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ULTRAFILTRATION OF GELATINOUS CORNSTARCH SUSPENSIONS

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ABSTRACT

It was the objective of this study to examine ultrafiltration of gelatinized starch to compare with other viscous streams and to develop a supporting data base. The objective was broadened to explain and model observations contrasted with other viscous materials. In particular, the results of ultrafiltration of starch are not consistent with diffusion-based theories of ultrafiltration; however, the resistance to flow is well modeled as a flowing filter cake. The results presented here may be useful for predicting the performance of a starch reactor wherein the goal is to convert the starch into sugars or alcohol via the action of special enzymes or hydrolysis.

INTRODUCTION

The gel layer concept introduced by Michaels [1] proposes that membrane flux is dependent primarily on achievement of a gel condition at the membrane which limits flux by the rate of counterdiffusion. Application of the gel theory to ultrafiltration, UF, was further developed by many researchers, especially Blatt et al. [2], Goldsmith [3], and Porter [4]. The gel concept, however, has been frequently challenged. An alternative hypothesis

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based on flux retardation via osmotic resistance was developed by Trettin and Doshi [5] and others. Le and Howell [6] deny the validity of the gel theory and propose instead that blocked pores in the membrane are responsible for changes in flux. Nakao et al. [7] indicate that the gel concentration is variable, dependent on both shear stress and feedstock concentration, whereas the original gel theory assumes a constant concentration. Nakao validated this theory by making measurements of the surface concentrations of residual material left behind on drained membranes. Le and Howell [6] and Clark et al. [8], challenge the gel concept on the basis that the fluids in question are not in gel state at the predicted concentrations.

Gill [9] attempted to define an entrance region over which the concentration of material on the surface of the membrane increases from an inlet value to its gel concentration. Gill's modeling resulted in the prediction of a position on the membrane at which a large rate of increasing concentration occurs. Leonard and Vassilieff [10] cite the importance of rheology in the prediction of flux. Rosen and Tragardh [11] used a numerical solution for flux and gel concentration to show large concentration increases at positions along the membrane.

Gaddis [12] used an integral model that allows the viscosity of the gel to vary with concentration. Using a predetermined profile of the concentration along the membrane, a crisis point is predicted at some point where the concentration rises infinitely. Bagchi [13] used a numerical model to calculate the position where this crisis point occurs. Beyond such a crisis point, any variation in concentration on the membrane surface results in an identical flux-versus-position curve. Bagchi's work is supported by UF experiments conducted with polyvinyl alcohol (PVA) and the conclusion of his work is that only the relative viscosity of the feedstock is required for the prediction of flux.

When the solute is a particulate, the separation is clearly mechanical and is simply a cross-flow filtration exercise, without diffusion. The resistance to flow is due to a filter cake, which may creep under the action of shear and whose resistance is determined by its concentration. Datta and

Gaddis have shown [14] that the properties of viscosity and resistivity may be unified by a cake whose concentration is dependent on the compressive action of the flow on the cake. For nondiffusive solutes these models are more appropriate than gel models and diffusion-limited fluxes.

Starch is a naturally occurring organic material that generally is a mixture of primarily linear α-1,4-glucan, amylose, and the highly branched, high-molecular-weight amylopectin. Corn is the primary commercial source of starch worldwide, while potato and wheat hold the balance of the significant shares of the market [15]. Gelatinized, or cooked, starch is a precursor for numerous chemical commodities and is present in many process and waste streams in the food industry. The conventional waste treatment of starch-laden streams is expensive and energy consumptive, so the recovery and possible utility value of starch represents a number of economic opportunities.

Starch becomes gelatinized when cooked under certain conditions of time, temperature, and agitation. In the process it is changed from a dense granular form to the expanded gelatinized form by absorption of water and the unraveling of the polymer molecules. Granular starch suspended in aqueous solvent becomes increasingly viscous as the gelatinization process progresses. Bakshi and Singh [16]; Case et al. [17]; Dolan and Steffe [18]; Kubota et al. [19]; Lai and Kokini [20]; Lund and Wirakartakusumah [21]; and Suzuki et al. [22] have all contributed to the understanding of the gelatinization process.

Another key conversion phenomenon that concerns the amylose component of starch is retrogradation. In the A-form, which forms for amylose in solution above 50 C, alignment of the linear amylose chains and subsequent hydrogen bonding leads to the formation of heavier amylose molecules that are completely insoluble [15]. The preparation of consistent suspensions of starch has been a substantial challenge; thus, the cooking processes here were performed as consistently as possible.

METHODS AND MATERIALS

The viscosity data of Kim [23], Evans and Haisman[24], and Christianson and Bagley [25] are presented in Figure 1, together with viscosity measurements of the actual starch solutions that were used in the UF experiments. The data are obtained at 25 C; however, it is assumed herein that the relative viscosity will be maintained at other temperatures. The data are represented by a model for the relative viscosity as a function of concentration of the form $\exp(\alpha C)$, where C is the concentration; for this study α is taken to be 0.86 for C as percent.

