Effect of Interparticle Electrostatic Double Layer Interactions on Permeate Flux Decline in Crossflow Membrane Filtration of Colloidal Suspensions: An Experimental Investigation

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A systematic study on the effect of electrostatic double layer interaction on permeate flux decline and deposit cake formation in crossflow membrane filtration of colloidal suspensions is reported. Three monodisperse silica suspensions with diameters of 47, 110, and 310 nm were used as model colloids, and a tubular zirconia membrane with an average pore diameter of 20 nm was used as a model membrane. The magnitude and range of the electrostatic double layer interactions were controlled via changes in solution ionic strength and pH. The coupling between colloidal interactions and hydrodynamic forces was investigated by changing the transmembrane pressure and particle size. The results indicate that the rate of flux decline is strongly dependent on solution ionic strength and, to a much lesser degree, on solution pH (for the investigated pH range 6.1–10.0). Variations in flux decline rate with solution ionic strength are especially significant as the particle size decreases. Particle cake thickness, permeability, and porosity generally increased with a decrease in solution ionic strength for a given particle size. For given physical and chemical conditions, the cake layer porosity increased with decreasing particle size, while cake permeability decreased with decreasing particle size. These trends are consistent with the increased importance of double layer repulsive forces in controlling the cake layer structure as the solution ionic strength and particle size decrease. Pressure relaxation experiments indicated that the particle cake layer is reversible, implying no irreversible deposition (attachment) of silica colloids onto the zirconia membrane surface.

Key Words: crossflow filtration; permeate flux decline; particle cake layer; interparticle interactions; colloid membrane filtration; concentration polarization; cake layer permeability; cake layer reversibility; membrane fouling.

1. INTRODUCTION

Crossflow membrane filtration is now an established process for the removal of colloidal particles from industrial and domestic wastewater and for the concentration of proteins and biological particles from suspensions (1, 2). The major advantage of crossflow filtration is that the suspension to be filtered flows parallel to the membrane surface, therefore reducing the accumulation of colloidal particles near the membrane surface. However, significant initial permeate flux decline cannot be avoided due to the hydraulic resistance of the accumulated particle (cake) layer (3–6). The observed decline in permeate flux during colloidal crossflow filtration is typically rapid at the start of the filtration process and then gradually diminishes until a steady-state (or pseudo-steady-state) flux is attained (4–6).

Permeate flux decline in crossflow filtration of colloidal suspensions is governed by the processes of concentration polarization and particle accumulation in a cake layer on the membrane surface (1, 4–7). These processes, in turn, are controlled by the hydrodynamic and physicochemical operating conditions, such as transmembrane pressure, particle size, crossflow velocity, ionic strength, and solution pH. There are numerous studies on permeate flux decline and the steady-state flux in crossflow membrane filtration of colloidal suspensions (4, 6–8, and references therein). However, systematic experimental and theoretical studies that consider the coupled effects of the above variables on permeate flux decline are rather scarce.

Since particle–membrane and particle–particle interactions are controlled by the physicochemical and hydrodynamic conditions of the filtration process (9–13), it is expected that changes in the solution chemistry (e.g., ionic strength and pH), particle size, and transmembrane pressure would result in marked changes in flux decline behavior and cake layer structure. For example, in a non-coagulating (stable) colloidal suspension, increasing the ionic strength would compress the diffuse double layer around the charged particles, allowing the particles to densely pack in the cake layer, thus reducing permeate flow (3, 11, 12). Variations in solution pH affect the surface charge density of the particles, thereby affecting the magnitude of the interparticle repulsive double layer forces (3, 12). As the applied transmembrane
pressure increases, compressive forces that act against the repulsive forces in the cake increase, resulting in a denser particle cake layer of lower permeability (3). Finally, as particle size decreases below about 100 nm, the range of interparticle electrostatic repulsive forces can approach, and may even exceed, the particle radius at low ionic strength, which results in a significant increase in cake layer porosity and permeability (3, 12, 14).

