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MEASUREMENT OF THE DEPOSIT FORMED BY A PARTICULATE SUSPENSION ON A MEMBRANE

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ABSTRACT

A technique of differential profilometry is reported which allows direct measurement of the deposits formed on a membrane. The technique is described and demonstrated to be capable of resolving deposits of one μm or less. Simultaneous measurements of the flux collected in a segmented manner along the operating membrane allow the calculation of the resistivity of the deposit formed. Microfiltration experiments at different velocities result in thinner deposits at higher velocities and higher fluxes. The deposits initiate downstream of the entrance, build somewhat erratically, then inexplicably diminish near the downstream end of the membrane. The method may lead to optical methods capable of continuous observations during operation.

INTRODUCTION

Porter (1) showed for some macromolecular solutes diffusion theory could offer solutions to the concentration polarization leading to specification of the permeate flux. He also found that particulate suspensions (e.g. PSL) deviated substantially from the expected behavior predicted by diffusive theory. Leonard and Vassilieff (2) cited the importance of rheology in the prediction of flux and assumed no diffusion.

Several investigators have begun to evoke shear-induced diffusion to explain the higher rates of filtration demonstrated by suspensions. Among these are Leighton and Acrivos (3), Zydney and Colton (4), and Romero and Davis (5). The latter measured the accumulation of solids on an operating membrane using a cathetometer in a rectangular flow passage. The particles were relatively large (40μm) and formed deposits of up to 5mm in a channel of depth 10mm. Their fluid was a glycerol solution controlled to yield a controlled density with a result of relatively low shear rates (about 15 to 60 s^{-1}). This result showed the deposits to conform to the expectation of a theory based in shear-induced diffusion.

In the shear-induced diffusion models, the particles are allowed to diffuse away from the membrane counter to the filter flow until their concentration at the surface exceeds the point where the slurry is immobile. Then the particles form an immobile cake under the diffusion zone of a hydraulic resistance just enough to retard the filter flux to the point of incipient addition to the cake. Song and Elimelech (6) have proposed a diffusive model, not based on shear-induced diffusion, which is otherwise similar, having a diffusion layer riding over a cake considered immobile.

In what may be equivalent to the diffusion models but of different vantage, Datta (7) viewed the accumulation as a cloudy layer overrunning a creeping cake. The cloudy layer was viewed as the unbounded-on-one-side manifestation of the normal stress of a sheared slurry. The cake Datta and Gaddis (8) showed to have a concentration dependent on the compressive stress of the accumulated pressure from resisted permeate. The particles are able to undergo some compression because of the dispersion and electrostatic forces, and the net effect was determined based on properties of the cakes achieved in steady state.

Regardless of which mental concept and mathematical model for the formation of cakes on operating membranes is used, the existence of such cakes is unquestioned and there are few experiments or methods to evaluate the actual deposits. The deposits are expected to have hydraulic resistance in concert with a Kozeny equation or Ergun's equation (9) or the equivalent. Herein the Carman-Kozeny equation following the lead of Zydney and Colton (4) will be used. In it the pressure drop through a bed of non-interacting spheres of radius, R, in concentration, C_c, and thickness, δ, can be expressed as

$$\Delta P = \frac{9KJ\mu_0 C_c^2 \delta}{R^2 (1 - C_c)^3}. \quad (1)$$

Here K is the Kozeny constant with an expected value of 5, though other values of K cannot be ruled out. J is the superficial flux through this packed bed and μ_0 is the solvent viscosity. A simple resistance model states that

$$\Delta P = r\delta J(x) = \Delta PTM - R_m J(x), \quad (2)$$

where ΔPTM is the total transmembrane pressure and $R_m J(x)$ is the pressure drop across the membrane. The trans-cake pressure drop, ΔP, from equation (1) may be

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clearly expressed as rδ, where r is a resistivity. The objective of this work was to perform a contemporaneous measurement of the thickness and resistance to flow of membrane cakes.