The fluid is a non-Newtonian, shear-thinning fluid, tested in apparatus generally at shear rates of a few hundred reciprocal seconds, corresponding to shear stresses typical of UF applications (100 N/m2) for solutions in the 6% range. Thus the model is believed to be applicable for the uses herein. Based on observations and cited reports, the fluid properties are poorly reproducible.

Since no published value of the diffusion coefficient of starch was found, and as mentioned, it is believed that these data may be important for predicting UF fluxes based on developed theories with similar materials like PVA, a goal was to implement an appropriate experiment in which the diffusion coefficient of polymers in solution could be measured. Optical interferometric techniques have been used [26] to measure the diffusion coefficient for PVA in solution, but the method required special equipment. Wall, Grieger, and Childers [27,28] have demonstrated a method suitable for measuring the mutual diffusion coefficient of polymer solutions such as PVA or starch. This technique has been employed for gelatinized cornstarch and the results are described herein.

METHODS AND MATERIALS

Cornstarch (ICN Biochemicals #902956) was dispersed in room-temperature water and heated to 95 C, while stirring continuously. After 10 to 15 minutes the granules begin to swell and gelatinize in the water. The

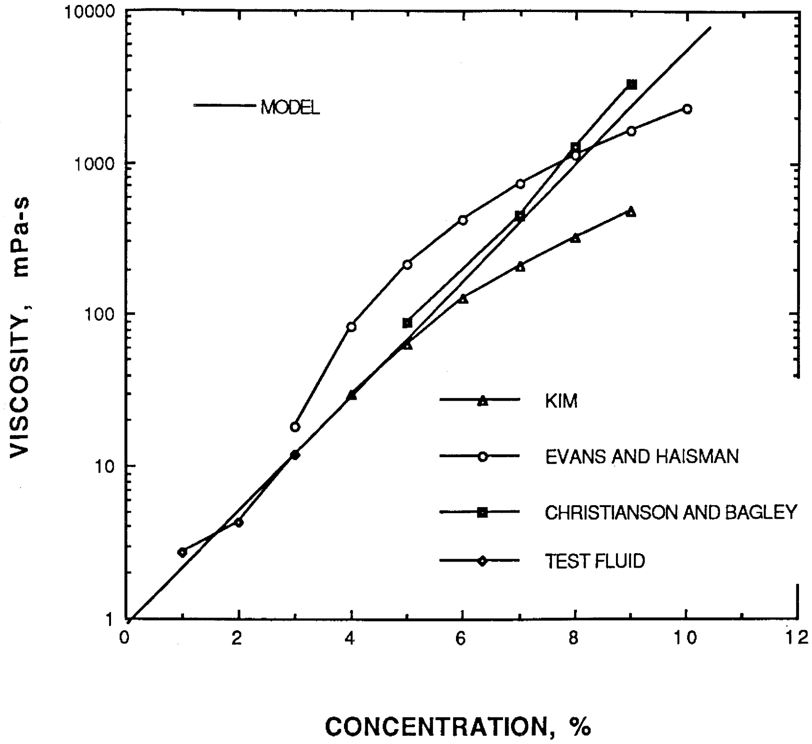

FIGURE 1. VISCOSITY OF CORNSTARCH.

initially milky white mixture becomes more translucent and its viscosity increases gradually. Care was used to provide sufficient agitation to avoid clumping and sticking to heated surfaces. The preferred heating for uniform heat transfer was achieved by placing the cooking vessel in a steam-heated bath. After 30 minutes at 95 C, the solution was considered fully gelatinized.

A beaker was used for small quantities in the laboratory and for the UF experiments (volume of about 80 liters) a commercial kettle equipped with a steam heating jacket and a motorized set of counterrotating, agitating, and wall-scraping blades was used.

The system used to conduct the UF experiments consisted of a diaphragm pump, a stainless steel steam-heated feed vessel, pressure and temperature instrumentation, and valves for controlling flow rate and pressure. The filter was a microporous membrane element from DuPont Separation Systems, Seneca, SC (currently Graver Separations, Inc.). The surface of this tubular membrane consisted of a layer of zirconium oxide hydrous gel coated over a dense layer of sintered titania embedded in a porous stainless steel substrate. The inner diameter of the membrane tube was 0.6 inches and the length was 36 inches. Figure 2 describes this system and identifies the key components. The starch mixtures were prepared at higher concentrations and diluted with filtered water in the feed kettle. The temperature of the solutions during filtering was 60 ± 2 C.

Membrane inlet pressure was varied in steps from 3.6 to 14 atm at a cross-flow velocity of 4.6 m/s. Permeate flow rates were determined by weighing samples obtained over a collection period.

