Classification of Resistance to Permeation Caused by Fouling during Ultrafiltration of Whey and Skim Milk

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To identify the cause of fouling of the membrane surface and pores during the ultrafiltration of whey or skim milk, these liquids were filtered through a membrane, allowed to adsorb to it, or both. Measurements of flux were made before and after gentle hand cleaning with a soft sponge, and resistance to permeation because of fouling was calculated and classified into four kinds: by adsorption to the surface, by adsorption in side the pores, because of filtration on the surface, and because of filtration in the pores. In the ultrafiltration of whey, resistance caused by fouling on the surface by filtration was great, and that caused by fouling in the pores by filtration was slight. In the ultrafiltration of skim milk, resistance caused by fouling by adsorption was great, and that caused by fouling on the surface by filtration was slight, probably because the casein micells in skim milk scrape fouling materials off the surface.

In ultrafiltration (UF), flux decline is still a problem. This decline is caused by fouling and concentration polarization. The authors have pointed out the importance of fouling in a study of an osmotic pressure model of membrane fouling in the UF of whey.

After Blatt et al. described a gel layer model to explain flux decline during UF, fouling on the surface of a membrane by gel layers or layers of deposits has been reported by many researchers. Several papers have suggested that fouling in the pores of membranes can occur, as well. We applied hand cleaning with a soft sponge to the surface of a fouled membrane after UF of skim milk to concentration factor 6, and found that fouling in pores contributed to permeate resistance. Nabetani et al. hand-cleaned the surface of membranes to which ovalbumin solution had absorbed and found that fouling by adsorption is not only on the surface but also in the pores of the membranes.

The importance of adsorption in the UF of bovine serum albumin solution, resulting in flux decline, was pointed out by Matthiasson. Tong et al. reported the adsorption of whey protein to the membrane during the UF of whole milk, and Meunier-Goddik et al. reported such adsorption during the UF of skim milk. Taddei et al. suggest that two kinds of fouling, protein adsorption and convective deposition of solid matter particles onto the membrane, occurs simultaneously and irreversibly during the UF of whey. It is likely that fouling occurs on the surface and in the pores of membranes by both adsorption and filtration.

The purpose of this study was to classify resistance to permeation because of fouling, \( R_f \), into resistance caused by adsorption, \( R_{ad} \), and resistance caused by filtration, \( R_{filt} \). We hand-cleaned the surface of fouled membranes with a soft sponge to classify both kinds of resistance into two kinds: that on the surface, \( R_{ad,s} \) and \( R_{filt,s} \), and that in the pores, \( R_{ad,p} \) and \( R_{filt,p} \). Here, resistance because of adsorption, \( R_{ad} \), is defined as the resistance caused by the adsorption of solutes to membrane. Resistance because of filtration, \( R_{filt} \), which may the same as a deposit layer, proposed by Taddei et al., is defined as the resistance which occurs only when filtration is in progress, adding to the resistance caused by adsorption. These resistances can be expressed by Eqs. (1) and (2).

\[
R_f = R_{ad} + R_{filt} \quad (1)
\]

\[
R_f = R_{ad,s} + R_{ad,p} + R_{filt,s} + R_{filt,p} \quad (2)
\]

This classification is shown in Fig. 1.

To find any differences in fouling between fresh and reconstituted solutions, both kinds of solutions were tested.

We assumed that resistance to permeation arising from fouling because of adsorption without UF was the same as resistance to permeation arising from fouling because of adsorption during UF, and that hand cleaning with a soft sponge could remove all fouling materials from the surface. Therefore, resistance to permeation, as defined in Eqs. (1) and (2) could be obtained as described below.

The pure water flux, \( J_{w,s} \), of the fouled membrane was expressed by the following equation, with use of the

![Fig. 1. Classification of Fouling Resistance.](image-url)
resistances described in the series model.\(^\text{10}\)

\[
J_{w,t} = \Delta P \left( \mu \cdot (R_m + R_f) \right)
\]

where \(\Delta P\), \(\mu\), and \(R_m\) are transmembrane pressure, the viscosity of the permeate, and the intrinsic resistance of the membrane, respectively.

