present (Fig. 2), the deposit becomes irregular until such a thick layer is formed that fouling starts to decrease again through the entrainment of these aggregates with the liquid flow. This size aspect also explains why whey proteins aggregated with casein micelles (see Fig. 13) are less prone to fouling.

The role of the free SH-, or thiol, groups in fouling, as suggested from the adsorption measurements by Elofsson et al. [46] in comparing native and NEM-blocked β-LG, becomes further apparent when considering the fact that the temperature not only has an effect on β-LG aggregation and subsequent adsorption, but also has an effect on the rate of adsorption. As can be seen from the data plotted in Fig. 14, the rate of adsorption of β-LG from BIPRO on chromium oxide as a function of holding time (i.e., the time the protein solution is kept at the given temperature before reaching the chromium oxide surface) shows a maximum if the holding time is varied. The maximum appeared at very short holding times. At 90°C, a similar maximum may have been present at even shorter holding times, but these shorter times could not be achieved experimentally. It is interesting to note that this maximum is predicted by the theory of Roefs and de Kruijf [34] for the kinetics of the heat-induced aggregation of β-LG, as the computer calculations by Jeurnink et al. [36] given in Fig. 15 for the relation between the concentration of B* and the holding time at temperatures between 70°C and 95°C show. In other words, dF/dt, the rate of adsorption of β-LG on chromium oxide, and hence the rate of fouling, seems to be proportional to [B*], the concentration of activated protein molecules, of which the thiol group plays a key role. As a consequence, all measures to minimize [B*] or dF/dt will reduce fouling. A typical example can be illustrated on the basis of the results presented in Fig. 16. As can be seen in Fig. 16, the rate of adsorption of β-LG onto chromium oxide shows a maximum at pH = 6.5, suggesting that, to minimize fouling, the pH of (cheese) whey (the normal pH of this system is 6.5) should be either reduced or raised. A possible explanation for the pH optimum is that, at low pH, the reactiv-
ity of the free SH-groups at 85°C is suppressed; whereas, at high pH, electrostatic repulsion starts to interfere with the aggregation process, leading to the same result. However, there is a limit to the reduction in pH because fouling starts to increase when the pH approaches the isoelectric pH of the protein.

**Bulk Fouling and the Role of Calcium Ions**

The difficulties that we had in obtaining a bulk deposit of whey proteins [14], as one observes in practice, led to an analysis of the role of calcium ions with regard to protein deposition following the observations of Delsing and Hiddink [48] that fouling is minimum in the absence of these ions. As a result, we observed that bulk deposition of whey proteins (ex BIPRO) onto stainless steel occurred only when 25–40 ppm calcium was added to the protein solution. According to Xiong [49], calcium ions indeed promote the bulk aggregation of whey proteins and hence fouling. A maximum in adsorption is found at 78°C (Fig. 6); that is, when the aggregation in the bulk through the presence of calcium ions has progressed to such a particle size that the aggregates are entrained with the flow. The role of particle formation in the bulk with respect to fouling was also observed when the pH of a whey protein–containing system was lowered to pH 5.1, the isoelectric point of β-LG, resulting in a sharp increase in fouling of whey proteins [50].

From this summary, one can conclude that, with respect to whey protein fouling, heat-, acid-, or calcium ion–induced particle aggregation seems to play a determining role. In this connection, it is not only the degree of unfolding or the reactivity of the whey proteins through the exposure of thiol groups as such that matters, but also the particle size, in view of the forces generated by the flow.

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**Figure 14.** The rate of deposition of β-LG from BIPRO onto chromium oxide as a function of holding time at various heating temperatures [36].

**Figure 15.** Computer simulations of [B+] as a function of the holding time [36].
Deposition and Fouling of Whey Proteins in Practice

For casein-free systems, it has been observed that the higher the (native) whey protein level, the spongier the deposit and the more lactose, when present, will be entrapped. A maximum in fouling mass is reached at 25% total solids (TS) for a given whey protein concentrate [51]. At higher concentrations, the deposits become so voluminous that all extra material deposited will be entrained with the fluid. These results suggest that whey protein fouling proceeds in the same way as whey protein gel formation, albeit only at the heating interface, where owing to the accumulation of material as a result of diffusion, the concentration exceeds the gelation concentration.