This paper presents a systematic experimental investigation of the effects of ionic strength, solution pH, particle size, and transmembrane pressure on the behavior of permeate flux decline in crossflow membrane filtration of aqueous colloidal suspensions. Also presented is an evaluation of the coupling between these parameters and their influence on permeate flux decline and cake layer formation. Changes in crossflow velocity were not examined since our recent work (4) demonstrated that, under laminar flow conditions, crossflow has a negligible effect on permeate flux decline during the initial stages of filtration, before a steady-state flux is attained. Another important goal of the study is to provide accurate and detailed experimental data that would enable validation and improvement of future fundamental crossflow filtration models that consider interparticle interactions.

2. MATERIALS AND METHODS

2.1. Preparation and Characterization of Colloids

2.1.1. Colloidal Suspensions

Three different silica (SiO₂) particles, denoted as ST-XL, PST-1, and PST-3 by the manufacturer (Nissan Chemicals, Tarrytown, NY), were selected as model colloids for the membrane filtration experiments. Dynamic light scattering (DLS) measurements and TEM images were used to confirm particle size and monodispersity. The mean hydrodynamic diameters of the PST-1 and PST-3 particles, measured by DLS (Nicomp Model 370, Particle Sizing Systems, Santa Barbara, CA), were 110 and 310 nm, respectively, with a coefficient of variation of 10%. The measured mean particle diameter by TEM of the ST-XL particles was 47 nm with a standard deviation of 14 nm. The densities of the ST-XL, PST-1, and PST-3 particles, obtained gravimetrically, were 2.36, 2.27, and 2.28 g/cm³, respectively. The colloidal stability of the silica suspensions for all pH and ionic strength conditions investigated in the crossflow filtration experiments was determined by measuring changes in particle mean hydrodynamic diameter with time using DLS.

2.1.2. Electrokinetic Measurements

Electrophoretic mobility measurements were used to determine the electrokinetic properties of the silica particles for the various experimental chemical conditions. These conditions included an ionic strength range of 10⁻⁴–10⁻¹ M KCl and the pH values of 6.1, 8.3, and 10.0. The measurements were conducted using a Lazer Zee Model 501 apparatus (Pen Kem Inc., Bedford Hills, NY) and a laser Doppler velocimetry apparatus (Zetaplus, Brookhaven Instruments Corp., Holtsville, NY).

2.2. Crossflow Membrane Filtration System

2.2.1. Zirconia Membrane

The membrane used for the crossflow filtration experiments was a 25 cm long tubular zirconia membrane (Membralox, US Filter Corp., Warrendale, PA) with a 7 mm inner diameter and an average pore size of 20 nm. It was mounted in a stainless-steel membrane module (US Filter Corp., Warrendale, PA). According to the manufacturer, the membrane can be used over a pH range of 0.5–13.5 and temperatures ranging from 4 to 316°C. The manufacturer also reported hydraulic membrane permeability of 1.07 × 10⁻³ – 1.18 × 10⁻³ m s⁻¹ Pa⁻¹ at 20°C.

2.2.2. Crossflow Membrane Filtration Test Unit

A schematic diagram of the laboratory-scale membrane test unit used in the crossflow filtration experiments is shown in Fig. 1. The colloidal silica suspension, held in a 5 liter polypropylene reservoir, was fed to the inlet port of the membrane module by a peristaltic pump (Easy-load, Model 7518-12, Cole-Parmer Instrument Co., Niles, IL). The flow rate of the feed suspension was measured by a flow meter (King Instrument Co., Huntington Beach, CA) connected between the pump outlet and the inlet to the membrane module. The transmembrane pressure was controlled by a needle valve installed on the outlet side of the membrane module. The transmembrane pressure was measured by a variable reluctance differential pressure transducer (Model DP15-44, Validyne Engineering Corp., Northridge, CA) connected to the inlet side of the membrane module and displayed by a digital transducer indicator (Model CD223,
Validyne Corp., Northridge, CA). Pressure measurements over a range of 20.7–62.1 kPa (3–9 psi) were made with a maximum error of ±0.5% of full scale. The temperature of the feed solution was controlled by immersing the feed container in a water bath. The water bath temperature was controlled by a stainless-steel coil with water fed from a recirculating water chiller (Model 6100, Fisher Scientific, Pittsburgh, PA). Permeate flux was measured by weighing permeate collected in a preweighed beaker.