RESULTS OF UF TESTING

Figure 3 contains traces of flux versus pressure at steady rates for pure water before starch exposure, and for 1, 2, and 3% gelatinized cornstarch. The data were obtained with increasing pressure and in order of increasing concentration. The flux increases linearly with pressure along a line characteristic of pure solvent until it begins to level off and approach an asymptotic permeate flux. For the 1, 2, and 3% solutions, these estimated flux asymptotes are 24.5, 16., and 11.3 μm/s (52, 34, and 24 gal/day-ft^2), respectively. Similarly viscous solutions of PVA have been measured routinely and would be expected to produce fluxes of no greater than 4.7 μm/s (10 gal/day-ft^2) --- much less than those of the starch.

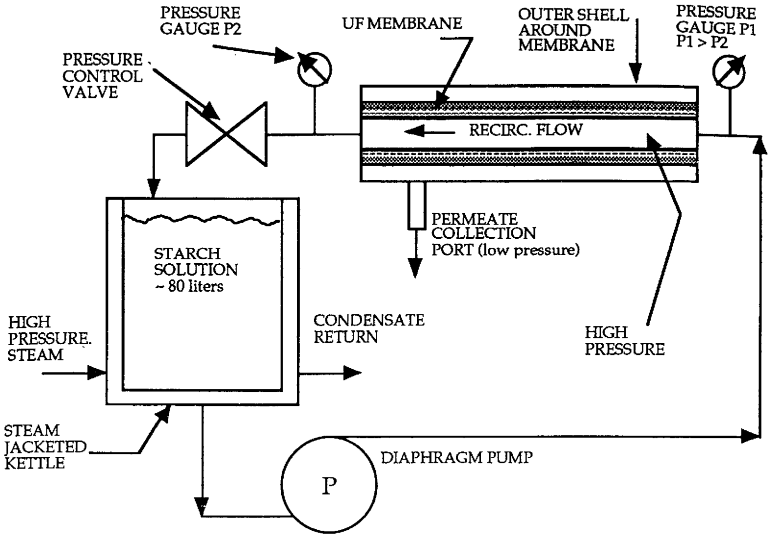

FIGURE 2. SCHEMATIC OF ULTRAFILTRATION TEST LOOP.

Anomolous high flux can result from poor solute retention, but rejection of the starch by the membrane appeared to be complete since the permeate collected was very clear and inviscid. Earlier unpublished measurements by D. See [29] were accompanied by permeate solids determination which routinely showed lack of starch penetration. The results of the See experiments are incorporated with the results of this study in Figure 3. The concentrations of cornstarch See tested, as shown in the graph, were 0.4, 0.7, and 1.5%. There were many differences between test conditions for her data and those for the 1, 2, and 3% tests which will be explored and summarized in detail at a later point. The See data are considered entirely consistent with the current results. It became a major point to determine why the starch fluxes were so definitely greater than the comparable PVA solution.

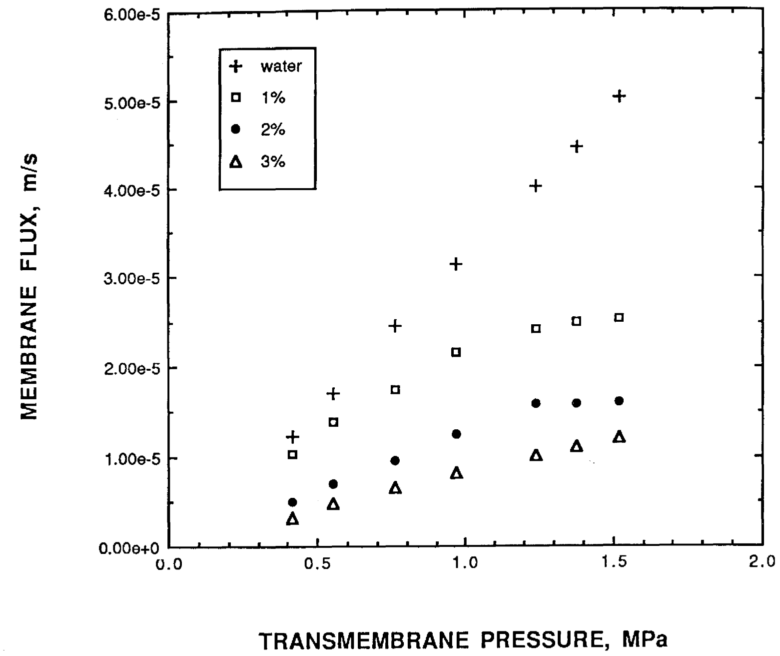

FIGURE 3. OBSERVED FLUX FOR GELATINIZED STARCH.

BENCH EXPERIMENTS

An experiment based on the work of Wall, Grieger, and Childers [27,28] was set up to determine the mutual diffusion coefficient of starch solutions. In this method the rate of weight loss from a frit saturated with mixture and suspended in solvent indicates loss of solute into the bath and the corresponding infiltration of solvent. Some preliminary runs were made on PVA, which provided the very reasonable result of $D \sim 2 \times 10^{-7}$ cm^2/s. Tests conducted at 75 C exhibited retrogradation of starch, wherein alignment of the linear amylose chains is followed by hydrogen bonding and the formation of heavier amylose molecules, which eventually become completely insoluble [15]. This insoluble material could be seen precipitating in large (1 to 3 mm) clumps and flakes. The temperature was therefore limited to 50 C.

