Engineering and Chemical Factors Associated with Fouling and Cleaning in Milk Processing

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The problem of fouling from food fluids is very severe, leading to the need for rapid and effective cleaning. Fouling of the process plant happens as a result of complex processes that occur when a fluid is heated: protein and minerals are both deposited on the surface. This review describes research into both the engineering and the chemical factors that lead to deposition. Fouling can be modeled by using data for the thermal behavior of \(\beta\)-lactoglobulin, coupled with models for the flows and temperatures of the process plant. The rate of cleaning depends on both the deposit present and the type of chemical treatment used. © Elsevier Science Inc., 1997

Keywords: food processing, heat transfer, milk, fouling, \(\beta\)-lactoglobulin, denaturation, aggregation, plate heat exchanger

FOOD FOULING

Thermal food processing is carried out to lower the concentration of harmful species, such as bacteria or their spores. In addition, heating deactivates enzymes that would otherwise cause quality losses. Thermal treatment of milk is the basis for a very large industry in which maintaining hygiene is vital. The milk system is thermally unstable; consequently, solid fouling deposit forms rapidly on the inner surfaces of the milk processing plant during both pasteurization and ultra-high-temperature (UHT) processes (Table 1). As well as causing an increased pressure drop and resistance to heat transfer, fouling deposit offers places where microbial growth can occur.

Fouling in the food industry is more severe than in other industries. In the petrochemical industry, cleaning is usually carried out yearly or less [2], whereas daily cleaning is often needed in food plants. Optimizing cleaning cycles is thus much more important to the food industry than to the process industries. Frequent cleaning of the plant is necessary, usually using complex and expensive cleaning-in-place (CIP) techniques, which have been developed empirically [3]. Two types of CIP treatment are found in milk processing [4]:

1. Two-stage cleaning, using alkali, commonly sodium hydroxide, and an acid wash of nitric or phosphoric acid. In the United Kingdom, alkali is used first.
2. Single-stage cleaning, using formulated detergents containing wetting and other surface agents as well as chelating compounds.

Selecting the correct cleaning strategy requires an understanding of fouling. For example, it has been suggested that, because whey deposits have a greater mineral content than do milk deposits, it may be better to reverse the cleaning stages, using acid and then alkali [5]. Two-stage cleaning is complex and may not achieve a clean surface [4, 6]. Single-stage methods decrease cleaning times but require more expensive chemicals, although Pritchard et al. [7] suggest that they reduce total costs by more economical use of chemicals, down time, wash water, and labor. Food processing generally uses equipment such as plate heat exchangers; however, fluids that foul heavily need expensive systems such as scraped-surface heat exchangers [8]. Fouling thus directly affects the economics of the process, in addition to cleaning costs. Additional costs can arise owing to the problem of disposal of cleaning chemical or effluent; this is becoming increasingly important.

In engineering practice, fouling is accounted for by including a fouling resistance, \(R_F\), in the equation relating the clean overall heat transfer coefficient, \(U_0\), to that after fouling, \(U\):

\[
\frac{1}{U} = \frac{1}{U_0} + R_F. \tag{1}
\]

For a uniform deposit of thickness \(x\) and thermal conductivity \(\lambda\), \(R_F = x/\lambda\); the product \(R_FU_0\) thus has the form of a Biot number, \(Bi\). The change in pressure drop can be represented in terms of the relation between the clean
pressure drop, \( \Delta P_0 \), and that after fouling, \( \Delta P \)—for example, as the dimensionless ratio:

\[
\frac{\Delta P - \Delta P_0}{\Delta P_0}.
\]

Fouling is a transient process; the exchanger starts clean and becomes fouled. There may be an induction period during which conditions do not change significantly, followed by a fouling period during which the heat transfer coefficient decreases and the pressure drop increases. In the limit pressure drop can become very high, owing to blockage of the equipment: such blockage can occur very rapidly. Figure 1 shows ways in which the fouling resistance may change; in food processing, falling rate or linear fouling is usual.

Heat exchanger fouling is common in the process industries but is still poorly understood. A variety of different effects can result in fouling, and the series of processes underlying deposit formation is complex and diverse. Many authors, such as Somerscales [9], Epstein [10], and Melo et al. [11], have described the chemical and physical processes leading to fouling. Much of the research in milk fouling has been to study the relation between product chemistry and the processing that the material receives. Fouling at a point in a heat exchanger depends on local thermal and hydraulic conditions, together with the chemistry and process history of the fluid.

This review aims to describe progress in understanding the processes of dairy fluid fouling and cleaning and attempts to model them. The complexity of the milk system and its thermal response is considerable and must be simplified for engineering analyses. Information obtained by food chemists is crucial in understanding fouling; however, the process engineering of the system—that is, the ways in which the flows and temperatures in the heat exchanger affect fouling—also is important.

**Figure 1.** Possible ways in which the fouling resistance can evolve with time.

### MILK FOULING

**Introduction**

Fouling problems associated with milk processing have been reported for more than half a century. Initial research concentrated on plant cleaning as a practical solution [12–14]. Bell and Sanders [15] found that the amount of fouling could be reduced by preholding milk at 75°C for 10 min and suggested that fouling was due to the denaturation of proteins and the decrease in solubility of milk salts with increasing temperature. This effect has been widely confirmed [16, 17]. Clearly, denaturation of whey proteins, especially \( \beta \)-lactoglobulin, during preheating reduces the amount of protein deposit later in the process. In practice, the selection of preheating temperatures is a matter of compromise between reducing downstream fouling without causing deposition in the preheating section [18].