The intrinsic resistance, \(R_m\), was calculated from the measured value for the pure water flux, \(J_{w,a}\), by Eq. (4).

\[
R_m = \Delta P \left( \mu \cdot J_{w,a} \right)
\]

The resistance to permeation of a membrane fouled by adsorption consists of \(R_m\), \(R_{ad,s}\), and \(R_{ad,p}\) and thus \(R_m + R_{ad,s} + R_{ad,p}\) was obtained from the pure water flux, \(J_{w,a}\), of a membrane fouled by adsorption by Eq. (5).

\[
R_m + R_{ad,s} + R_{ad,p} = \Delta P \left( \mu \cdot J_{w,a} \right)
\]

The value of \(R_{ad,s}\) plus \(R_{ad,p}\) was deduced from the pure water flux, \(J_{w,sp}\), of the membrane after adsorption and then hand cleaning of its surface, by use of Eq. (6), because \(R_{ad,s}\) could be assumed to be zero.

\[
R_m + R_{ad,p} = \Delta P \left( \mu \cdot J_{w,sp} \right)
\]

Then the value of \(R_{ad,s}\) plus \(R_{ad,p}\) was calculated by Eq. (7) from the pure water flux, \(J_{w,t}\), of the membrane, fouled by UF of a test liquid.

\[
R_m + R_t = \Delta P \left( \mu \cdot J_{w,t} \right)
\]

After hand cleaning of the surface of the fouled membrane, the measurement of the pure water flux of the membrane, \(J_{w,tp}\), gave the following equation.

\[
R_m + R_{ad,p} + R_{tit,p} = \Delta P \left( \mu \cdot J_{w,tp} \right)
\]

From Eqs. 2–8, \(R_m\), \(R_{ad,s}\), \(R_{ad,p}\), \(R_{tit,s}\), and \(R_{tit,p}\) were calculated.

In practical uses, the flux, \(J_p\), measured with a permeate instead of pure water, was also used to calculate fouling resistance, from the viscosity of the permeate. In such a calculation fouling is defined as the irreversible resistance that remains after the permeate is used for rinsing instead of water.

Materials and Methods

Membrane and apparatus. The membrane tested was a polyacrylonitrile UF membrane (type IRIS 3038, Rohne Poullanc Co., France; mol. wt. cut-off, 20,000). The apparatus used was a cell with a magnetic stirrer (Type MC-2A, Ulback Service Co., Japan), pressurized with nitrogen gas and with an effective membrane area of 12 cm\(^2\). Flux was measured, with a weight balance and a computer data-gathering system.

Preparation of test solutions. Fresh skim milk was obtained from a dairy plant (Zenrakure Tokyo Factory). Fresh Gouda cheese whey was obtained from the Snow Brand Cheese Laboratory in Yamanashi Prefecture.

For preparation of reconstituted skim milk and whey, skim milk powder and Gouda cheese whey powder (both Snow Brand Milk Products Co.) were dissolved in deionized water to give 8.5 wt% and 6.0 wt%, respectively, of the total solids, and stored before use for 24 hr at 10°C.

The gross composition of each feeding solution is shown in Table I. The protein content in skim milk was much higher than that in whey because casein is the main component of protein in skim milk.

Sodium azide (0.02%) was added to all feeding solutions to prevent microbial contamination. Pure water, microfiltered with a membrane (pore size, 0.8 \(\mu\)m) and deionized, was used.

UF test and flux measurement. A new membrane selected for a set level of pure water permeability, was used each time for UF of a test solution.

### Table I. Gross Components of Whey and Skim Milk

<table>
<thead>
<tr>
<th>Component</th>
<th>Whey</th>
<th>Skim milk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Reconstituted</td>
</tr>
<tr>
<td>Total solid</td>
<td>5.98</td>
<td>5.95</td>
</tr>
<tr>
<td>Lactose</td>
<td>4.41</td>
<td>3.61</td>
</tr>
<tr>
<td>Protein</td>
<td>0.79</td>
<td>0.85</td>
</tr>
<tr>
<td>Ash</td>
<td>0.57</td>
<td>0.50</td>
</tr>
<tr>
<td>Fat</td>
<td>0.19</td>
<td>0.07</td>
</tr>
</tbody>
</table>