On the other hand, when the level of native whey proteins is reduced (e.g., by preheating or by interaction with the casein micelles in milk) whey protein fouling will be limited to a great extent. Depending on the pH, β-Lactoglobulin will be deposited onto these micelles through a linkage with the κ-casein present on the micellar surface (pH = 6.5) or β-LG will react with the free nonmicellar κ-casein in the serum (pH = 7.0) [20]. As a result, the reactivity of β-LG toward other surfaces will be diminished and may even be prohibited. However, whey proteins in the presence of casein, may still play a role in fouling (e.g., as a bridging agent between the casein micelles and the heating surface or as such when present in excess with respect to the level of casein, as illustrated in Fig. 13).

Summary

The process of whey protein denaturation resulting in aggregation and ultimately gelation is controlled by a range of parameters, including pH, calcium concentration, and temperature. The determining factor in bulk fouling is found to be the formation of activated aggregates in a limited size range in the bulk of the liquid and the subsequent deposition. Knowledge of whey protein particle formation therefore seems crucial in understanding and controlling fouling.

A compilation of the various phases of the process of protein deposition on the basis of the foregoing survey is given in Figs. 12 and 13. At room temperature and neutral pH, individual molecules of native β-LG in dimer form (B2) adsorb onto stainless steel (step 1). Upon heating to approximately 50°C, the dimer dissociates into two monomers (step 2), which are adsorbed onto the heating surface (step 3). Above 65°C, the only free SH-group of β-LG is exposed (B*; step 4) and able to bind to the already adsorbed molecules—for example, through SH/SS interchange (step 5a) or to κ-casein at the casein micelle surface (step 5b) through an S–S bridge (Fig. 13). Only in the presence of calcium ions (step 6) do large aggregates of β-LG (B*) form, leading to bulk deposition (step 7). Heating at temperatures above 85°C leads to bulk aggregation (step 8), whereby the particle size becomes so large that the aggregates are entrained with the flow and deposition no longer occurs.

In presence of casein micelles (Fig. 15), the activated molecule of β-LG (B*), formed at temperatures above 65°C, may also react through a heat-induced interaction with κ-casein (step 5b) at the casein micelle surface. The so-formed particles may be subsequently bound to the surface through mediation of the attached whey protein molecules (step 9).

MINERAL PARTICLE FORMATION AND FOULING

Introduction

The second major contribution to fouling in milk processing at elevated temperatures is related to the presence of calcium and phosphate ions. Mineral fouling is due to the inverse solubility of calcium phosphate salts with temperature. The precise crystalline form and the amount of the
mineral deposited depends on the components present in milk and the severity of heating.

Because calcium phosphate particles—the mineral deposits are always particulate in nature—play such an important role in the process of fouling, it is relevant to see under which conditions these particles are formed and how the process of particle formation is affected by the other components present in milk or by various additives. This knowledge may help us in finding options and conditions for reducing the degree of fouling in the processing of milk and other dairy fluids. The formation of insoluble calcium phosphate particles in general (depending on the type of complex formed) leads to a lowering of the pH, as in

\[ \text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{CaHPO}_4 \downarrow + \text{H}^+ \]

**Calcium Phosphate in Milk**

In milk, the calcium and phosphate ions in the serum phase (9.5 mM and 11.2 mM, respectively) are on the verge of precipitation; the remaining part (20.6 mM and 9.7 mM, respectively), is bound to the casein micelle in the form of a colloidal, noncrystalline, calcium/Mg phosphate-citrate complex. For the complicated way in which these inorganic constituents link the individual casein micelles together, the reader is referred to the work of van Dijk [52] and Holt [53] for their in-depth account of the way in which calcium and phosphate ions are possibly bound to the various casein molecules in the casein micelle.

Complexes with citrate and proteose peptone prevent the noncasein-bound calcium ions in the serum phase of milk from precipitation [54]. In other circulating body fluids that are supersaturated with respect to calcium precipitation and ultimate hydroxy apatite (HAP) formation (saliva, plasma), this role is played by pyrophosphates (Na_4P_2O_7) or, in saliva, by M-statherin, a proline-rich phosphopeptide [55]. In this respect, it is interesting to note that both citrate and pyrophosphate addition to milk from precipitation [54]. In other circulating body fluids that are supersaturated with respect to calcium precipitation and ultimate hydroxy apatite (HAP) formation (saliva, plasma), this role is played by pyrophosphates (Na_4P_2O_7) or, in saliva, by M-statherin, a proline-rich phosphopeptide [55]. In this respect, it is interesting to note that both citrate and pyrophosphate addition to milk have been found to reduce fouling. Other inhibitors that were found to prevent calcium phosphate from precipitating are poly-aspartate, poly-glutamate, and ethylenediamine tetraacetic acid (EDTA) [56].