METHODS AND MATERIALS

A membrane test cell with a rectangular flow channel was constructed. The dimensions of the membrane surface are: width — 58 mm × length — 240 mm and the height of the channel — carefully determined by direct measurement and by confirmation of pressure drop — 3.5 mm ±0.05mm. The membrane was constructed of 1.2-mm thick stainless steel filter stock (Mott Metallurgical 0.5-μm rating). The pores in the filter stock, of dimensions roughly 2 to 5 μm at the surface, were impregnated with titania slurry and sintered as in Gaddis and Jernigan (10). The surface thus formed is smooth to within a few microns and porous with intervening metal solids of characteristic dimension in the plane of 20 μm. The permeate chamber is divided into ten segments estimated to collect the flow separately and proportionately. The center eight are equal and the ends are slightly larger; it is estimated that no significant crossover flow should occur.

Suspensions of titania (rutile, R101, duPont) having a near-uniform size distribution of diameter 300nm were used for all testing. Water was RO permeate. To mixtures of 70% titania, 30% water, were added NaOH to pH= 10 and 0.3% Nopcosperse 44 dispersant. This mixture was placed into an attritor mill with 1.5 mm media and blended 15 min. The slurry was removed and separated from the media and used for stock suspensions for the testing. This same mixture was used by Datta (7) to obtain viscosity data at volume concentrations up to 0.548, where the material becomes lumpy, probably a Bingham plastic. This value is very near the volume concentration range of 0.54-0.58 which Datta found to satisfy the average cake properties in agreement with both his data and Porter's (1).

Profilometry and Differential Profilometry

For measurement of the cake thickness, a Taylor-Hobson profilometer was employed which used a 0.5-mm radius ball-tipped stylus. This relatively dull stylus was selected after trials with a sharper (2.5-μm radius) stylus to afford a profile of the cake by gliding over individual crevices and documenting an average height over a specified traverse length. The stylus was connected to an inductive transducer that measured the displacement of the stylus over its travel of 100 mm. To address the membrane length of 240 mm, a custom template was constructed to index the membrane in segments with the precision of identical replacement of position, estimated as 5 μm. The instrument can produce surface profiles comprising up to 120,000 data points during a single traverse, corresponding to a hor-

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izontal resolution of about 2 μm. The vertical resolution is approximately 10 nm using the Talysurf interferometric principle. In practice, using the techniques employed herein (careful but not special) the instrument was able to detect a thickness of 0.5 μm while traversing in the horizontal plane.

A series of tests was run to check both the resolution of the instrument and to demonstrate consistent placement of the membrane into the template made specifically for this profilometer. The differential profilometry tests consisted of consecutive runs without moving the membrane, consecutive runs with removal/replacement of the membrane, and consecutive runs with an intervening test having exposure of the membrane to foulant and subsequent partial cleaning.

The consecutive runs testing amounted to placing the test membrane onto the profilometer and taking an initial reading. Without disturbing or removing the membrane, a second run of the profilometer was then performed. The displacement for the second run was subtracted, point by point, from the displacement of the first run to get a difference in the profiles. This test was run using a clean test membrane, on which no cake had been previously deposited. An example is presented in Figure 1 of such a run. Since both runs were performed using the same membrane then it was expected that the profiles would match identically. In reality, the profiles show deviations on the order of a micron, with a mean difference of essentially zero. There is no detectable difference in the mean height based on the two consecutive runs and the signal is basically noisy. The reason for the profiles not being identical is presumed due to the inability to replace the stylus precisely (on the order of microns) and perhaps due to unquantified vibrations or environmental conditions.

The replacement test involved taking an initial run on the clean membrane. The test membrane was then removed, reinstalled onto the template of the profilometer and another run was performed. The difference in results of the two test runs was made as before to judge the effect of replacing the membrane onto the profilometer. A typical test result is shown in Figure 2. The mean difference is

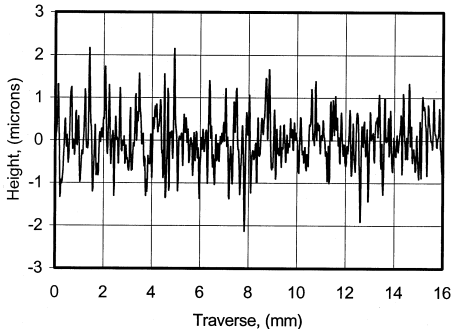

Figure 1. Differential profilometer run with undisturbed membrane.