### 2.3. Crossflow Filtration Experiments

#### 2.3.1. Experimental Procedure

Flux measurements for all experiments were taken over a period of 120 min, except for the pressure−relaxation experiments (Section 2.3.3), for which measurements were taken for a total period of approximately 180 min. Each permeate sample was collected over a period of 4 min during the first 80 min of the experiment and over a period of 9 min during the last 40 min of the experiment. Several of the filtration experiments were repeated more than twice, and the results were very reproducible.

The filtration system was cleaned by pumping NaOH (pH 11) and HCl (pH 3) solutions through the membrane at zero transmembrane pressure for a period of 2 h before each experiment. The membrane was then conditioned by flowing a particle-free solution, having solution chemistry (described later) identical to that used in the subsequent colloidal filtration, for approximately 1 h.

#### 2.3.2. Experimental Conditions

The effect of ionic strength on permeate flux decline and cake layer structure was studied by varying KCl concentration (10⁻¹, 10⁻², 10⁻³, and 10⁻⁴ M). The three different pH conditions used were obtained by the addition of NaHCO₃ solution (to obtain pH of 6.1 and 8.3) and by the addition of NaOH from a 1 M stock solution (to obtain pH 10.0). The varied physical parameters included transmembrane pressure of 20.7, 41.4, and 62.1 kPa (3, 6, and 9 psi) and the three different particle sizes (47, 110, and 310 nm). The crossflow velocity of 0.246 m/s corresponded to a shear rate of 280 s⁻¹ and a Reynolds number of 1720 (based on the crossflow velocity and inner membrane diameter).

#### 2.3.3. Pressure Relaxation Experiments

Pressure relaxation experiments were conducted to investigate the reversibility of the cake layer of the 47 nm particles at three different ionic strengths (10⁻¹, 10⁻² and 10⁻³ M) and a transmembrane pressure of 41.4 kPa (6 psi). Once the filtration experiment was terminated, the needle valve (Fig. 1) was completely opened to reduce the transmembrane pressure to zero. As a consequence, permeation through the membrane was eliminated, while maintaining the same crossflow velocity. After 1 h, the valve was partially closed again to obtain a transmembrane pressure equal to that used in the initial membrane filtration experiment (i.e., 41.4 kPa). Flux measurements were then resumed for a period of 60 min.

#### 2.3.4. Quantification of Cake Layer Mass

The variation of cake mass with time during the course of the crossflow filtration process was also determined experimentally. The mass of the deposited cake layer was determined by sampling the feed solution at predetermined time intervals during the filtration experiments. A feed sample was collected at the start of the experiment and every 2–10 min for the duration of the experiment. Samples were collected using a 20 ml volumetric pipette and subsequently analyzed for particle concentration by UV absorbance measurements (Model 8452A, Hewlett Packard, Palo Alto, CA). The corresponding mass of the particles deposited on the membrane surface was calculated from a simple mass-balance, using particle feed concentration values obtained during the filtration runs.

### 3. RESULTS AND DISCUSSION

#### 3.1. Colloidal Suspensions and Zirconia Membrane

The stability of the colloidal suspensions at different ionic strengths and pH levels was evaluated by DLS particle size measurements. Suspension stability was indicated by invariance of particle size with time. An exception was the highest ionic strength of 10⁻¹ M at which a very slow aggregation was observed for all particle sizes. Therefore, deposited mass measurements were not conducted at that ionic strength.