Upon heating of milk, part of the soluble calcium will become insoluble owing to the inverse solubility product of calcium phosphate salts with temperature and will precipitate as a calcium phosphate salt. This precipitate may be formed in solution as such or it may associate with the already present casein micellar calcium phosphate (MCP) or with the \( \beta\)-LG aggregates in the serum phase or with both (see Fig. 13). With time, the precipitate will ultimately form a deposit on the stainless steel wall of the processing equipment. At temperatures below 100°C, the precipitate may redissolve again upon prolonged low (room) temperature storage, as long as no HAP has been formed [20]. This typical example of crystallization fouling [57] involving nucleation and diffusional and removal phenomena is too complex (i.e., too many processes are operating at the same time) to enable mathematical modeling.

**Mineral Composition of Deposits**

Analysis of deposits has shown that the calcium phosphate deposited onto a PHE is a mixture of dicalcium phosphate dihydrate (DCPD) (\( \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \)) and octacalcium phosphate (OCP) \( [\text{Ca}_8\text{H}_2(\text{PO}_4)_6\cdot 5\text{H}_2\text{O}] \) which at prolonged heating is eventually transferred to the least soluble calcium phosphate complex, hydroxy apatite \( [\text{Ca}_10(\text{OH})(\text{PO}_4)_6] \), having a Ca:P ratio of 1.6 [58].

Mineral deposits were found by Schraml and Kessler [51] to have a Ca:P ratio of 1.5 containing citrate, the more citrate, the lower the pH. Apparently, not all calcium phosphate was transferred to HAP.

At relatively low temperatures (e.g., upon pasteurization of milk), the deposits are richer in proteins; at high temperatures, as in ultra high temperature (UHT) processing, the deposits are richer in calcium phosphate salts. The overall level of minerals in both cases is substantially higher than in the starting fluid—for example milk (see Table 1). In the former case (pasteurization), it is suggested that the calcium phosphate is associated with the whey protein particles and to a certain extent to the casein micelles; in the latter case, the proteins are entrapped in the calcium phosphate matrix (see Fig. 13).

Scanning electron micrographs of a pure mineral deposit (ex SMUF (simulated milk ultrafiltrate)) show a matrix of calcium phosphate particles with a “house of cards” structure (Fig. 17). In the presence of whey proteins, such a structure can no longer be formed, and the deposit appears to consist of individual calcium phosphate particles embedded in a protein matrix (Fig. 4).

Bowman et al. [13], on the basis of scanning electron micrographs, found that calcium phosphate deposits consisted of more or less spherical particles ranging in size from about 0.2 to 2 \( \mu m \), suggesting an amorphous structure, which may have transferred to the more crystalline structure of hydroxy apatite. The question remains how the other components in milk are affecting and determining the ultimate crystalline habitat of the calcium phosphate in the deposit.

**Milk Dialysate / SMUF**

To better understand the processes taking place during the heating of dairy fluids, it is interesting to see what

![Figure 17. Scanning electron micrograph of a SMUF deposit.](image-url)
happens to the milk salt system when it is heated as such. The heating of milk dialysate containing salts and lactose only (respectively its synthetic equivalent devoid of lactose, SMUF), above 40°C in the pH range 6–7 causes the precipitation of calcium phosphate as OCP \([\text{Ca}_8\text{H}_2(PO_4)_6.5\text{H}_2\text{O}]\) owing to the negative thermal coefficient of its solubility product; upon cooling, the OCP redissolves again. The higher the pH of the solution, the lower the temperature of transition.

The heating of SMUF to 60°C results in the precipitation of 40% of the calcium and 25% of the phosphate; at 90°C, these percentages are 60% and 30%, respectively, whereby, in the latter case, the pH drops with 0.64 units [59]. At the pH of milk (6.7), the thermodynamically stable, microcrystalline HAP \([\text{Ca}_3(\text{PO}_4)_2\cdot\text{OH}]\), initiated by a heterogeneous nucleation step, is formed when the heating temperature is sufficiently high. The formation of this spongy material is preceded by a precursor phase, depending on the pH of the system. At pH = 6.7, the precursor will be OCP, which is spherical in nature; whereas, at pH 5–6, it is either the structureless amorphous calcium phosphate, ACP \([\text{Ca}_3(\text{PO}_4)_2\cdot\text{H}_2\text{O}]\) or brushite DCPD = \(\text{CaHPO}_4\cdot2\text{H}_2\text{O}\), which has a typical thin platelet crystalline structure [60].