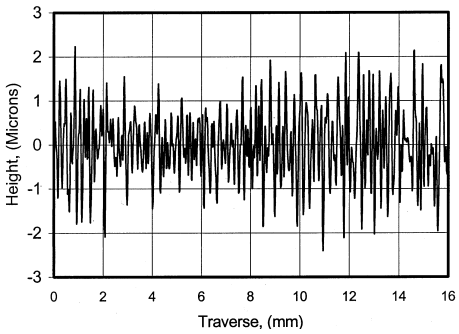

Figure 2. Differential profilometer run with membrane replaced.

again at or close to zero. Compared to Figure 1, there is a noticeable increase in the deviation of the signal beyond the mean height line, up to approximately 2 microns. The reason for this increase is that there is a detectable effect associated with the placement of the membrane back onto the profilometer.

The third test produced a difference in profile of a clean membrane and that of a fouled and partially cleaned membrane. The objective of this test was to determine the minimum deposit that the profilometer could detect, and based on this data, how to tell if the test membrane was actually clean. The clean membrane was placed onto the profilometer and an initial profile was taken. Then the membrane was fouled in crossflow microfiltration and cleaned until virtually no slurry was evident on the membrane. The test membrane was then placed back onto the profilometer and another run was performed. The difference in profile for the two runs was determined at points along the length of the membrane, as shown in Figure 3. This figure shows that there is a nonzero mean height upon which fluctuations of ± 2 microns occur, thus suggesting that accumulations of material were

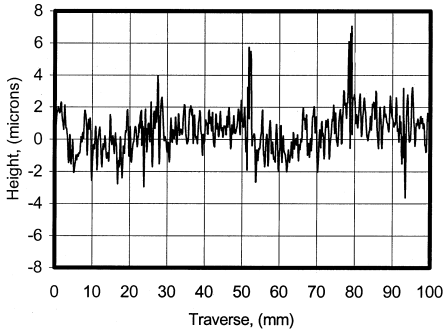

Figure 3. Differential profilometer on membrane following fouling and cleaning.

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detected on the surface of the membrane. The traverse was increased from 16 mm to 100 mm for this test compared with the former two. The data suggest that deposits of 1 micron can be detected effectively by the profilometer. This is a basic illustration of the instrument's resolution as used in these experiments.

Normally, the particular clean membrane used had the metallic appearance of brushed steel; however, a small accumulation on the membrane turns the surface slightly white. As the deposit on the membrane increases the surface whitens until no metal can be seen. The same deposit detected in the experiment reported in Figure 3 was, on close examination, also visually detectable. This suggests that an optical method calibrated with the differential profilometer should be possible and which has obvious possibilities. Multiple tests of each of the three types mentioned above were run in order to develop confidence in the techniques of membrane placement and profilometer proficiency. These tests allowed for confidence in the accuracy of the results obtained under less controlled outcomes.

Test Loop

The microfiltration flow system consisted of a steam-heated tank feeding a triplex diaphragm pump with a flow-control bypass returning to the suction line of the pump. The primary flow passes a pressure-measuring station, enters and exits the test section, passes through a valve used for pressure control, and passes through a magnetic flow meter and a heat exchanger from which it returns to the tank. The test section has a pressure gauge at each end and a gauge in its center for observing both pressure drop and central transmembrane pressure.

In all runs approximately 70L of RO permeate water was adjusted to pH 10 ± 1 and stock slurry was added to provide a particle volume fraction of 0.001. The conditions for operation were: temperature, 40C, transmembrane mean pressure, 345kPa, and the velocity, (varied by run) from 2 to 5 m/s. All runs were operated for about 4 hours until steady filtrate flow prevailed. Data were obtained for the flux rate for each of the ten collection segments along the membrane. The runs were terminated and the fluid drained from the test section carefully. The test section was disassembled and the caked membrane removed. After draining, blotting with absorbent towels from the backside, and a 30-minute air exposure the membrane was placed into the profilometer template for measurement.