For a mixture of 5% starch at 50 C, the resulting mass loss data are shown in Figure 4. A decay line for D of 1.1 x 10^{-7} cm^2/s seems to fit the initial portion of the data trace, but it was desired to extend the observations for W(t)/W(0) to 0.5. The readings, however, reach a nearly constant weight at W(t)/W(0) somewhere between 0.9 and 0.85. For the portion of the curve for t > 200 minutes, assuming an adjusted initial mass, an upper bound for D can be established as 5×10^{-10} cm^2/s.

Lower concentrations of starch exhibited the same type of behavior: an initial drop in mass of up to 10% in 200 seconds was followed by a very slow mass decline, representative of a diffusion coefficient of less than $10^{-9} cm^2/s$. During the initial 200 minutes of this process small isolated clumps of concentrated material could be seen falling under the action of gravity from the disc. Clearly the sides and rim of the disc have a coating of some amount when loaded into the solvent vessel. It is suspected that this coating, together with some of the cell contents of the disc, flowed under the influence of gravity in creeping motion and was able to exit the disc. When all such viscous flow had ceased, the mass became quite constant as diffusion was ineffective.

The conclusion from these experiments was therefore that the mutual diffusion coefficient for gelatinized cornstarch and water at 50 C can be no greater than 7 x 10^{-10} cm^2/s. To give a perspective on what this number means, similarly viscous PVA exhibits a diffusion coefficient 300 times the estimated upper limit for starch. Combined with the flux results already presented, wherein the fluxes on starch were considerably greater than for PVA under comparable conditions, it is impossible to employ any diffusion-limited concept to explain the data.

It was desired to estimate the resistivity, r, for a layer of known mass and volume of starch. Resistivity, as employed here, is the ratio of applied pressure gradient to the superficial velocity of the solvent. A layer of starch of known initial thickness and concentration was placed on a flat segment of membrane material. Solvent flow, forced by pressure through the starch

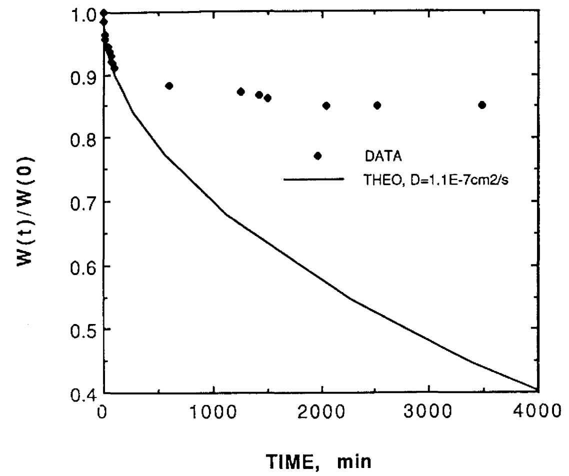

FIGURE 4. WEIGHT LOSS TREND FOR A SATURATED FRIT.

layer and the membrane, was interpreted in terms of the resistivity of the starch layer. In the experiment the flow rate declines slightly over a brief period but resolves to a steady flow rate of solvent. The overall resistance DP/J is equated to the sum of the predetermined resistance of the membrane itself (R_m) and the resistance of the starch cake layer, $r\delta$. This basic relationship is expressed by Equation 1, where the left-hand side contains

$$(\Delta P / J) = (r\,\delta + R_m) \qquad \text{N-s/m3} \tag{1}$$

parameters from the steady-operation portion of the test, and R_m and δ are known constants.

The initial value of thickness, $\delta_o = 0.32$ cm, is used for the purpose of calculations of the value of r_o, the resistance equivalent of an uncompressed layer. The actual thickness of the cake layer may be reduced by compression during the run, and the corresponding concentration may increase. In applying the model, the value of r will be scaled while the observed value of resistance in the experiment is maintained according to Equation 2.

$$(r/r_o) = (\delta_o/\delta) = (C/C_o) \tag{2}$$

This simple scheme maintains fidelity to the observation but is weak in that it is based on uniform assumptions for the compressed layer of solute which could well be resistive disproportionately to its mass.

Figure 5 is a diagram of the unstirred-cell bench-top filter apparatus. The membrane used is a round plate made of the same materials used in the cross-flow filtration experiments. A rubber gasket approximately 10 cm in inside diameter and 0.32 cm thick sits on top of the membrane and retains the starch solution when initially loaded into the device as well as during the experiment. The cavity created by the gasket allows consistent installation and estimation of the initial thickness, δ_o, of the starch layer placed on the membrane. In these experiments, the solvent is pressurized by air on the top side of the solvent chamber at pressures ranging from 1.5 to 4 atm. The solvent chamber consisted of 30 to 35 ml in a tube. Insulation and constant temperature water heat tracing of this tube were employed to maintain solvent temperatures consistent with those of the UF experiments. An initial layer concentration of 5% was chosen because of preliminary calculations based on viscosity. The accumulated mass of permeate was monitored at intervals for a duration on the order of 2 hours, at which time the supply of water was exhausted.