Many significant physicochemical factors are involved in dairy fouling. On heating, protein denaturation and aggregation reactions as well as the insolubilization of calcium phosphate and change in solution pH occur. Each reaction is important, and their effect appears interrelated. The literature is now extensive; for conference proceedings, see Hallström et al. [19], Lund et al. [20], Kessler and Lund [21], and Fryer et al. [22]. The chemistry is well understood, and some progress has been made toward reducing fouling in commercial plants—for example, by using different preheating strategies.

### Factors Affecting Fouling

Dairy fluid fouling is a function of many variables, both chemical and physical. Some parameters, such as temperature and flow rate, can be determined by the process designer; others, such as the chemistry of the product, cannot be changed. Milk is a complex biological fluid subject to compositional variations [23] (Table 2). Burton [24–27] and Grandison [28–30] have reported seasonal changes in the amount of fouling during milk processing. Parris et al. [31] showed that genetic variants of \( \beta \)-lactoglobulin exhibited different degrees of fouling. Burton [26] proposed that cattle feeding regimes affected deposition, as did the state of lactation [27], although Grandison [30] was unable to correlate diet and fouling. Fryer et al. [32] found that the total amount of deposit from whey protein concentrate increased linearly with protein concentration. Jeunmink [33] also reported that fouling increased with serum protein concentration and that calcium deposition was coupled with this increase. Schraml and Kessler [34] found that fouling increased to a maximum concentration of 25% total solids (TS), after which deposition decreased. The reason for the decrease was thought to result from two competing mechanisms: (1) aggregation of whey protein and (2) crystallization of salts. Up to 25% TS, aggregation dominates; however, beyond 25%, TS greatly exceeds the solubility limit, giving a greater amount of salt precipitation [35], which gives a more compact deposit resulting in reduced fouling mass.

Reconstituted milk exhibits much less fouling than fresh milk. The reason for this is unclear, however it is known that 25% of the \( \beta \)-lactoglobulin is denatured during evaporation and drying in reconstituted milk production [36].

### Table 1. Composition of Pasteurizer and Sterilizer Deposits

<table>
<thead>
<tr>
<th>Composition</th>
<th>Pasteurizer, 72°C</th>
<th>Sterilizer A, 90°C</th>
<th>Sterilizer B, 138°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein (%)</td>
<td>50</td>
<td>50</td>
<td>12</td>
</tr>
<tr>
<td>Mineral (%)</td>
<td>15</td>
<td>40</td>
<td>75</td>
</tr>
<tr>
<td>Fat (%)</td>
<td>25</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Other (%)</td>
<td>10</td>
<td>9</td>
<td>10</td>
</tr>
</tbody>
</table>

From Tissier et al. [1].

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![Diagram of fouling categories](image-url)
In addition, calcium concentration and ion activity is reduced by 9% and 11%, respectively. Each of these factors could contribute to reduced fouling.

Holding milk for 24 h prior to processing significantly reduces deposition [26], although longer-term aging increased fouling [26, 37]. The reasons for the initial drop are unknown, but the rise may be due to the action of proteolytic enzymes, formed by psychrotrophic bacteria in the milk [37].

The effect of pH on the stability of milk and on deposit formation has been widely studied [38-43]. Milk pH typically varies between 6.6 and 6.8. Skudder et al. [39] showed that the amount of fouling increased markedly at acid pH but was unaffected by alkaline pH. Hegg et al. [44] and Hege and Kessler [40] explained this effect in terms of increased β-lactoglobulin adsorption toward its isoelectric point (pH 5.15).

Lalande and Corrieu [45] correlated the rate of deposit formation in a heat exchanger and the amino nitrogen level of the milk. This may depend on the association of amino concentration with urea content [18]. Added urea is known to increase milk heat stability [46, 47] and decrease deposit formation. Al-Roubaie and Burton [48] reported that the addition of capric acid, a fatty acid, to milk decreased deposit formation by increasing casein micelle stability. However, other fatty acids increased fouling or had no effect.

Mineral deposition occurs because of the lower solubility of calcium phosphate at higher temperatures [26, 41]. Barton et al. [49] suggested that calcium phosphate deposition occurred by precipitation fouling; the rate of precipitation is a function of both temperature and supersaturation [50]. The system is complex; aqueous equilibrium involves 13 ionic reactions including five different solid-phase reactions [51]. Hydroxyapatite is the most stable, but Singh and Creamer [52] were unable to determine the form in which calcium phosphate precipitated.

In general, the amount of deposit increases with time. Deposition at both pasteurization and UHT temperatures in a tubular exchanger shows the three phases of Fig. 1 [40, 53]. However, in plate heat exchangers, induction periods can be significantly shorter; deposit formation increases exponentially at pasteurization and UHT temperatures until the exchanger is shut down [54]. This variation between the two heat exchangers may be due to the difference in flow geometries [55].

Most of the foregoing parameters cannot be varied in operation. Processing parameters that can be changed include temperature, velocity, and air content. Gynning et al. [56] found that deposition is reduced if the air content of milk is reduced. The air content of bovine milk may be increased by entrainment during milking [57]. Bubble formation, from either dissolved air or nucleate boiling, can significantly enhance fouling [53] and cause a shift in protein deposition from serum proteins to caseins [36]. Bubbles will form during nucleate boiling; it is important to maintain a high enough pressure in the process plant to avoid bubble formation and the resulting severe fouling and to minimize air entrainment during processing. The absolute fluid velocity in a heat exchanger affects deposit formation. Belmar-Beiny et al. [58] studied fouling from both laminar and turbulent fluids and showed a decrease in fouling with increasing turbulence. Gordon et al. [59], Fryer [53], and Gotham [60] demonstrated that both the rate and the amount of fouling decreased with increasing flow rates in a tubular heat exchanger. Here, flow rate can be easily related to the shear stress in the equipment; this is more difficult in plate heat exchangers because of their complex flow geometries. The dependence of fouling on flow rate and temperature is further discussed below.