Cake Properties

The cake resistivity was determined using a dead-end filtration cell and forcing solvent through a fixed slurry on a porous stainless steel membrane coupon. Initially, the membrane resistance was determined by forcing RO water, with pH 10 ± 1, through the bare membrane. The circular membrane of diameter

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Table 1. Resistance Cell Observations

Applied Pressure, kPa	100.	200.
Temperature, °C	22.3′	22.3
Membrane Resistance, ΔP/J, Pa-s / m^3	8.11 E 8	9.68 E 8
Steady Flux , m / s	1.93 E-6	3.2 E -6
Resistivity, Pa-s / m^4	1.29 E13	1.56 E 13

10 cm was covered with a four-millimeter thick paste which had been concentrated from stock suspension by evaporation to 55% volume concentration. One hundred milliliters of filtrate was collected and the time needed to collect a given volume was recorded. The rates were steady during the run. The test parameters and results are shown in Table 1.

At applied pressures of 1 bar and 2 bar, the membrane resistance was found to be slightly different, probably due to inadequate cleaning between runs, but the membrane resistance was small compared with the resistance of the slurry cake. Using the data of Table 1, the resistivity $\Delta P/(J\delta)$ of the cake shown in Table 1. was calculated using Equation 2. The Carman-Kozeny resistivity values for 300nm spheres at 55% concentration is, for reference, 0.664 E13 Ns/m^4. At least part of this difference could be due to the relative inability to form a uniform cake of 4 mm on the membrane. The cake could be considered slightly compressible by putative models.

Datta (7) measured the viscosity of the concentrated titania slurries used in this study. The shear rate dependence may be expressed through a power law model as in the following equation:

$$\eta - \eta_\infty = m\gamma^{n-1} \tag{3}$$

where η_∞ is the viscosity at infinite shear rate, m is a pseudoviscosity with dimensions Pa-s^n, γ is the shear rate in s^{-1}, while n is a dimensionless parameter. Since n is small compared to one, the fluid is shear thinning, and the psuedo viscosity, m, is a strong function of the concentration. The large-shear viscosity value is similarly affected by the concentration. Table 2 gives the values of constants for Equation (3) from Datta (7).

Table 2. Constants for Viscosity Model

Volume Concent.	m	n	η_∞
0.58	55.755	0.1385	0.769
0.5485	37.472	0.1448	0.5326
0.5067	18.854	0.1548	0.2828
0.46	10.629	0.1466	0.6462
0.3883	3.529	0.2105	0.0590
0.3539	2.238	0.1225	0.0457

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RESULTS AND DISCUSSION

Experiments were performed at 2, 3, 4, and 5 m/s crossflow velocity and the stated conditions. Figure 4 shows the measured profile of the cake obtained at the 2 m/s run. The figure shows accumulations of slurry begin at the 20 millimeter location with a ramp in thickness to 5 microns at 27 millimeters. A maximum cake thickness of 18 microns is reached at 215 millimeters followed by a decrease in thickness to 4 microns at the 240 millimeter position. The shear stress value at 2 m/s was determined to be 12.04 Pa with an average flux value of 3.91 E-6 m/s.

Figure 5 is a photograph of the test membrane taken at 2m/s crossflow velocity. It is plain to see that the deposits are not uniform and that the positions where thickness is over 10 μm are thoroughly white. The corners of the membrane channel have significantly greater deposits than the central flat region. And the downstream exit zone has a greatly thinned region, though not clearly evident in the photograph. Figure 6 shows the flux measured at the various collection cavities of the membrane. The inlet region has higher flux, as expected, and the flux generally declines along the membrane from entrance to exit. The exit region has a high relative flux consistent with a thin layer.