Following each test the general condition of the layer was examined. For all five experiments, the starch layer remained uniformly spread and appeared to be slightly compressed. For most runs, three layers were distinguished and were assayed for solids content. The top layer contained the bulk of the original mass, about 90%, and was only slightly changed in concentration from the original 5% layer. The middle layer, containing about 5% of the original mass, had concentrations ranging from 5.5 to 9.0%, depending on the applied pressure. The most viscous layer had to be gently scraped from the membrane surface for sampling purposes and had concentrations from 17 to 25%, again depending on applied pressure.

The resistivity values obtained from the experiment are tabulated in Table 1 and varied from 1.53 to 2.94×10^{14} Pa-s/m^2. The variations were not clearly related to pressure or temperature. Scatter, not unlike that anticipated

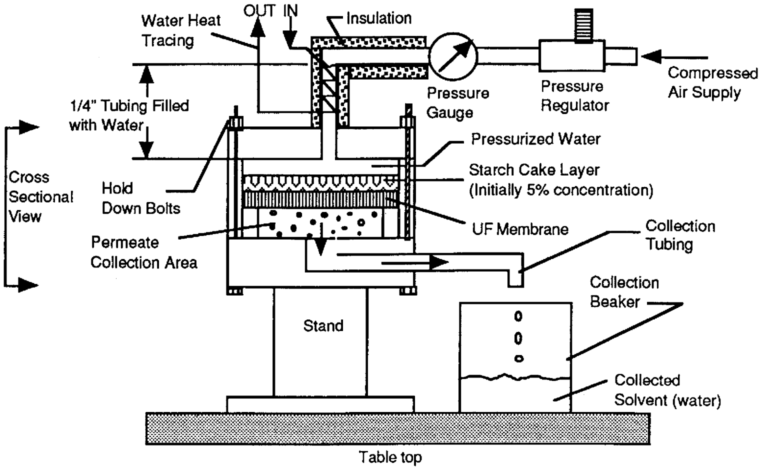

FIGURE 5. SCHEMATIC OF RESISTIVITY CELL.

Table 1. Data Summary --- 5% Gelatinized Starch Layer Resistivity

Run #	Avg flow rate	Flux	$\Delta P/J$	Resistivity	Avg Ccake
ΔP [atm]	[g/min]	J [m/s]	[N-s/m^3]	r_o [Pa-s/m^2]	[Wt %]
		T = 25 C			
(1) 2.7	0.2140	4.69×10^{-7}	5.87×10^{11}	1.73×10^{14}	n/a
(2) 2.7	0.1737	3.81×10^{-7}	7.23×10^{11}	2.16×10^{14}	5.3%
		T = 60 C			
(3) 4.1	0.1941	4.25×10^{-7}	9.71×10^{11}	2.94×10^{14}	6.9%
(4) 2.7	0.2402	5.26×10^{-7}	5.23×10^{11}	1.53×10^{14}	6.7%
(5) 1.35	0.0660	1.45×10^{-7}	9.52×10^{11}	2.88×10^{14}	6.4%
		AVERAGE r_o:		2.40×10^{14}	

for other properties of starch based on subtle effects during cooking, is clearly evident. The duplicate condition run resulted in a 25% difference. From these data, a value of about 2.4 x 10^{14} Pa-s/m^2 is taken to be representative of the resistivity at 5%, with adjustments for cake concentration according to Equation 2. The initial flux rates from these tests all indicated a resistance value of about 1.25 x 10^{14} Pa-s/m^2, and the membrane itself had a resistance two orders of magnitude lower than the cake resistance. Therefore, compression increased the resistivity of the starch layer from 22 to 135% over its original value. Because only 5 to 10% of the layer mass was significantly compressed, the entire increase in compression could have been focused in this relatively small amount of the whole. The specific resistance (resistance per mass) could then have increased to 20 times its original value in the small region.

MODELING AND ANALYSIS

The schematic diagram shown in Figure 6 describes an infinitesimal segment near the surface of the UF membrane where the bulk solution, of concentration C_b, is separated from zero-concentration filtrate. The action of filtration results in the formation of a resistive layer of concentration C_c and thickness δ. The volume flux, J(x), is dependent on the membrane and the properties of the resistive layer. The hydraulic resistance of the membrane, R_m, is assumed uniform over the membrane. It is recognized that gelatinized cornstarch is a foulant for membranes; consequently, the resistance levels measured prior to an experiment could not be subsequently restored by flushing with pure solvent. The membrane resistance could be restored by using an acidic solution. In conducting the tests reported herein, however, the system was not acid-washed between runs. The value for R_m, for the 2 and 3% cases, was based on the applicable fouled state of the membrane by using the low-pressure slope of the J vs P curve in Figure 3.