Deposit Composition

A number of analyses of milk fouling deposits have been reported. Burton [26] described two types of fouling; see also Lyster [61]:

1. Type A: soft and voluminous; formation starts above 75°C, is greatest in the range 95–110°C. The deposit is 50–70% protein and 30–40% minerals [1, 26, 54]. At low temperatures, most of the protein is β-lactoglobulin; but, at the high end, it is predominantly casein [1, 62]. Figure 2 shows a scanning electron micrograph of a deposit obtained with a plate heat exchanger after 200 min contact with whole unpasteurized milk. The pasteurizer deposit (Fig. 2a) consists largely of proteins and is typical of type A deposit.

2. Type B: forms at higher temperatures than type A, above 120°C. It is hard and granular; 70–80% minerals and 10–20% protein [26, 54, 61]. Figure 2c shows type B deposit, which is much more crystalline than type A.

Tissier et al. [1] gave a detailed chemical analysis of fouling deposits over pasteurization and UHT temperature ranges (see Table 1). The pasteurizer deposit was similar to type A, whereas the sterilizer contained both type A and type B deposits. Amino acid analysis was used to determine protein composition (Table 3); type A deposit (100°C) contained mainly whey proteins and im-

![Figure 2](image-url)
Table 2. Composition of Cow’s Milk

<table>
<thead>
<tr>
<th>Component</th>
<th>% w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>87.0</td>
</tr>
<tr>
<td>Lactose</td>
<td>5.0</td>
</tr>
<tr>
<td>Lipids</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Lipids 4.0

Proteins:
- Caseins 2.5
- /β-Lactoglobulin 0.3
- α-Lactalbumin 0.07
- Other proteins 0.19

Minerals:
- Calcium 0.13
- Sodium 0.05
- Potassium 0.15
- Phosphate 0.21
- Chloride 0.10
- Other 0.30

From Walstra and Jenness [23].

munoglobulins, whereas the sterilizer type B deposit contained entirely casein proteins. There are large differences between deposit and raw milk protein compositions; fouling results from preferential deposition of certain components.

Type A deposit is white and spongy [26, 61]. Tissier and Lalande [63] reported that, for process times greater than about 1 h, type A deposits consist of two layers: a protein-rich outer layer and a layer near the heat exchange surface rich in calcium and phosphorus [64-67]. Tissier and Lalande [63] attributed the formation of the sublayer to the diffusion and subsequent crystallization of insoluble calcium phosphate.

Type B deposit is hard, granular, and brittle [54, 61]. Foster and Green [68] studied the structure and profile scanning electron micrograph and found no distinct layers, but, as in type A deposits, protein was concentrated near the outside of the deposit with calcium, phosphorus, and magnesium near the heat exchange surface.

Lyster [61] noted that calcium and phosphate typically formed 90% of the mineral content of milk fouling deposit but composed only 30% of mineral content in raw milk. The calcium/phosphate ratio for type A deposit was shown to be about 1.5. This has been found by others [54, 63, 69, 70] and indicates the presence of calcium triphosphate. Fat appears to play an insignificant role in milk fouling [71]; it is a negligible constituent of both type A and type B deposits. Even in the processing of 36% fat cream, fat content is still a negligible component of fouling deposits [72].

Protein Thermal Stability and Fouling

Lyster [61] proposed that changes in the stability of milk proteins at high temperature were important in deposit formation. /β-Lactoglobulin is the milk protein most sensitive to heating [73], but the thermal stability of other milk proteins also is important. When heated above about 70°C, the structure of /β-lactoglobulin is irreversibly altered by denaturation and aggregation. The protein first unfolds in molecular denaturation, an intramolecular process that exposes the hydrophobic molecular core, together with reactive disulfide and sulfhydryl bonds. This unstable configuration becomes stabilized by polymerization with other denatured molecules in intermolecular aggregation. Denaturation is reversible, but aggregation is not; the resulting aggregates are insoluble in water. One difficulty is that the two processes are very difficult to separate; the whole process is often described as denaturation.

/β-Lactoglobulin forms mixed aggregates with other heat-labile proteins, such as κ-casein [74]. Heat treatment of caseins in the UHT range increases the micelle size [75]; this may be related to interaction between the micelle and whey protein [76-79] or to a shift in the location of calcium phosphate [80]. Mixed aggregates may be involved in fouling [33, 37], but the processes are not yet understood.

Skudder et al. [70] showed the importance of aggregation in fouling, which could be significantly decreased by adding potassium iodate to milk before pasteurization. This oxidizes the sulfhydryl (-SH) groups exposed during denaturation. Denaturation is reversible, but aggregation is not; the resulting aggregates are insoluble in water. One difficulty is that the two processes are very difficult to separate; the whole process is often described as denaturation.

Adding calcium ions increases deposition [29, 65, 82]. Burdett [83] found that adding sodium pyrophosphate to raw milk significantly decreased UHT fouling and suggested that this decrease was due to the inhibition of calcium phosphate precipitation and increased casein micelle stability. De Wit [84] and de Wit and Klarenbeek [85] showed that calcium affected whey protein aggregation.

Varunsitian et al. [86] found that the presence of calcium and magnesium ions promoted whey protein concentrate (WPC) thermal denaturation and aggregation. Xiong [87] notes that calcium can cause bridging between adjacent carboxyl groups and stabilize aggregates. Jeurnink and de Kruijf [88] found that both an increase and a decrease in calcium concentration compared with that of normal milk increased fouling, with a greater amount of casein. Low-calcium milk exhibited swollen casein micelles, from which a large proportion of the κ- and β-casein was dissociated. These “depleted micelles” are less heat stable because of the lack of κ-casein, resulting in increased fouling. High-calcium milk showed shrunken micelles and very little dissociation. It was hypothesized that changes in mineral content and composition reduced electrostatic and steric repulsions between the casein micelles, leading to increased interaction and thus lower heat stability; see also Jeurnink and de Kruijf [89] and Jeurnink [90].