The deposition pattern of the 2 m/s run is also observed at higher velocity. Figure 7 incorporates the data from 2 m/s and adds the data at 3, 4, and 5 m/s velocity. Each shows a clear entrance, a ramp and fairly steady increase in thickness, followed by a drop in thickness near the exit. The position at which the deposit starts occurs systematically further downstream with higher shear stress. And the thickness generally is less at the higher shear conditions. Table 3 summarizes the results for position of the initial cake edge, maximum thickness achieved, and flow parameters of velocity and shear stress.

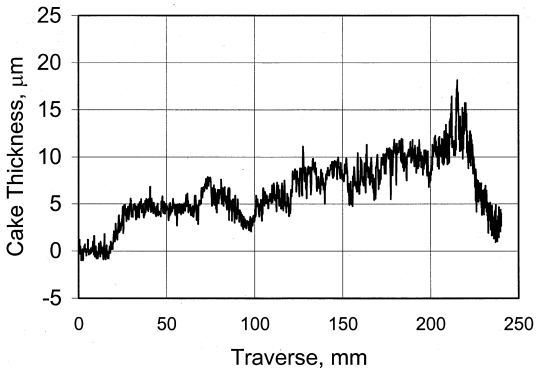

Figure 4. Thickness profile for crossflow velocity of 2 m / s.

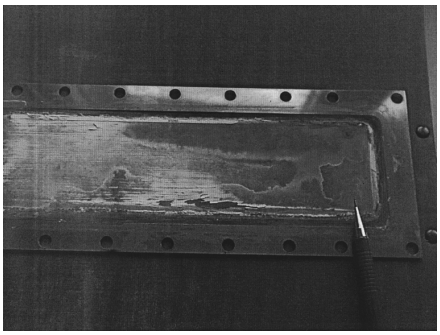

Figure 5. Photograph of membrane deposit formed at 2 m / s.

Figure 8 shows the measured local flux values taken for individual segments along the length of the membrane. The flux values tend to decrease from the first tap to last along the membrane except for the sudden increase registered regularly at the exit port. This general increase is anticipated because of the increasing cake thickness towards the aft segments of the membrane. The flux values at 5 m/s are greater than those at 2 m/s due to the generally thinner cake.

Although the experimental flux values did show a decreasing trend, each tap did not necessarily follow this pattern as shown in Figure 8. Flow at some particular taps is higher than the preceding tap. This is presumably due to irregularities in the deposit on the membrane, which did not increase continuously, but rather leveled off, peaked and then decreased. The average flux of the filtrate through the membrane is anticipated to increase as the crossflow velocity increases in response to the cake thickness. Figure 9 shows the experimental average flux values that confirm this prediction. This figure indicates the average flux values increase with the crossflow velocity to a power of 0.46.

The measured local fluxes from Figure 8 and the local mean thicknesses of Figure 7 may be used to determine by Equation 2 the resistivity of the cake at positions along the membrane. The resistivity of the deposits thus determined is in-

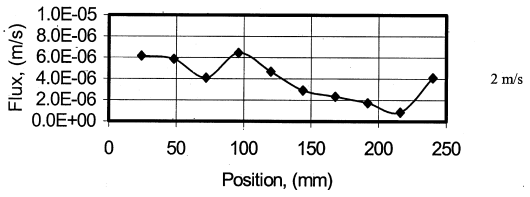

Figure 6. Segmented flux along the membrane at 2 m / s.