*Fig. 2. Effect of Concentration Polarization on Permeation Flux, \(J_p\), of a Permeate with a Fouled Membrane versus Pressure. \(J_{bt}\) and \(J_{tf}\) are permeation fluxes of permeate for the fouled membrane before and after its being cleaned by hand with a soft sponge.*

All measurements of \(J_p\) were done at 25°C and at the stirrer rotation of 800 rpm. After 3–5 hr, when the flux reached a steady state at 0.4 MPa, the pressure dependency of \(J_p\) was measured in the range of 0.1 to 0.4 MPa. Whenever 10% of the initial feed amount had been filtered, the permeate was returned to the cell to keep the feed concentration approximately constant. After \(J_p\) was measured and the solution was discharged, the cell was rinsed with pure water or permeate. Then, the fluxes of the fouled membrane, \(J_{bt}\) or \(J_{tf}\), were measured with pure water or permeate. To remove the fouled layer, the surface of the membrane was gently cleaned by hand with a soft sponge. The fluxes of the membrane, \(J_{bt}\) and \(J_{tf}\), were also measured.

Adsortion test and flux measurement. The adsorption test was done under the same conditions as the UF test without the application of pressure (\(J_p = 0\)). The test continued for two days so that fouling because of adsorption would not be underestimated. Then, \(J_{bt}\), \(J_{bt}\), \(J_{bt},\) and \(J_{bt}\) were measured by the same procedure as for the UF test.

Flux measurement with permeate instead of pure water. For measurement of the flux for the fouled membrane, with use of permeate, the flux versus pressure was checked first, because the linearity of the flux against pressure might be affected by a difference in osmotic pressure between the two sides of the membrane which was caused by concentration polarization of lactose, which does not pass through a fouled membrane.\(^\text{11}\)

Typical fluxes of the membrane fouled by whey before and after hand cleaning with a soft sponge are shown in Fig. 2. The linearity of both flux and pressure was maintained at 0.1 MPa or less. At more than 0.1 MPa, flux seemed to be affected by the concentration polarization of lactose, mentioned previously. Therefore, all fluxes of the permeate for the fouled membranes were measured at 0.05 MPa.

A stirrer rotation of 100 rpm, which would not affect the status of fouling, was chosen.

Results and Discussion

Comparison of permeation fluxes of pure water and of the permeate for membranes fouled by adsorption and UF.

Resistance to permeation of a fouled membrane is generally calculated from its pure water flux. Nakanishi and Kessler\(^\text{13}\) reported that pure water cleans fouled mem-
branes, so we compared permeation fluxes of pure water and a permeate.

As a typical example, permeation fluxes of pure water and permeate for membranes fouled by the UF of fresh whey (Fig. 3) and because of adsorption (Fig. 4) are shown. Fluxes, \( J_{w,p} \), \( J_{p,p} \), \( J_{w,ap} \), and \( J_{p,ap} \), measured after hand cleaning with a soft sponge are also shown.

The flux in the UF of whey, \( J_w \), is shown for reference. In Fig. 3, \( J_w \) was less than \( J_{p,p} \) because of resistance to permeation because of concentration polarization of rejected solutes (whey protein and lactose), as discussed before.\(^1\)

The permeation fluxes of pure water and permeate for the membranes fouled by UF were almost identical with and without hand cleaning (Fig. 3). When fouling was caused by adsorption of whey, the fluxes were different depending on hand cleaning (Fig. 4). Permeation fluxes of pure water, \( J_{w,a} \) and \( J_{w,ap} \), were higher than those of permeate, \( J_{p,a} \) and \( J_{p,ap} \). This suggests that some of the fouling material may be cleaned away with pure water. The permeate, not water, goes through the pores during the UF of dairy liquids, so all resistances to permeation in this study were calculated from permeation flux data obtained with a permeate instead of pure water.

**Intrinsic resistance to permeation of the membrane**

The intrinsic resistance to permeation of the membrane was \( 1.70 \times 10^{12} \) m\(^{-1} \). This was only 9\% of the total resistance to permeation during the UF of fresh skim milk, showing how much fouling contributes to flux decline during the UF of dairy liquids.