The other main whey protein, α-lactalbumin, also is heat labile and present in fouling deposits. Denaturation of α-lactalbumin is reversible to about 85°C, but the denatured form is more surface active than native protein and can be an active constituent of milk fouling deposits [91].

The behavior of /β-lactoglobulin, the most prominent protein in fouling deposit, has formed the basis for a number of fouling models. The amount of deposition at any point in a heat exchanger has been correlated to the local amount of denaturation of /β-lactoglobulin, determined by the local temperature [62, 64, 72]. Tissier et al.
The controlling reaction occurs. The chemistry of unfolding begins at contact points between heat exchanger plates. A denaturation to aggregation. Hege and Kessler [40] and been found, with a change in the energy at about 90°C, different controlling reactions have different rate-limiting steps and therefore different activation energies. Table 4 summarizes published data for the thermal stability of β-lactoglobulin; a wide variety of activation energies have been found, with a change in the energy at about 90°C, where the controlling reaction switches from unfolding (denaturation) to aggregation. Hege and Kessler [40] and Kessler and Beyer [17] concluded that β-lactoglobulin denaturation is the governing reaction in fouling, whereas Lalande and René [97] suggested that, above 90°C, surface aggregation is the governing reaction. Gotham et al. [98] noted that the effect of pH on fouling was the same as the effect of pH on aggregation and thus suggested that aggregation is the governing reaction. It is still not clear where the controlling reaction occurs. The chemistry of the protein reactions in fouling is further discussed by Visser and Jeurnink [99].

Initial Stages of Fouling

If the processes that govern the induction period were understood, it might be possible to extend it. The sequence and the rate of events that make up the induction stage are thus important. For example, Delplace et al. [100] and Schreier [101] both demonstrated that fouling begins at contact points between heat exchanger plates. A number of techniques can characterize surfaces, including X-ray photoelectron spectroscopy, Auger spectroscopy, secondary ion mass spectrometry, ion scattering spectroscopy, and Rutherford backscattering [102]. It is very difficult to obtain a full understanding of events during fouling by using a single technique. Arnebrant et al. [103] studied β-lactoglobulin adsorption onto chromium-covered glass slides and found that, above the denaturation temperature, conformational changes of the protein must take place before surface aggregation begins. Lag phases of 500 s and 1200 s were found at 78°C and 76°C, respectively. Dalgleish [104] also reported that both the disappearance of denatured whey proteins and the appearance of aggregated proteins in solution appeared to have an initial stage followed by a faster process. Brassart [105] conducted X-ray photoelectron spectroscopy studies to characterize the adsorption of different amino acids and β-lactoglobulin. The adsorption of β-lactoglobulin was studied at 20°C and 70°C; at 20°C, the protein adsorbs in a way resembling its native form; whereas, at 70°C, it undergoes significant unfolding.

Several studies [66, 106, 107] have found that the nature of the surface becomes unimportant when the first fouling layers are adsorbed; when a surface is covered, deposit–deposit rather than deposit–metal surface interactions are the most significant. Britten et al. [66] found that coating the heating surface affected the strength of adhesion but not the amount of deposit; the interfacial energy of the surface appeared to be the main factor affecting adhesive strength. These results concurred with Arnebrant et al. [108] and Brassart [105]. The first material to adsorb may be responsible for the strength of the deposit–surface bonds; which may affect the cleaning rate.

The final deposit contains calcium phosphate concentrated at the deposit–metal interface [63, 65, 109]. It was thus suggested that minerals are the most likely to adsorb first. However, other workers found that proteins adsorbed first, such as Baier [110]. Delsing and Hiddink [82] followed by Daufin et al. [65], found, by using X-ray photoelectron spectroscopy and different test fluids, that proteins were the main, though not the only, species to adsorb first. Foster and Green [68] studied milk fouling onto stainless steel disks at wall temperatures of 140°C, using secondary ion mass spectrometry. They found that the distribution of elements changed with depth, concluded that minerals diffuse through the deposit, and suggested that minerals and protein layers are built simultaneously. The early stages of fouling from whey proteins onto stainless steel have been studied at pasteurization temperatures by Belmar-Beiny and Fryer [111, 112] for contact heating times down to 4 s. X-ray photoelectron spectroscopy, scanning electron microscopy and X-ray elemental mapping were used to interpret the data. Scanning electron micrographic images showed that clean metal surface first (ca. 120 s) became covered by a layer of material on which aggregates grow or adhere. The aggre-

<table>
<thead>
<tr>
<th>Table 3. Analysis of Protein Deposits</th>
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<tbody>
<tr>
<td><strong>Composition (%)</strong></td>
</tr>
<tr>
<td><strong>β-Lactoglobulin</strong></td>
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<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td><strong>β-Cassein</strong></td>
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<td></td>
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<tr>
<td><strong>Immunoglobulins</strong></td>
</tr>
<tr>
<td><strong>Other</strong></td>
</tr>
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<td>From Tissier et al. [1]</td>
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<table>
<thead>
<tr>
<th>Table 4. Activation Energies for β-Lactoglobulin Denaturation and Aggregation</th>
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<tr>
<td><strong>Activation Energy (kJ / mol)</strong></td>
</tr>
<tr>
<td><strong>Lyster [95]</strong></td>
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<tr>
<td></td>
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<tr>
<td><strong>Lalande and Corrieu [45]</strong></td>
</tr>
<tr>
<td><strong>Hegg and Kessler [40, 64]</strong></td>
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<tr>
<td><strong>Dannenberg and Kessler [96]</strong></td>
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<td><strong>de Wit [157]</strong></td>
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From Tissier et al. [1]
gates range in size from 0.2 \( \mu m \) to 0.7 \( \mu m \) and are packed in clusters, forming bridges between each other.