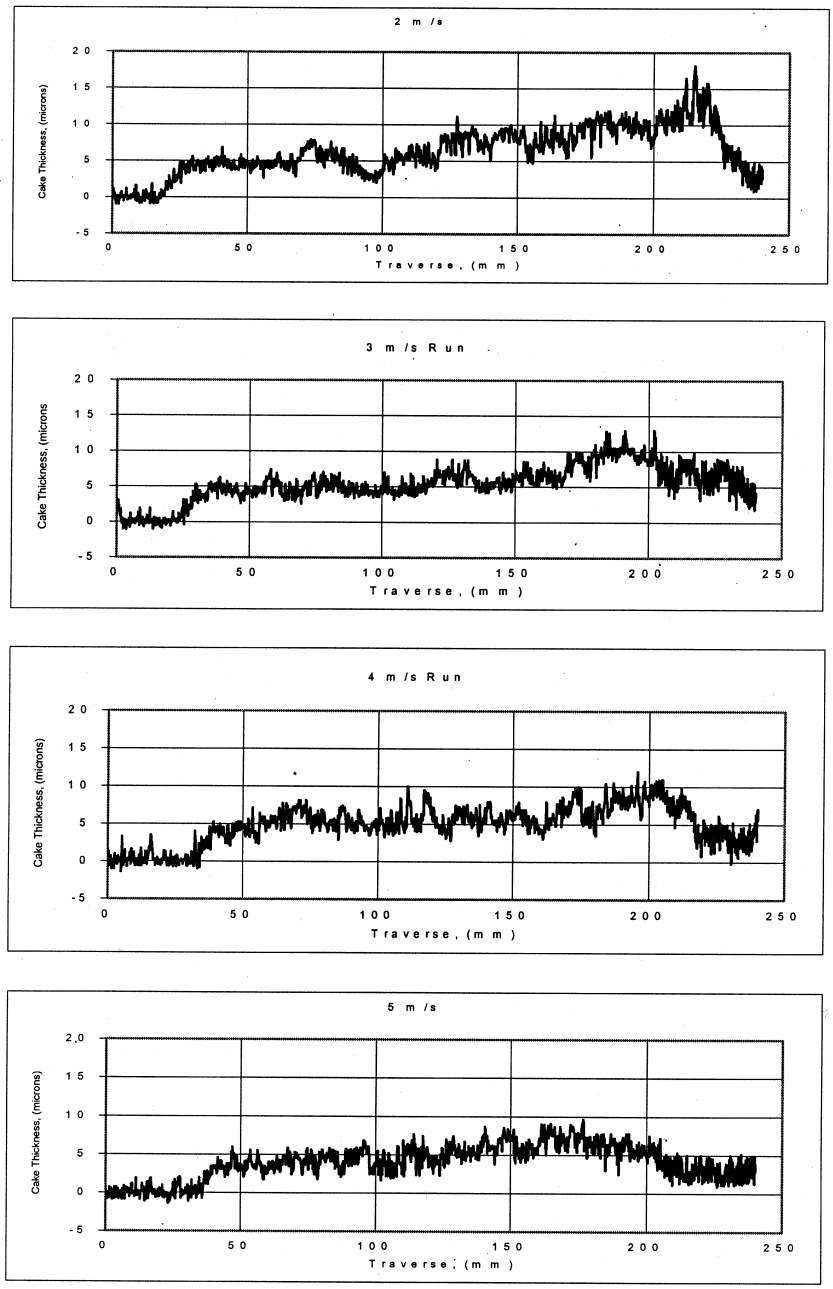

Figure 7. Thickness profiles for crossflow velocities at 2, 3, 4, and 5 m / s.