The electrophoretic mobility of the smaller (47 and 110 nm) particles studied (Table 1) became less negative with increasing ionic strength, while remaining relatively constant from pH 10.0 to 8.3. The electrophoretic mobilities are also seen to decrease from pH 8.3 to 6.1. These results are expected for silica which has a point of zero charge (PZC) of about 2 (15) and generally exhibits a constant electropho-
The initial permeate flux of the particle-free electrolyte solution increased as the pH was lowered and approached the PZC of zirconia, which is reported to be at pH 5.8 (16). Membrane initial permeate flux also increased at higher ionic strengths at pH 8.3 and 10.0. The increase in membrane permeate flux is postulated to be due to the decrease in the apparent viscosity of the permeating solution near the surface of the membrane pores at low pH or high ionic strength conditions. This view is supported by the studies of Bowen and Jenner (3) and Levine et al. (17) who demonstrated that, as surface charge of narrow capillaries approaches zero, or when the counterionic environment near a charged surface is dense, the apparent viscosity of the flowing solution in the capillaries decreases. Previous experimental studies by Henniker (18) with porcelain filters and KCl solutions of various concentrations, and by Huismann et al. (19) with an α-alumina microfiltration membrane using NaCl and MgCl₂ solutions, also confirm the above explanation.

The influence of capillary (or pore) surface charge and solution ionic strength on the liquid apparent viscosity can be explained by the so-called electroviscous effect. This effect refers to the back-flow of counterions and water in the double layer adjacent to the capillary pore surface due to a streaming potential that develops between the capillary ends. The electroviscous effect is least pronounced at high ionic strength or near the capillary surface point of zero charge where double layer effects are negligible. At high ionic strength or low surface charge, the permeating solution appears to exhibit a reduced viscosity when its flow rate is compared with the flow at low ionic strength and high surface charge.

Permeate flux decline curves for the 47 nm colloidal suspension are depicted in Fig. 3. The initial permeate flux (at \( t = 0 \)) is highest for the higher ionic strength and lower pH conditions. These observations are attributed to the electroviscous effect, as discussed above. Despite differences in the initial flux, permeate flux values at the end of the filtration experiments, where cake layer resistance dominates membrane resistance to permeate flow, are essentially identical for all pH values at a given ionic strength. This result demonstrates that, at a given ionic strength, the dominating cake layer resistance is essentially independent of the solution pH investigated. At the pH values of 10.0 and 8.3, the particle electrophoretic mobility does not vary significantly (see Table 1) and, consequently, the magnitude of the interparticle double layer repulsive forces changes only slightly. Even though the electrophoretic mobility became less negative from pH 8.3 to 6.1, changes in the magnitude of the repulsive double layer forces and their effect on cake layer resistance to permeate flow are apparently insignificant when compared to variations in the range of these forces, which is controlled by the solution ionic strength, as discussed in the following subsection.
3.2.2. Effect of Ionic Strength

When the ionic strength increases, the permeate flux decline becomes more severe, and the approach to steady-state flux is faster than in the low ionic strength case. This behavior is demonstrated in Fig. 4 in which permeate flux is normalized with respect to the initial flux. The above trend can be rationalized by noting that the interparticle distance in the cake layer decreases at higher ionic strengths due to a decrease in the range of the electrostatic double layer repulsive forces (3, 10, 11, 14); consequently, the cake layer is more densely packed and the resistance to permeate flow increases.

A measure for the range of the electrostatic repulsive force between charged colloidal particles and, thus, for the interparticle distance, is the Debye screening length, $\kappa^{-1}$. For a 1:1 electrolyte, the Debye screening length (in SI units) is given by

$$\kappa^{-1} = \left( \frac{2 \times 10^3 e^2 N_A I}{\epsilon_i \epsilon_0 kT} \right)^{-1/2}, \quad [1]$$

where $e$ is the elementary charge, $N_A$ is Avogadro’s number, $I$ is the ionic strength (mol/L), $\epsilon_i$ is the dielectric permittivity of water, $\epsilon_0$ is the permittivity of free space, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. Equation [1] indicates that when the ionic strength increases, the range of the repulsive force between the colloidal particles decreases; the experimental results given in Fig. 4 are in qualitative agreement with this trend. Similar observations were made by McDonogh et al. (10, 11), Bowen and Jenner (3), and Zhu and Elimelech (20). McDonogh et al. (21) also noted that for particles with diameters smaller than