Figure 3 shows the X-ray photoelectron spectra (250 eV and 1500 eV) obtained for the adsorption of a deposit formed by WPC 75 at 73°C fluid inlet temperature, for contact times of 4 and 150 s, together with the spectrum of a clean unfouled stainless steel surface. Protein was followed mainly through carbon and nitrogen peaks of binding energy appropriate to the peptide bond. Inserts 1 and 2 correspond to the carbon spectrum for unfouled and fouled surfaces. As contact time increased, the peaks corresponding to the metallic surface decreased and the carbon and the nitrogen peaks increased; the initial layer is a protein film. Belmar-Beiny and Fryer [112] found that the composition of this film was close to the theoretical composition of pure \( \beta \)-lactoglobulin. Only after 150 s contact time were sulfur and calcium detected; no phosphorus was found. X-ray elemental mapping was carried out on thicker deposits. For exposure times of 150 s, a nonuniform deposit was found. Aggregates contain both sulfur (indicating the protein nature of the deposit) and calcium. No phosphorus was detected. After 60 min, however, calcium and phosphorus were found concentrated at the deposit–stainless steel interface, similar to other work [63, 65, 68, 82, 109], suggesting that the structure changes with time.

In whey fouling, there appears to be a lag phase in which no aggregates appear in the surface, during which the surface becomes covered with a proteinaceous film. The results of Belmar-Beiny and Fryer [112] suggest that the lag phases observed in protein adsorption by previous workers [103, 104] are similar to those at pasteurizing conditions. Further work [113] has been to study deposition on surfaces with UHT temperatures. The initial stages of fouling were similar, save that the coverage of the initial layer was not total; some regions of the surface became covered with aggregates before all the metal had been covered. Under some conditions, aggregates similar to those in pasteurizer fouling are seen, but highly amorphous deposits also can form. The reason for this is unknown.

These results indicate that proteins are likely to be the first species to adhere. The role of calcium and phosphate ions in milk and whey fouling is complex. Visser and Jeurnink [99] discuss these problems in detail. In the bulk, calcium ions promote \( \beta \)-lactoglobulin aggregation both by binding to the \( \beta \)-lactoglobulin molecule and by decreasing the denaturation temperature [87]; on the surface, calcium
will form bridges between adsorbed protein and protein aggregates formed in the bulk and then adhered to the surface. The way in which minerals eventually become concentrated at the interface and between deposit and the metal surface is still unclear.

THE INTERACTION BETWEEN FLUID MECHANICS AND CHEMISTRY

Surface and Bulk Effects

If a mathematical model for fouling were available, it would be very useful to process designers; Fryer and Slater [114] showed how the effects of fouling could be modeled, and Fryer [55] outlined the advantages of applying fouling models to a full-scale plant during design and operation. To model fouling, both the fluid mechanics and the chemistry of the process must be considered.

Early work, such as that of Lund and Bixby [115] and Lalande and Corrieu [45], was largely empirical. More recently, attempts have been made to use models that reflect the fluid mechanics of the system. Studies of deposition from solutions of soya proteins [116] found that fouling increased significantly when the temperature in the turbulent core of the fluid exceeded that at which the soya becomes thermally unstable. Results were explained in terms of a “thermal damage layer” where the temperature was hot enough to cause protein denaturation. Similar conclusions were reached [53, 117] by interpreting fouling data from a tube; for a fluid bulk temperature of 60°C and wall temperatures between 85 and 110°C, the initial rate of fouling after the induction period was found as:

$$\frac{dBi}{dt} = \frac{(4.85 \pm 0.4)}{Re} \times 10^{13} \exp\left(\frac{-(87 \pm 6) \times 10^3}{RT_i}\right),$$

(3)

where Bi is the fouling Biot number \((Bi = ReU_0^0)\) and \(T_i\) is the temperature at the deposit-fluid interface. The activation energy found here is similar to that reported by Dannenberg [96]. Paterson and Fryer [117] explained the simultaneous temperature and velocity, \(u\), dependence of Eq. (3); that is,

\[ \text{initial rate of fouling } \propto \frac{\exp(-E/RT_w)}{u}, \]

(4)

in terms of a bulk reaction. Because below about 70°C the rate of protein reaction is negligible [118], in these experiments the only regions of the fluid hot enough for protein to react were the hot surface and the fluid boundary layer next to it. Two effects of flow were considered: (1) the change in the volume of the “reactor” (the hot wall layer) —as Reynolds number increases the thickness of this layer decreases; and (2) a decrease in the sticking probability of foulant resulting from the increase in surface shear stress with Reynolds number.

If fouling involves bulk processes rather than just a surface reaction, it will result from a sequence of stages:

1. Reaction in the liquid;
2. Mass transfer to the surface;
3. Surface reaction into the deposit; and
4. Possible transfer back to the bulk; that is, reentrainment.

The slowest process will be rate controlling. Two cases can be envisaged:

1. If fouling is mass transfer controlled, transfer of reacted protein to the wall is the slowest step; deposition will not be a strong function of temperature.
2. Fouling reaction in different places. If fouling is controlled by surface processes, deposition will be a function of the wall but not the bulk temperature. If the controlling reaction for fouling takes place in the bulk, the adhering species could be generated either in the wall layer or throughout the fluid, depending on the temperature distribution.