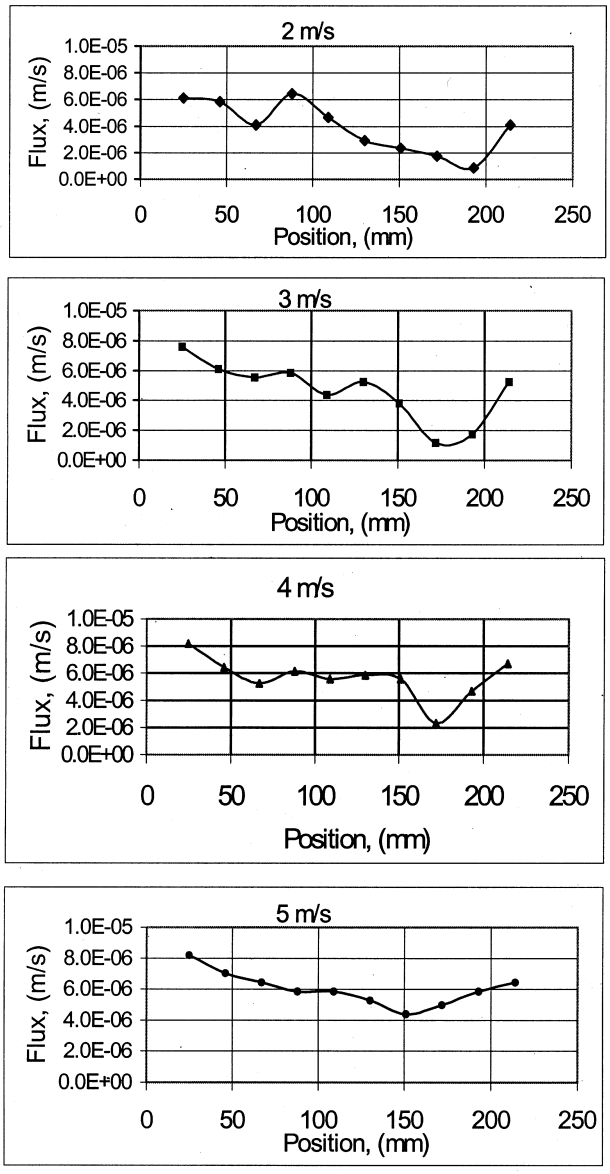

Figure 8. Flux distributions for crossflow velocities at 2, 3, 4, and 5 m / s.

Table 3. Summary of Deposit Features

Velocity	Initial Position	Maximum thk.	Final thk.	Shear Stress	Ave Flux
2	20. mm	18. μm	4. μm	12.0 Pa	3.91μm/s
3	24. mm	13. μm	3. μm	26.6 Pa	4.67 μm/s
4	36. mm	12. μm	5. μm	46.4 Pa	5.67 μm/s
5	38. mm	10. μm	5. μm	74.7 Pa	6.01 μm/s

dicated in Figure 10 for velocities 2, 3, 4 and 5 m/s, respectively. The first flux collection segment has such a slight thickness that its values of resistivity are poorly determined; the others are not as significantly afflicted. The combined resistance of cake and membrane generally yield resistances quite reduced from the resistance value of the clean membrane, 9.3 E9 N-s/m^3. This means that uncertainty in either determination does not have an exaggerated effect on the results. The values of cake resistance are relatively high, by three orders of magnitude, compared to the resistivity of Carman-Kozeny and the values measured for the stationary captured slurry cake. This result is interpreted to indicate contamination by external material or possibly by physical degradation in the suspension. While the values do not correlate with the expected result for resistivity, the method shows promise in detection of the actual deposits formed on the operating membrane.

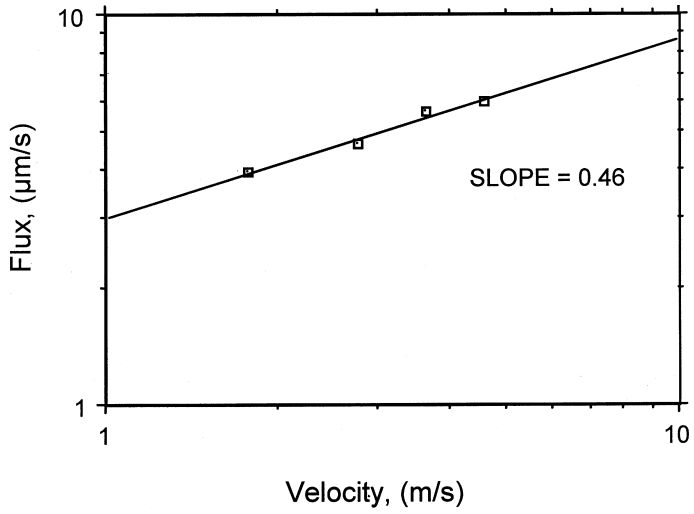

Figure 9. Average flux versus velocity.