<table>
<thead>
<tr>
<th>Particle diameter (nm)</th>
<th>Ionic strength (M)</th>
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<tr>
<td></td>
<td>$10^{-4}$</td>
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<tr>
<td>47</td>
<td>0.8</td>
</tr>
<tr>
<td>110</td>
<td>1.8</td>
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<tr>
<td>310</td>
<td>5.1</td>
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strength rises, the particle packing density is expected to increase (Section 3.2.2). Also, as the transmembrane pressure increases, the higher permeation drag and compressive forces exerted on the cake layer favor a thicker and more densely packed cake layer. In contrast, at low ionic strength conditions (10^{-3} and 10^{-4} M) and the lowest transmembrane pressure (20.7 kPa), particle deposition and cake layer buildup were not significant enough to cause a rapid initial flux decline (see also Section 3.3). Indeed, only an 11% overall decline in permeate flux (from 1.45 \times 10^{-5} to 1.29 \times 10^{-5} m/s) was observed for the lowest ionic strength (10^{-4} M) and the lowest transmembrane pressure (20.7 kPa) filtration conditions. This observation is indicative of operation approaching the critical flux in crossflow membrane filtration, which is the permeate flux below which particles do not deposit on the membrane surface (9, 22).

The results depicted in Fig. 5 seem to indicate that, at a given ionic strength, nearly the same steady-state flux limit is reached regardless of the applied transmembrane pressure. This apparently pressure-independent steady-state flux value is known as the limiting flux. At the limiting flux regime, an increase in the applied pressure results in a corresponding increase in cake layer buildup so that the overall resistance to permeate flow remains nearly unchanged. This observation, however, is somewhat misleading, since a close inspection of the data in Fig. 5 and Table 3 reveals that, at a given ionic strength, the actual permeate flux values at the steady-state limit differ by as much as 24%. As expected, the above results indicate that the terminal flux is higher at low ionic strength (1.29 \times 10^{-5} m/s for 10^{-4} M and 20.7 kPa) than at high ionic strength (0.80 \times 10^{-5} m/s for 10^{-2} M and 20.7 kPa) because of the greater cake permeability.

It is important to note that, when the above results are analyzed as normalized flux versus cumulative permeate volume rather than time, the obtained normalized flux decline curves still exhibit greater flux decline at higher transmembrane pressures, as illustrated in Fig. 6 for the 10^{-4} and 10^{-3}

![FIG. 5. Effect of transmembrane pressure on permeate flux decline at ionic strengths of 10^{-4}, 10^{-3}, and 10^{-2} M KCl. The filtration conditions employed were particle size, 47 nm, pH 10.0, particle volume concentration, 0.01%, crossflow velocity, 0.246 m/s, and temperature, 20.0°C.](image)

about 100 nm, the effect of double layer repulsive forces on permeate flux decline behavior becomes quite significant. Our results in Fig. 4 show that as the particle radius \( a_p \) decreases and the Debye screening length approaches values comparable to the actual particle size (i.e., small \( \kappa a_p \) as shown in Table 2), changes in solution ionic strength have an important effect on permeate flux behavior. Furthermore, for a given ionic strength, initial permeate flux decline becomes more rapid as the particle size decreases, as can be seen from the slopes of the curves in Fig. 4. In their theoretical analysis, Bowen and Jenner (3) indeed demonstrated that, for small colloidal particles (less than ca. 100 nm), the electrostatic double layer repulsive force is, by far, the dominating interparticle force in the cake layer when compared with other interparticle surface forces.