These ideas were tested by Gotham [60], who studied fouling from whey protein concentrates in a tube. Although the mineral content of the deposit was fairly uniform, the amount of protein changed down the tube. Figure 4 shows the results of a series of experiments for the same temperature profile and different flow rates. An increase takes place when the bulk temperature exceeds about 75°C; that is, where bulk reaction of protein becomes significant. Similar effects are seen in other types of exchanger [119]. The nonuniformity of the deposit suggests that mass transfer does not control. Belmar-Beiny et al. [58] outline two simple models, based on wall and bulk reactions, and show that wall reactions are not the controlling process. A possible reason for the importance of bulk processes was suggested with the use of models proposed by Fryer and Slater [120] and Vatistas [121] to consider the balance between adhesion and flow in the near-wall region. Fluid bursts, distributed randomly over the surface, will convect fluid to and from the bulk. If a burst brings a protein to the wall, it will begin to adhere. The force between protein and wall will increase with time and will eventually be so large that the protein cannot be removed by subsequent bursts. The shorter the time required for adhesion, therefore, the more likely that it will occur. Adhesion will be faster for denatured or aggregated proteins, which have reactive groups already exposed, than for native protein. Protein that has reacted in the bulk will thus adhere faster, and the amount of deposit will be related to the amount of hot fluid; Epstein [122] has given a model for surface adhesion.

Computational Models for Fouling

A number of workers have described computational models of heat exchangers to model fouling [54, 123]. Some models for the conditions in a plate heat exchanger are now available [124, 125]. De Jong et al. [126] studied the relation between \(\beta\)-lactoglobulin denaturation and fouling in a plate heat exchanger for temperatures between 70 and 122°C. Mass transfer of reacted protein from the bulk to the wall was modeled, and reasonable fits between experiment and theory were found for temperatures up to 100°C. This is further evidence that bulk reactions must be considered in fouling. De Jong et al. [127] integrated reaction models into a program to optimize a UHT plant with respect to product quality and operational costs. This method found an optimum that reduced operational costs by more than 50% while maintaining product quality, using a 13-min hold at 90°C.

Delplace [125] and Delplace and Leuliet [128] developed a model to predict dry masses of deposit in the
channels of a plate heat exchanger by calculating the heat denaturation of \( \beta \)-lactoglobulin. Fouling by whey proteins onto two types of plate geometry (straight corrugated and herringbone), incorporating different flow arrangements, was studied together with the effect of Reynolds number, mean residence time, and the concentration of native \( \beta \)-lactoglobulin in the inlet of the plate heat exchanger. Fouling was monitored by recording the change in the heat transfer coefficient for the whole section with time. Inlet and outlet temperatures as well as mean residence times were determined, using the method of René et al. [124]. The second-order kinetic model for \( \beta \)-lactoglobulin denaturation [95] (Table 4) was used to calculate inlet and outlet concentrations of native \( \beta \)-lactoglobulin for each channel:

\[
C(t) = \frac{C_0}{1 + kC_0 t}
\]

where \( C(t) \) = concentration of native \( \beta \)-lactoglobulin at time \( t \) (kg/m³), \( C_0 \) = initial concentration of native \( \beta \)-lactoglobulin (kg/m³), and \( k \) = second-order rate constant [m³/(kg s)]:

\[
\log_{10} k = 37.95 - 14.51(10^3/T) \text{ where } T \leq 363.15 \text{ K};
\]

\[
\log_{10} k = 5.98 - 2.86(10^3/T) \text{ where } T \geq 363.15 \text{ K}.
\]

With use of the approach of Lalande et al. [62], the concentration difference between inlet and outlet native \( \beta \)-lactoglobulin concentration (\( \Delta C_i \)) was calculated. Delplace et al. [100] and Delplace [125] observed a linear evolution of deposit mass with time in the plate heat exchanger channels. Only a small fraction of denatured \( \beta \)-lactoglobulin was involved in deposit formation. The relation between deposit mass and the volume of fluid hot enough to produce denatured and aggregated proteins, proposed by Belmar-Beiny et al. [58], was used to develop a model. After accounting for the volume of fluid processed, \( V_i \) (m³), and surface area of different plate geometries, \( S_i \) (m²), the following equation was developed by a combination of analysis of experimental results and numerical simulations:

\[
\frac{m_{di}}{SV_i} = 0.127\Delta C_{i0.5},
\]

where \( m_{di} \) = dry mass of deposit in a channel \( i \) (kg) and \( \Delta C_i \) = the difference between inlet and outlet native \( \beta \)-lactoglobulin concentrations of the channel (kg/m³). Irrespective of Reynolds number or flow arrangement (and therefore mean residence times), this model predicted dry mass of deposit in each channel to within 20% accuracy. At constant flow rate, dry mass of deposit in each channel appeared to be proportional to the volume of treated fluid and then proportional to time. Dry deposit mass in the plate heat exchanger channel was dependent on \( \Delta C_{i0.5} \); for very low concentrations of denatured \( \beta \)-lactoglobulin, deposit was proportionally greater (i.e., the fraction of denatured \( \beta \)-lactoglobulin in deposit formation is greatest when denatured quantities are very small). The deposit mass also depends on the mixing in the plate heat exchanger channel. This is included in the numerical coefficient, calculated as 0.127 for straight corrugated plates. For herringbone plates, the coefficient was calculated as 0.06 [125]; fouling in this geometry was found to be half that of straight corrugated plates under the same thermohydraulic conditions. The decrease in fouling was explained by the use of the work of Gaiser and Kottke [129] to determine mixing intensity in corrugated channels. Mixing intensity may reduce fouling by promoting aggregate formation in the bulk instead of on heat transfer surfaces.