**Factors Affecting the Crystalline Structure of Calcium Phosphate**

The process of ACP-OCP-HAP formation in moderate supersaturated calcium phosphate solutions [61] upon heating is strongly dependent on the overall composition of the system and is affected by various additives.

\[
\text{soluble calcium and phosphate} \rightleftharpoons \text{ACP} \rightleftharpoons \text{OCP} \rightleftharpoons \text{HAP} \rightleftharpoons \text{DCPD}
\]

For example, pyrophosphate and Mg enhance the formation of ACP, whereas citrate and poly-L-glutamate always inhibit its formation [62]. However, when ACP has been formed, these ions stabilize ACP against redissolution or alteration into other crystal modifications.

The conversion of ACP into HAP through OCP upon heating (see scheme) is inhibited by Mg ions when the Mg:Ca ratio equals 0.2, and crystalline DCPD is formed instead. When low levels of Mg ions or when citrate ions are present, the crystal growth of OCP and hence the formation of HAP is retarded, with the structure of DCPD crystals being affected [63].

HAP precipitation can also be retarded by the addition of EDTA, α-LA, β-LG, small levels of casein at pH = 6.7, and Mg ions. Precipitation can be accelerated by poly-L-glutamic acid [64].

HAP aggregation is inhibited by citrate and pyrophosphate ions [65]. When HAP aggregates have formed, however, their dissolution is retarded by the adsorption of α- or β- or κ-casein [66]. The more phosphosorines per molecule present, the stronger the binding of these caseins. κ-casein has a positive effect on HAP formation. In presence of the other caseins (e.g., α- or β-casein), the precursor phase (OCP) is stabilized and the formation of HAP is prohibited.

All these effects together may explain why there is such a large variation in fouling between different milks and between milk and whey—for example, as a consequence of the natural variation in Mg and citrate levels or of the presence of casein.

**Conclusions**

From the preceding review on calcium phosphate particle formation in milk and in SMUF and the factors affecting the crystalline structure of calcium phosphate, it is clear that the process of calcium phosphate particle formation during fouling is a very subtle one, whereby the pH, the temperature, and the other components present play a crucial role. A schematic representation of the various options is given in Fig. 13: calcium and phosphate ions may form calcium phosphate particles (step 10) or bind to the micellar calcium phosphate in the casein micelles (step 11). The calcium phosphate particles may deposit directly onto the stainless steel heating surface (step 12) or indirectly (step 14) after binding to whey protein aggregates (step 13).

The observed effect of pyrophosphate, citrate, and Mg both on fouling and on the crystalline habitat of calcium phosphate suggests a link between the two parameters. Hence, more in-depth knowledge on calcium phosphate particle formation and how this formation can be affected by specific additives or by altering the processing conditions may help to control the process of fouling. As yet, the complexity of the milk system at this stage does not permit a more quantitative relation. Such a relation, however, may be a clue to solving the problem of mineral fouling.

**PROCESSING AND OTHER FACTORS AFFECTING FOULING**

**The Role of Processing**

A great deal of attention has been paid in the literature to the role of processing conditions on fouling, in particular because this is one of the few options that can be altered at liberty without legal constraints within the limits of the definition of pasteurization, sterilization, and so forth. Typical factors that play roles in this area are the temperature difference between the heating surface and the fluid to be heated [67]; the flow regime, including the Reynolds number [68]; and the level of turbulence. Because these aspects are treated in great detail in the paper by Changani et al. in this issue [69], we will only briefly touch upon them in our contribution.