### 3.2.3. Effect of Transmembrane Pressure

Permeate flux declines faster at high transmembrane pressures and high ionic strength conditions as depicted in Fig. 5. This trend is attributed to the higher convective mass of particles toward the membrane surface at higher pressures and to the dependence of the cake layer packing density on ionic strength and transmembrane pressure. As the ionic strength rises, the particle packing density is expected to increase (Section 3.2.2). Also, as the transmembrane pressure increases, the higher permeation drag and compressive forces exerted on the cake layer favor a thicker and more densely packed cake layer. In contrast, at low ionic strength conditions (10^{-3} and 10^{-4} M) and the lowest transmembrane pressure (20.7 kPa), particle deposition and cake layer buildup were not significant enough to cause a rapid initial flux decline (see also Section 3.3). Indeed, only an 11% overall decline in permeate flux (from 1.45 \times 10^{-5} to 1.29 \times 10^{-5} m/s) was observed for the lowest ionic strength (10^{-4} M) and the lowest transmembrane pressure (20.7 kPa) filtration conditions. This observation is indicative of operation approaching the critical flux in crossflow membrane filtration, which is the permeate flux below which particles do not deposit on the membrane surface (9, 22).

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### Table 3

<table>
<thead>
<tr>
<th>Ionic strength (M)</th>
<th>Transmembrane pressure (kPa)</th>
<th>Initial Flux (10^{-5} m/s)</th>
<th>Final Flux (10^{-5} m/s)</th>
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<tr>
<td>10^{-4}</td>
<td>20.7</td>
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<td>1.29</td>
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</tr>
<tr>
<td>10^{-3}</td>
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<td>10^{-2}</td>
<td>20.7</td>
<td>1.50</td>
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<tr>
<td>10^{-2}</td>
<td>61.2</td>
<td>4.57</td>
<td>0.99</td>
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M runs. This observation clearly indicates that permeation
drag and compressive forces are indeed important factors
in controlling the flux behavior at different transmembrane
pressures (4, 23). Song and Elimelech (23) have recently
presented a theoretical investigation of particle deposition
onto a permeable surface under laminar flow conditions.
Their theoretical analysis indicates that the rate of colloid
deposition onto a permeable surface is controlled by an inter-
play between double layer repulsion and the opposing hydro-
dynamic force (permeation drag) resulting from the convect-
tive flow toward the membrane. This unique mechanism,
which is nonexistent in particle deposition phenomena onto
impermeable surfaces, can account for the differences in
the permeate flux behavior shown in Fig. 6 for the various
transmembrane pressures.

3.3. Particle Cake Layer Porosity and Mass

Permeate flux decline, in the present study, was attributed
to the buildup of a concentrated particle cake layer near the
membrane surface. The accumulation of particles in the cake
layer, expressed in terms of the mass of the cake layer per
unit membrane surface area, is shown in Fig. 7 for the three

![Graph](image)

**FIG. 6.** Normalized flux as a function of total accumulated permeate
volume for the filtration experiments at $10^{-4}$ and $10^{-3}$ M shown in Fig. 5.
Accumulated volume was obtained from integration of the permeate flux
with respect to time.

![Graph](image)

**FIG. 7.** Variations in deposit cake layer mass with time at different
ionic strengths for the 47, 110, and 310 nm particles. The filtration condi-
tions employed were pH 10.0, transmembrane pressure, 41.4 kPa (6 psi),
particle volume concentration, 0.01%, crossflow velocity, 0.246 m/s, and
temperature, 20.0°C.

particle suspensions at three different ionic strengths. The
mass of the cake layer for all experimental runs, regardless
of particle size, pH, or ionic strength, increased with time.
These results are consistent with the permeate flux data (Fig.
4) which indicate decline in permeate flux due to increased
resistance of the cake layer to permeate flow as particles
accumulate in the cake layer. It is also noted that more mass
was deposited in the case of the 47 nm and, to a lesser
extent, the 110 nm particles at lower solution ionic strengths.
No variation in the mass of deposited particles with solution
ionic strength was observed for the largest, 310 nm, particles.
A closer examination of Figs. 4 and 7 reveals that, even
though the mass of deposited particles for the cake layers
of the 47 and 110 nm colloidal suspensions is greater at
lower ionic strengths, the corresponding permeate fluxes are
also greater than those at the higher ionic strengths. These
rather interesting results may be better analyzed in terms
of the dependence of cake layer resistance, porosity, and
thickness on solution ionic strength as described below.