**Resistance to permeation because of fouling**

The resistance to permeation because of fouling of whey and skim milk are shown in Figs. 5 and 6, respectively. Some differences in the profiles of the fresh and reconstituted solutions were observed in the state of fouling. The results suggested that the heat-denatured foulant in the reconstituted solution penetrated less into the pores of the membrane than the non-denatured foulant in the fresh solution. Therefore, \( R_{ad,a} \) was larger for the reconstituted whey than for the fresh whey (Fig. 5), and \( R_{ad,w} \) was larger for the fresh skim milk than for the reconstituted skim milk (Fig. 6), because of the effect of casein, discussed below.

With whey, resistance to permeation because of fouling on the surface by filtration, \( R_{f,s} \), was the largest factor, and resistance to permeation because of fouling in the pores by filtration was the smallest factor (close to zero).

Resistance to permeation at the surface (by adsorption and...
by filtration) exceeded 70% of the total resistance because of fouling. These results are consistent with previous reports that fouling, which causes flux decline, occurs mainly on the surface.\(^2,3\)

For skim milk, resistance to permeation because of fouling by adsorption (on the surface and in the pores) was the main factor in fouling, causing about 60% of total resistance to permeation. Resistance to permeation because of fouling on the surface during filtration was the smallest factor with skim milk, but the largest factor for whey. Resistance to permeation because of fouling in the pores during the filtration of skim milk exceeded that for whey. Probably the smaller resistance caused by fouling on the surface during filtration corresponded to the larger resistance caused by fouling in the pores during filtration. In the UF of whey, the greater resistance caused by fouling on the surface during filtration may correspond to the prevention of fouling in the pores.

Fouling materials in the UF of whey have been thought to be mainly whey protein.\(^10\) Fouling materials in the UF of skim milk have been reported to be whey protein.\(^9,11\) Therefore, we expected the state of fouling in the UF of whey to be similar to that in the UF of skim milk. However, as mentioned previously, they were different. What accounts for the difference? There are two main ways in which whey and skim milk differ: their pH, and the presence of milk protein (casein), which is abundant in skim milk, but not in whey.

Nilsson\(^17\) reported that resistance because of fouling by adsorption was higher at pH 6.0 than that at pH 6.8 in the UF of reconstituted whey protein solution. In our study, the resistance because of fouling with skim milk at pH 6.9 was higher than that with whey (at pH 6.4). Therefore, the difference in fouling caused by adsorption with skim milk and whey is not caused only by the difference of pH.

There are two ways in which casein might prevent fouling on the surface: one is by covering the surface as a deposit, and the other is by scraping off of fouling on the surface by the casein micelles. Because casein has not been detected as a foulant\(^13\) and because resistance to permeation because of fouling in the pores by filtration increased (Fig. 6), it is more likely that the latter way takes place.

The resistance to permeation caused by fouling in the pores is the largest and other kinds of resistance are close to zero for membranes fouled during the UF of skim milk to concentration factor 6, when the hand-cleaning method is used.\(^9\) The more the UF concentrates the skim milk, the larger resistance caused by fouling in the pores becomes, because resistance caused by fouling on the surface is small.

Understanding the difference in the fouling states with skim milk and whey, the use of different methods to prevent fouling has to be considered. In the UF of skim milk, membranes with a low adsorption effect are preferred, and care should be taken to use detergent that more easily goes through the pores to remove fouling materials during cleaning. In the UF of whey, the method should be aimed at decreased fouling on the surface, by, for example, intermittent cleaning with a sponge ball for a tubular module.

The total permeation resistance caused by fouling was 1.67 for fresh whey, 1.91 for reconstituted whey, 2.30 for fresh skim milk and 1.87 for reconstituted skim milk (units, $10^{13} \text{ m}^{-1}$). The values were not as different as the flux differences (Fig. 7). Therefore, the large difference in fluxes with whey and skim milk was not caused by fouling resistance but probably by casein, although the mechanism of flux decline because of casein is not known.

The fluxes of the reconstituted solutions were higher than those of the fresh solutions (Fig. 7). Mohamed et al.\(^18\) reported that the flux during the UF of reconstituted skim milk is higher than that of fresh skim milk, and suggested that whey protein, denatured by heat, caused less fouling and resulted in a higher flux. In our study, the results support their suggestion, because the total resistance to permeation because of fouling by reconstituted skim milk was smaller than that with fresh skim milk. The results with whey were opposite.

### References