Engineering measurements of fouling (i.e., change in pressure drop and heat transfer coefficient) also have been related to protein denaturation, using the same basic approach. Schreier [101] and Fryer et al. [130] describe experiments on a pilot-scale plate heat exchanger. Changes in both heat transfer and pressure drop could be correlated in terms of the local reaction rate of \( \beta \)-lactoglobulin,
Figure 5. Response surface for fouling rate, expressed as ΔBi, in the UHT section of a pilot-scale plate heat exchanger, showing the effects of two process variables, flow rate and the amount of reacted protein in the plate exchanger section [130].

expressed as grams of protein reacted per square meter of surface per second. Multiple linear regression [131] was used to develop empirical polynomial models to characterize the system behavior. Figure 5 is an example of the results, displaying data from the UHT section of the plate heat exchanger together with the fitted model. It shows the effect of the significant process variables, flow rate and amount of reacted protein, on the response variable, Biot number, calculated from the overall heat transfer coefficient (see the section titled "Food Fouling"). The lattice surface represents the model, black and white dots show the relative positions of the experimental data, below and above the model surface respectively. The amount of protein reacted was found from the kinetic data of Lyster [95] and measured temperatures in the exchanger. Modeling and statistical analysis of the data showed the change in Biot number (and thus overall heat transfer coefficient) to be significantly affected by the amount of protein reacted and to a lesser extent by flow rate. The correlation between protein reacted and fouling found in the studies reported here confirms that the use of these reaction kinetics is a good starting point for understanding fouling even at UHT temperatures.

Although considerable progress has been made in modeling deposition, some problems still remain. For example, difficulties arise in going from laboratory to industrial scale; if there are a number of mechanisms involved in fouling, they will scale upward in different ways. Three parameters (constant Reynolds number, surface shear stress, and temperature change for fouling fluid), for which surface and bulk processes vary, were tested as candidates for scale-up strategy [132]. Results showed that there is no simple scaling parameter for fouling and emphasized the need to understand local processes of fouling kinetics to enable modeling and prediction of fouling in industrial-scale plants. The interrelation of chemical reactions and the fluid mechanics of heat transfer equipment also results in problems when modeling fouling. Toyoda et al. [133] have developed a model for milk fouling from turbulent fluid in a tubular exchanger, incorporating bulk and surface processes. The mathematical model proposed incorporated temperature difference between the bulk and the boundary layer of the fluid, realistic protein denaturation and aggregation kinetics, and realistic protein mass transfer and wall reaction terms. The numerical solutions showed a good fit with experimental data for several flow rates and protein concentrations. However, results were highly sensitive to the reaction parameters, especially activation energy. For example, Fig. 6 shows the large change in the predicted fouling pattern shown by even a 5% change in activation energy. Given the variability of data shown in Table 4, this suggests that it may be difficult to model fouling accurately; however, the models are now at a stage where they can be used to suggest improvements in plant design and operational strategy.

CLEANING OF DEPOSITS

Introduction

The processes by which fouled deposit is cleaned are even more poorly understood than fouling. Many of the protocols used by the food industry are anecdotal; for example, the cleaning solution velocity of 1.5 m/s often quoted as necessary for cleaning [3] has no theoretical justification. Cleaning is a multistage process [135] comprising steps that may be controlled by mass transfer, diffusion, or reaction. Cleaning chemicals must be transported to the solid-liquid interface and then must contact and penetrate the deposit. The solution then reacts with the deposit, which can then be removed. Any step may control the whole process; for example, mass transfer in low shear areas will be slow, leading to slow cleaning [55]. Observation of cleaning [136, 137] shows (1) that, on contact with sodium hydroxide, protein deposit swells and (2) that cleaning is not uniform but includes uneven removal of
lumps of swelled deposit from the surface. If just sodium hydroxide is used, minerals are left on the surface; acid wash is needed to remove that layer. Single-stage cleaners allow this layer to be removed with the protein.

The Effect of Process Parameters in Cleaning

For kinetic studies, it is necessary to have a uniform deposit that can then be removed under quantified conditions. Much of the research, however, has used a process plant, such as plate heat exchangers, that fouls unevenly. Only a few studies have been reported from uniform deposit; Grasshoff [138] uses uniformly fouled plates, whereas Bird and Fryer [137] report experiments using uniformly fouled tubes. Figure 7 gives a typical cleaning curve, showing the rate of removal of deposit as a function of time. The shape is similar to those found by others, such as Perlat [139].

Early research established that the time taken to clean is a function of temperature, flow rate, and the cleaning chemical concentration [140]. Other factors affect cleaning, such as the finish on the heat exchanger surface, the geometry of the heat exchanger, and the overall process design [141, 142]. Attempts have been made to characterize cleaning in terms of the fluid velocity [143], Reynolds number [144], and the mean wall shear stress [145]. Other models have used mass transfer effects, incorporating flow velocity [146, 147]. Bird and Fryer [137] found a smooth decrease in cleaning rate with increased flow velocity, in experiments down to Re = 340; they found that the cleaning rate becomes significantly higher above 50°C. Gallot-Lavallée and Lalande [147] and Perlat [139] fitted Arrhenius models to cleaning data and found activation energies in the order of 80 kJ/mol. It is, however, difficult to identify the controlling factor.

The effect of cleaning agent concentration is complex. An optimum cleaning agent concentration exists that minimizes the cleaning time [5, 148–150]. Figure 8 shows the effect of changing sodium hydroxide concentration on the cleaning of a uniform deposit; a clear minimum is found in the region of 0.5 wt.%. Bird [151] shows that the same effect can be seen in both WPC and milk deposits. Subsequently, optima have been found for starch removal [152], albeit at a very high level (at 14 wt.% NaOH). The use of

Figure 6. Sensitivity of the fouling amount to the activation energy for the protein denaturation reaction: a 5% variation in the activation energy gives very large changes in the amount of fouling [134].

Figure 7. Typical cleaning curve, showing a whey protein soil (35% protein) cleaned with 1 wt.% sodium hydroxide at 70°C and a flow velocity of 0.175 m/s.