**Dissolved Gas**

Fouling is severely enhanced if \(\text{CO}_2\) is used to acidify milk [70] or through gas bubble formation when milk is heated and dissolved air is released at temperatures above 40°C. Burton [71] suggested that air in milk encourages deposit formation only if it is separated as bubbles at the heating surface. Thom [72] reported that air bubbles are nuclei for the formation of a deposit. When these bubbles are generated at the heating surface at local irregularities, they become stabilized by casein micelles at their (gas–liquid) interface. As long as the bubbles remain small, they will not be entrained by the flow and will continue to stick to the heating surface. Their presence may lead to local overheating of the heating surface, ultimately resulting in
the collapse of the adhering bubbles in question and the additional "deposition" of the stabilizing casein micelles, accumulated at the gas–liquid interface, onto the heating surface, as Jeurnink has shown [73]. On the basis of this knowledge, to minimize fouling, either degassing a dairy fluid to be heated before processing is recommended or processing under a back pressure, for example, 10^5 Pa (1 bar) to keep the dissolved air in the fluid. If degassing is not possible, one could apply a high flow velocity to entrain the particles from the wall.

The Role of the Heating Surface (Stainless Steel)

Apart from the whey proteins and calcium phosphate—the two major components in dairy fluids responsible for fouling—the surface to which these foulants are adhering also has an effect on the degree of fouling. As yet, attempts to minimize fouling by coating the stainless steel surface with Teflon and polysiloxane [74], for example, have not been successful on an industrial scale.

Factors that affect fouling of a stainless steel surface include:
1. the presence of a chromium oxide or passive layer, 2–4 nm thick [75], that inhibits corrosion and further oxidation;
2. the surface charge, or zeta potential, which depends on the cleaning treatment and on the industrial finishing conditions [75];
3. the surface energy or degree of hydrophobicity [76];
4. the surface microstructure—for example, roughness and other irregularities;
5. the presence of active sites—for example, positively and negatively charged metal atoms [42];
6. residual proteins [77] and other contaminants from previous processing operations—for example, detergent molecules, rust particles, and so forth; and
7. the type of steel or metal used.

Not much is known about the precise role of each of these factors on fouling. In membrane fouling and in fouling of milking machine components where lower processing temperatures are applied, similar parameters play a role; in particular, the surface charge and surface energy of the polymer have been found to be important parameters [1].

The Role of Fat

Although fat is present in milk and milk-based products and is found in fouling deposits, its level in the latter is too low to be of importance in the processes that affect fouling. Dalgleish [78] has shown that, upon heating whole milk, the whey proteins associate with the fat globule membrane constituents. Hence, the mechanism by which the fat globules are entrapped in the whey protein matrix may be through its whey protein covered surface.

Milk Preheating, Reconstitution of Milk from Milk Powder, and Prolonged Cold Storage of Milk

Two processing operations, preheating and reconstitution, lead to a substantial reduction in fouling partly because of the denaturation of whey proteins [73], whereas, in the prolonged cold storage of raw milk, the opposite takes place, owing to the action of proteolytic enzymes ex psychrotrophic bacteria. The increase in fouling upon storage of milk for 10 days at 5°C was the result of additional protein deposition [79]. As a result of these observations, to minimize fouling, one keeps T as low and ΔT as small as possible and the flow velocity as high as possible, and preferably one degasses the fluid before heating.

CONCLUSIONS

Fouling of metal surfaces upon heating dairy fluids such as milk is a severe problem in the dairy industry, causing loss of processing time, cleaning costs, and effluent problems due to intermittent cleaning.

The major components in fouling deposits are the heat-sensitive whey proteins and the heat-induced precipitation of calcium phosphate salts. Important parameters are the pH, the temperature, the presence of calcium ions and casein molecules, the surface characteristics of the equipment used, and the flow regime.

As soon as a protein-containing solution comes in contact with a metal surface even at room temperature, adsorption will take place. The adsorption itself will not lead to fouling; it only modifies the surface. The precise mechanism by which the protein is initially bound is not known, although there are indications of a chemical linkage. Nor is it known whether the protein changes its conformation or there is an orientation effect or both.

The protein-modified surface, however, may be the basis for the further attachment of particles of colloidal dimensions, generated in the bulk of the solution upon heating. Because it takes time to form these particles, a lag time in fouling is observed. The particles that seem to be attached to the demetalized surface first are primarily mineral in composition and form the backbone of the fouling layer, into which the proteins are entrapped.

Because particle formation is affected by parameters in milk that are seasonal (and lactation) dependent (e.g., pH and calcium level), the degree of fouling may vary from day to day.

A summary of the general trends observed in fouling is given in Table 2. A schematic representation of the processes taking place during deposition when whey proteins, calcium phosphate, and casein micelles are heated is presented in Figs. 12 and 13.

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