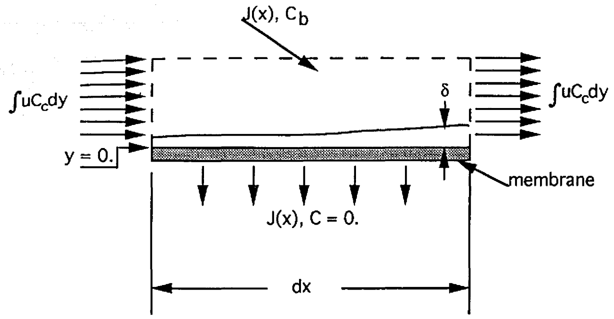

FIGURE 6. CONTROL VOLUME USED FOR MODELING.

The second assumption is that the concentration of the viscous cake layer is uniform. It is possible to create a more responsive model in which the cake concentration is allowed to vary longitudinally and transversely; however, more extensive testing would be needed to provide proper data for evaluation. The use of this assumption is to isolate the average properties for the layer. Also because the layer is thin in comparison with the dimension of the channel, the shear stress in the cake is considered constant.

The concentration of the cake, while considered spacially uniform, is allowed to respond to the applied pressure. Although the cake concentration may be influenced by many factors, the compressive stress due to the applied pressure is believed to have a primary effect on the structure and concentration of the viscous cake.

The goal is to predict the average flux, J_{avg}, for the membrane having a flux distribution, J(x), according to Equation 3.

$$J_{avg} = \frac{1}{L}\int_{0}^{L} J(x)\,dx \qquad (3)$$

To determine the average flux, it is first of benefit to perform a mass balance on the element of Figure 6, which is described by Equation 4. The integral from y = 0 to ∞ can be broken into the sum of two integrals: the first representing the mass excess of solute in the cake layer itself, and the second representing the mass excess in the region between the free stream and the cake layer.

$$J_{avg} C_b L = \int_0^L J(x) C_b \, dx = \int_0^\infty u (C - C_b) \, dy = \int_0^\delta u (C - C_b) \, dy + \int_\delta^\infty u (C - C_b) \, dy \tag{4}$$

Since it has been determined that mutual diffusion for gelatinized starch is negligible, the second of these two integrals can be neglected for this analysis. The concentration, C, in the zone of the cake is designated as uniform, C_c. Equation 4 reduces to the form shown in Equation 5.

$$\int_0^L J(x) C_b \, dx = \int_0^\delta u (C_c - C_b) \, dy \tag{5}$$

The shearing velocity, u, for a fluid of constant composition at constant shear is simply $\tau \, y/\mu_c$. Substituting this expression into Equation 5, integrating over y, and differentiating both sides with respect to x gives Equation 6.

$$J(x) = \frac{\tau}{\mu_c} \left(\frac{C_c}{C_b} - 1 \right) \frac{d}{dx} \frac{\delta^2(x)}{2} \tag{6}$$

An additional expression relating the two dependent variables J(x) and δ(x) is provided as the resistance model in Equation 7, which is the same as Equation 1 but expressed locally.

$$J(x) = \frac{P}{(R_m + r_o \, \delta(x))} \tag{7}$$

Substitution of Equation 7 into Equation 6 and integrating gives Equation 8.

$$\frac{\tau}{\mu_c P}\left(\frac{C_c}{C_b} - 1\right)\left(R_m\frac{\delta^2}{2} + r\frac{\delta^3}{3}\right) = x \tag{8}$$

Equation 8 constitutes a relationship for the local cake thickness, $\delta(x)$; the value of r is related to C_c as $r = r_o(C_c/C_o)$. The local flux, J(x), evaluated from Equation 7, allows the average flux, J_{avg}, to be obtained from Equation 1.

According to Equation 8 the thickness will increase downstream along the membrane and with increases in pressure, viscosity, and bulk concentration and with reductions in shear stress. All these features are intuitively satisfying. The cake concentration, C_c, linked to both viscosity, μ, and resistivity, r, is undetermined. Table 2 below lists the parameter values which have been measured or estimated for the UF experiments.

Predictions of the flux, J_{avg}, for various cake concentrations were compared with the starch filtration data, under the provision that a 5% tolerance was allowed so that the cake concentration data could assume a smooth dependence on pressure over the operating range. Figure 7 shows the resulting cake concentrations obtained. The cake concentration values for the 1% data increase with increasing pressure, from 4.5 up to 6.9%. The cake concentration values for the 2 and 3% cases, however, were constant over the entire range of pressures, at 6.6 and 7%, respectively, except for the highest pressure point of the 2% case, where the concentration increased from 6.6 to 7%. The four measured values of mean cake concentration for the bench-test resistance experiments were 5.3, 6.4, 6.7, and 6.9% (see Table 1). Since the range of concentrations shown in Figure 7 is near these values, it is felt that the resistivity data are as responsive as any constant value model can be.