Figure 8. Variation of cleaning time as a function of sodium hydroxide concentration, showing the existence of an optimum for deposit cleaned at 50°C and 0.174 m/s [151].
concentrations above the optimum both increases cleaning times and raises the amount of effluent produced.

Other ways of enhancing cleaning have been sought. It has been found that the addition of oxidizers and complexing agents can increase cleaning efficiency by a factor of ten compared with pure 0.25% sodium hydroxide [153]. However, if one component becomes exhausted, then efficiency can decline considerably. Enzyme cleaners are not commonly used for cleaning milk heaters [153]. They are too expensive (three times conventional commercial cleaners) and require neutral pH, temperatures of about 60°C, and considerably more time to digest deposits than the usual acid/alkali cleaners. Ultrasonic oscillators also have been investigated. However, because the ultrasonic field is effective only over a few centimeters, it would be difficult to design a cleaner for a plate heat exchanger [153]. Energy expenditure also would be considerably increased. For these reasons, ultrasonics is not currently being considered seriously for cleaning plate heat exchangers.

Models for Cleaning

The importance of predicting a cleaning rate has been reflected in the number of efforts made to model it. It has been found convenient to model removal in terms of the deposit per unit surface area, m. Schlussler [146] suggested a zero-order model for milk deposit removal:

$$\frac{dm}{dt} = -k_0.$$  \hfill (7)

Other workers have used rate laws that are first order in both deposit mass per unit area and cleaning chemical concentration, c [154, 155]:

$$\frac{dm}{dt} = -k_2c.$$  \hfill (8)

This has been found useful for comparing different cleaning chemicals. Grasshoff [138] studied the removal of fouling deposits from 50-mm prefouled discs and expressed results in terms of a first-order rate constant. This was found to vary with time, suggesting that such a simple model is insufficient to model the process fully.

Gallot-Lavalée and Lalande [147] and Perlat [139] describe a four-stage cleaning model, which assumes that deposit is changed by hydroxyl ions (OH⁻) from an initial state to an intermediate state prior to removal. The cleaning process then comprises four stages: (1) mass transfer of OH⁻ from the bulk to the deposit; (2) diffusion of OH⁻ through swelled deposit; (3) reaction with unswelled deposit; and (4) removal of swelled deposit. Deposit removal was found to control; however, the activation energy fitted to this reaction (138 kJ/mol) is high enough to suggest a chemical reaction. Bird and Fryer [137] used a simpler, two-stage model for cleaning. No model exists that can predict cleaning times in a process plant; more work is needed in this area.

FUTURE WORK

Three factors have made the problem of dairy fouling in food processing so severe: (1) the highly complex chemistry of the processes that give rise to deposition, (2) the rapid rate of fouling, and (3) the complexity of the temperature and flow fields within process plant. The rates and amount of fouling change with both physical factors, such as temperature and flow rate, and chemical factors, such as pH and protein concentration. Without accurate models for the local temperatures and shear stresses in equipment, it is very difficult to interpret fouling data in terms of the basic kinetics. The lack of such data hampers the development of procedures to minimize fouling. In the authors' view, experiments on plant where it is difficult to determine flows and temperatures are of little fundamental value. It is necessary to understand the basic processes of fouling and cleaning. Models for the operation of plate heat exchangers, such as that of de Jong et al. [126] and Delplace [125], potentially represent a significant advance; however, if they are to be used to predict the behavior of different industrial plants then some kinetic expression for fouling is needed.

Three approaches to reduce or eliminate fouling are possible:

1. Modifications to the heat treatment that the fluid receives, such as changes in the temperature profiles. The use of holding sections has been found to reduce fouling, but holding times and temperatures may not be optimal.
2. Modifications to the design of the heat exchanger, either by changing its configuration or the surface finish.
3. Modifications to the dairy fluid, such as the addition of oxidizing agents to prevent aggregation and the addition of calcium phosphate inhibitors to prevent its destabilization and further precipitation. In many cases, this may be precluded because the product specification is constrained.

The second approach may offer the greatest scope for engineering advance. However, Yoon and Lund [156] studied different surfaces, such as teflon, polysiloxane, and different metals, finding very little difference in fouling rates. Interestingly, they also tested a magnetic "descaling" device and found it to have no effect. Understanding the mechanisms of fouling is critical here. For example, if fouling is controlled by a bulk process, then surface modifications may not be able to prevent deposition. However, if fouling is a surface process, to modify the exchanger surface, it is necessary to determine which species are deposited first and design the surface to resist such deposition or to extend the induction period for as long as possible. The work described above suggests that it may be possible to use protein-resistant coating to prevent the first layer of adhesion. However, the processing temperatures are such, particularly in UHT, that calcium phosphate will still precipitate and adhere to the surface. In selecting surfaces, both fouling and cleaning must be considered; any fouling-resistant system must still be capable of being cleaned because of possible bacterial contamination or equipment breakdown, so the surface must be capable of resisting cleaning.

Developments in the process plant will evolve as a result of advances in the understanding both of the chemistry of the milk system and of the way in which that chemistry is affected by the flows and temperature that occur in the process plant. Type A deposit appears to be
formed by adhesion to the wall of proteins that have reacted in the bulk of the fluid either by unfolding or partial aggregation. Preheating can give aggregates that have less tendency to adhere. However, the interaction between proteins and calcium phosphate in deposition is still unclear, as are the processes that control adhesion and the rate of adhesion. The controlling kinetic step in UHT fouling is not known. More work is needed in a number of areas; there are a number of processes, such as vaporization, that have not been thoroughly studied for which the mechanism of fouling is not known. Equally, there are a number of modified milk products that have not been well studied whose behavior may be significantly different from those discussed here.

REFERENCES