The cake porosities at filtration time $t = 120$ min were
calculated using the permeate flux and cake layer mass data
(Figs. 4 and 7, respectively) as follows. The specific cake
where $M_c$ is the total number of particles (per unit area) accumulated in the cake layer, as calculated from the deposited mass data and particle density, and $\epsilon$ is the porosity obtained from Eq. [3].

The calculated cake layer porosities and thicknesses for the three particle suspensions are given in Fig. 8. It is observed that cake layer porosity and thickness are highest ($\epsilon = 0.744$ and $\delta_c = 60.5 \mu m$) for the smallest (47 nm) particles and when the solution ionic strength is lowest ($10^{-4}$ M). The results demonstrate a significant increase in cake layer porosity and thickness with decreasing solution ionic strength for the 47 nm particles, and to a lesser degree, for the 110 nm particles. No significant changes in cake porosity or thickness with solution ionic strength were obtained for the 310 nm particles. Examination of the data in Table 2 and Fig. 7 reveals that the increase in cake porosity with decreasing ionic strength for a given colloidal suspension correlates with the decrease in the parameter $kappa p$. For the 47 nm particle suspension, very porous cake layers are formed when $kappa p$ approaches values comparable to 1 ($\epsilon = 0.744$ for $kappa p = 0.8$). These significantly higher porosities of the smaller particle cake layers explain the unusually high permeate flux and cake layer thickness obtained in the filtration of the smaller particles.

![Fig. 8](image_url)  
**Fig. 8.** Particle cake layer porosity (a) and thickness (b) for the 47, 110, and 310 nm particles.

Resistance can be calculated from Darcy’s law which relates the permeate flux, $J$, to the total resistance to permeate flow:

$$J = \frac{\Delta P}{\mu (R_m + R_c)}, \quad [2]$$

where $\Delta P$ is the transmembrane pressure, $\mu$ is the liquid viscosity, $R_m$ is the membrane resistance, and $R_c$ is the cake resistance. The latter may be expressed in terms of the specific cake resistance, $\alpha$, as $R_c = \alpha M_a$, where $M_a$ is the accumulated mass per unit area on the membrane surface. The specific cake resistance can be further related to the cake porosity (or void fraction), $\epsilon$, via the Carman–Kozeny equation

$$\alpha = \frac{45(1 - \epsilon)}{\rho a_p^2 \epsilon^2} \quad [3]$$

where $\rho$ is the particle density and $a_p$ is the particle radius. Cake layer thickness, $\delta_c$, can also be calculated from the deposited mass data using a simple mass balance on the cake layer (7):

$$\delta_c = \left( \frac{2 \pi a_p^3}{\epsilon} \right) M_c, \quad [4]$$

![Fig. 9](image_url)  
**Fig. 9.** Variations in deposit cake layer mass with time for a range of transmembrane pressures at high ($10^{-2}$ M KCl) and low ($10^{-4}$ M KCl) ionic strengths. The filtration conditions employed were particle size, 47 nm, pH 10.0, particle volume concentration, 0.01%, crossflow velocity, 0.246 m/s, and temperature, 20.0°C.
In addition to changes in solution chemistry, variations in the transmembrane pressure can also significantly affect cake layer formation, as illustrated in Fig. 9 for the 47 nm particles. The results indicate that higher particle mass accumulates in the cake layer at higher applied transmembrane pressures. The results also demonstrate that there is an increase in the mass of deposited particles at the lowest ionic strength ($10^{-4}$ M) for all transmembrane pressures. Under these conditions, at which cake layer porosity and permeability are higher, particle convection to the membrane surface is expected to increase, resulting in a thicker cake layer.