The corresponding cake thickness evaluated at the end of the membrane, x = 0.914 m, are shown in Figure 8. The thickness of the cake shown all tend to increase with increasing pressure as expected for this kind

Table 2. Model Variables and Values

VARIABLE	VALUE	DESCRIPTION / COMMENTS
τ - shear stress	45 [N/m^2]	Calculated from pressure drop
μ_c - cake viscosity	[Pa-s]	$\mu_c = \mu(H_2O) \exp(86\ C_c)$, based on Figure 1
P - pressure	3.6 -14 [atm]	Seven pressures each run
C_b - bulk conc.	0.01, 0.02, 0.03	Feed concentrations
C_c - cake conc. (average)		For each C_c, P, there is one C_c which will fit the experimental data.
R_m - membrane resistance	3.7 x 10^{10} [Pa-s/m] 6.4 x 10^{10} 9.7 x 10^{11}	Pure water, no starch on membrane After 1% starch fouling After 2% starch fouling
r - cake resistivity	[Pa-s/m^2]	$r = (C_c/0.05)r_o$; where $r_o = 2.4 \times 10^{14}$
L - mem. length	L = 0.914 [m]	

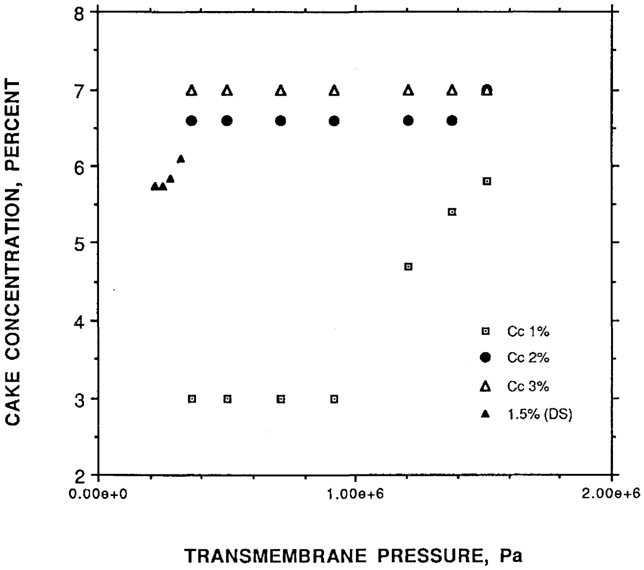

FIGURE 7. CAKE CONCENTRATION NEEDED FOR DATA AGREEMENT.

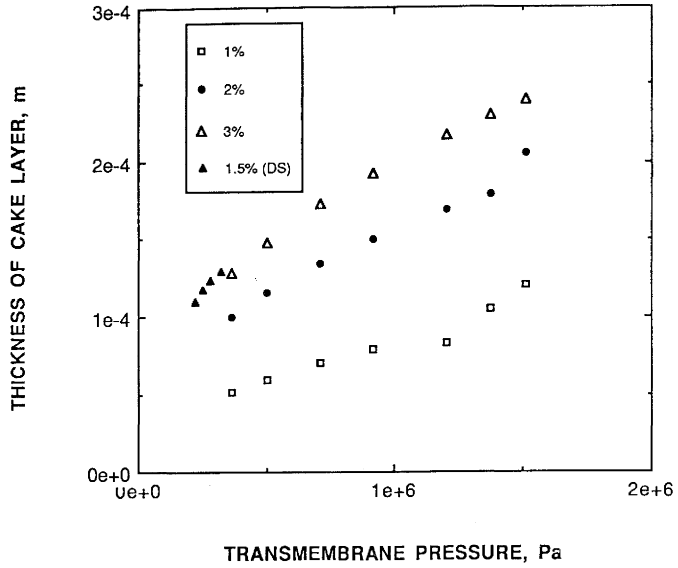

FIGURE 8. THICKNESS OF CAKE LAYER ON MEMBRANE.

of UF process. The cake thickness calculated by the model for the 1, 2, and 3% starch data range from about 50 to 250 μm. The thickness of the enriched-concentration layer predicted by diffusion is expected [13], to approximate 2D/J or about 2 μm, two orders of magnitude smaller than the cake thickness of Figure 8. While the greater starch mass may present a problem in some filtration applications, it should actually be very beneficial in a reactor process, where the highly concentrated layer would constitute a region of enhanced production when combined with a high concentration of catalyst.