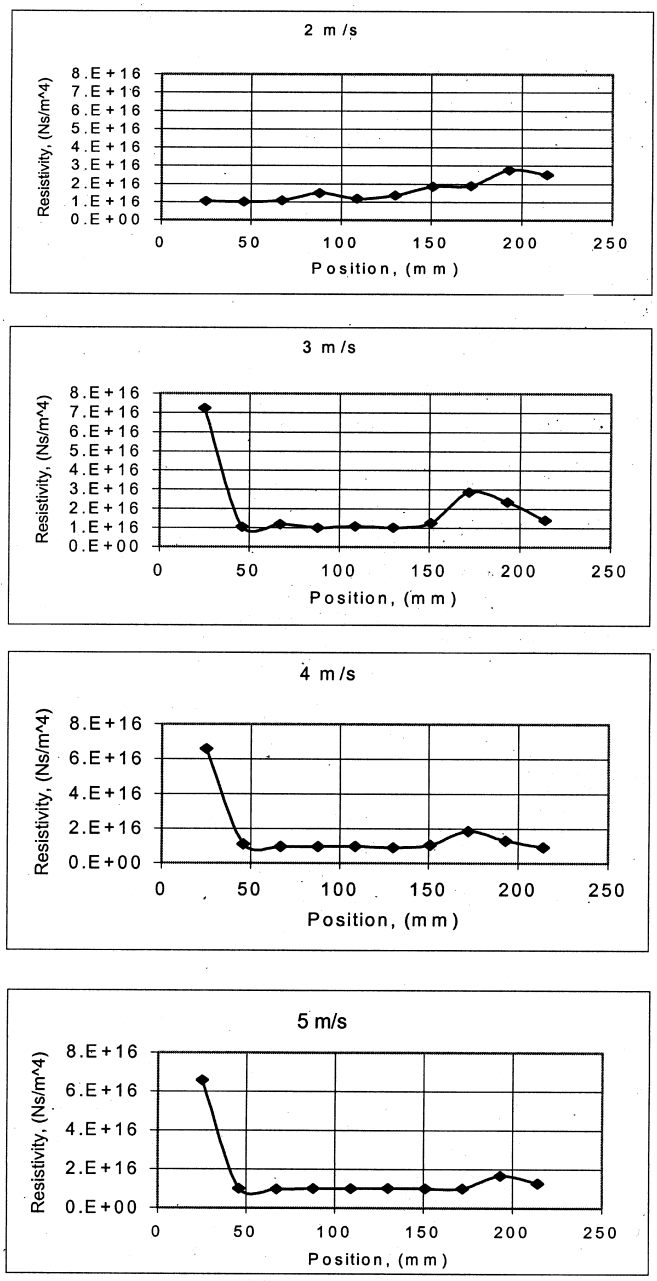

Figure 10. Resistivity distributions at 2, 3, 4, and 5 m / s.

CONCLUSIONS

A flat membrane cell with a removable membrane has been fitted with a segmented permeate chamber allowing local collection of permeate along a membrane operated in crossflow conditions. The membrane, formed of metal with a ceramic active surface, has been placed carefully into a high resolution profilometer to allow differential profilometry of the surface and any deposit thereon. The technique is shown to be capable of detecting deposits within about one μm. When operated to filter suspensions of 300 nm particles, deposits on the surface are formed and range up to 20 μm. Simultaneously, the local flux determination allows calculation of the flow resistance of the deposit. The deposits observed have a flow resistance per unit thickness in the range of 1 E16 N-s / m^4, a value much higher than a prepared bed of concentrated particles identical to those in the suspension. The difference is attributed to contamination by a small amount of flow-resisting material, perhaps from degradation of suspension particles during the experiments.

There is a short section of membrane having little or no deposit at all velocites studied. The deposit does build, but the thickness is not monotonic as suggested by theories. The exit region in fact has a greatly depleted thickness in contrast will all known theories. The deposit is greater at low crossflow conditions and the flux is lower in agreement.

The technique is expected to be useful in fouling studies. In addition informal observations of the optical properties and the thickness suggest that there may be a correlation between gray scales and thickness resulting in an in-place method of measurement.

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