In view of the above trends in cake layer accumulation and porosity, a mechanism for cake layer formation for the smaller particles is suggested for the two extreme conditions of high and low solution ionic strengths. During the initial stages of the filtration process, in the absence of a substantial cake layer, the particles are transported by convection to the membrane surface with a maximum convective driving force. The convection of particles to the membrane surface decreases with decreasing permeate flux and cake buildup. However, the permeate flux, and hence cake buildup, is more pronounced at low ionic strengths for which double layer repulsive forces between particles are significant (both in range and in magnitude), resulting in the formation of a thicker and more porous cake layer.

Finally, it should be noted that the electroviscous effect, which was shown to influence the intrinsic membrane resistance and initial permeate flux (Section 3.2.1), may also influence the permeate flow through the particle cake layer. However, Bowen and Jenner (3) pointed out that, for cakes of small (<100 nm) charged colloidal particles, the electroviscous effect is important only at low solution ionic strength and high particle zeta (surface) potential. Nevertheless, under such conditions, the electroviscous effect is expected to be of secondary importance to the very pronounced effect of the repulsive double layer interactions on cake layer structure and permeate flux.

### 3.4. Pressure Relaxation and Cake Reversibility

Transmembrane pressure relaxation experiments were conducted to examine the reversibility of the cake layers at different solution chemistries. Figure 10 demonstrates that permeate flux decline before and after pressure relaxation was essentially the same at all solution ionic strength conditions. These results suggest that cake formation is reversible, and membrane fouling (i.e., permanent, irreversible attachment of particles in the membrane pores or onto the membrane surface) did not occur under the experimental conditions used. Namely, when the transmembrane pressure is relaxed, the colloidal particles diffuse away from the higher concentration region at the membrane surface back into the bulk solution.

![Permeate flux decline before (open symbols) and after (filled symbols) relaxation of transmembrane pressure for a range of ionic strengths.](image)

**FIG. 10.** Permeate flux decline before (open symbols) and after (filled symbols) relaxation of transmembrane pressure for a range of ionic strengths. The filtration conditions employed were particle size, 47 nm, pH 10.0, transmembrane pressure, 41.4 kPa (6 psi), particle volume concentration, 0.01%, crossflow velocity, 0.246 m/s, and temperature, 20.0°C.

### 4. CONCLUSION

The structure and mass of the deposited cake layer in crossflow membrane filtration of colloidal suspensions are markedly affected by solution chemistry and hydrodynamic filtration conditions. In turn, the cake layer structure significantly affects permeate flux decline behavior. Solution ionic strength controls the range of the interparticle electrostatic double layer interactions and, hence, has a pronounced effect on cake layer porosity and the resulting permeate flux. A marked effect of ionic strength on permeate flux decline is observed for small colloidal particles (the 47 nm and, to a lesser extent, the 110 nm colloidal suspensions), but it is negligible for larger colloidal particles (the 310 nm colloidal suspension). In contrast, solution pH (in the range investigated) has a marginal effect on permeate flux behavior. The results suggest that cake layer structure and permeate flux behavior are determined by the coupled effects of permeation drag, which is governed by the applied transmembrane pressure, and the electrostatic double layer repulsion between the colloidal particles, which is governed by solution ionic strength. For instance, when the transmembrane pressure and solution ionic strength are low (20.7 kPa and $10^{-4}$ M, respectively), the permeation drag force is sufficiently low so that electrostatic double layer repulsion significantly inhibits cake layer buildup. In fact, under these conditions, the small reduction of only 11% in the initial permeate flux for the smallest (47 nm) particle suspension indicates operation very near to the critical flux. The unique coupling between permeate flux and cake layer properties also explains the higher deposited (cake layer) mass and permeate flux for...
crossflow experiments with small colloidal particles at low ionic strength conditions.

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