The predicted flux of the model, using the cake concentrations shown in Figure 8, is compared with the results of testing in Figure 9. Each concentration run has seven operating pressures obtained in an increasing sequence. The first four points for the 1% experimental data form an approximately linear relationship between permeate flux and average

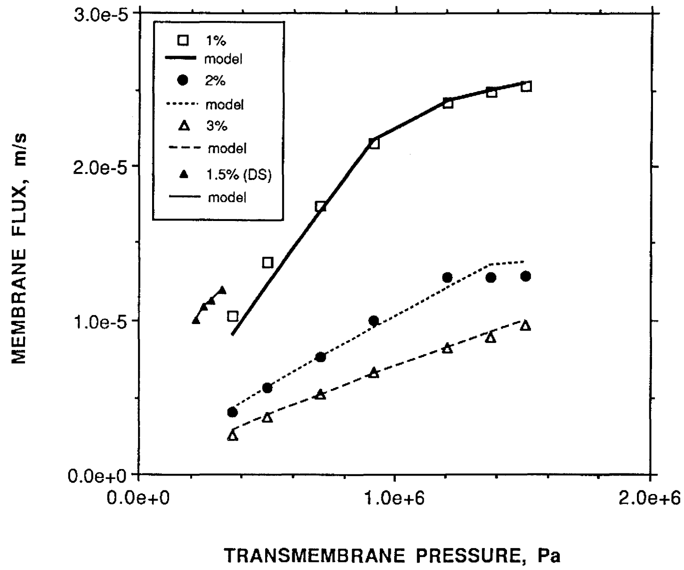

FIGURE 9. COMPARISON OF PREDICTED FLUX WITH OBSERVATIONS.

transmembrane pressure. Above the fourth level of pressure, the data show a progressively decreasing slope, where further increases in pressure cause progressively smaller increases in flux.

The middle group in Figure 9, for 2% bulk starch concentration, exhibits similar, but less responsive changes in flux with increasing pressure. The theoretical portion of the data is more nearly a straight line over the range of pressures than that of the 1% run. The lower group in Figure 9, for 3% starch, has the most linear response of flux to pressure of the curves.

The unpublished data of See [29] offer some independent assessment of the trends noted. In these similar UF experiments with wheat, rice, and potato as well as cornstarch, the membrane was cleaned between runs. The tests of gelatinized cornstarch of 0.4, 0.7, and 1.5% were conducted under slightly different conditions. The membrane used was similar, but had a significantly lower value of membrane resistance, $R_m = 1.36 \times 10^9$ Pa-s/m at 65 C, compared with the value here of 3.7×10^{10} Pa-s/m. The temperature was 5C higher, the transmembrane pressures was lower, the shear stress was about half the level reported in this work, and the membrane was 30% shorter. The 1.5% data of See have been analyzed according to the model, and it was found that a cake concentration of 6% causes agreement of flux versus pressure as shown in Figure 9 for the short curve (labeled DS) within 2% of the flux reported.

CONCLUSIONS

Ultrafiltration of viscous suspensions of swollen, gelatinized starch produces permeate fluxes surprisingly high compared with those of PVA, a similarly viscous material. While PVA fluxes have been associated with diffusion-limited models, the increased starch flux cannot be interpreted on a diffusion basis, because diffusion in the starch suspension has been measured to be much lower or zero. The resistive nature of the concentrated layer of starch formed by the action of solvent removal adjacent to the membrane must depend on the nature of a filter cake or slime, in particular on its hydraulic resistivity and viscosity.

A primitive experiment has been used to estimate the hydraulic resistance of a layer of prepared starch. An average resistance value has been used because the obtained values, contained by approximately ±35%, were not clearly related to operating conditions of pressure and temperature. This resistance value, together with viscosity values from the literature and corroborated herein, forms the basis for a simple model to interpret the flux data. The model has shown the ability to predict UF membrane flux, from which concentrations and thickness of cake can be deduced. The composite model based on the starch data obtained herein, as well as on the independent data of Dawn See, provide a credible model for the observed behavior.

The cake thickness and concentration behave systematically with the operating conditions. The concentration of starch in the cake layer varies for the conditions observed from 4.5 to 7%, becoming higher systematically with operating pressure. The thickness increases from zero at the inlet edge of the membrane to values from 50 to 250 μm at the end of the 0.9-m membrane surface. The thickness of cake increases with flux (higher pressure) and decreases with higher applied shear stress, as expected. What is different is that the value of thickness is far greater than the thickness of a diffusive layer and implies that the content of starch in the concentrated zone is two orders of magnitude more than previously anticipated by diffusion-based models. This offers new viewpoints for the prospects of a membrane reactor.

It is encouraging that results of simple bench-scale experiments can be incorporated into a fluid model to provide agreement with experimental data in an active UF experiment. While the data were applied as an average for the composition-dependent properties of resistivity and viscosity, the results appear to have general consistency with experience. With further development these measurements can lead to detailed models of resistance and strain rate as dependent on compressive stress and applied shear for a comprehensive model.

The observations --- that a membrane can be cleaned and that fouling from the starch causes hysteresis in the flux-versus-pressure data --- are indications that fouling of UF membranes by starch could be a problem when trying to justify or implement commercial processes.

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REFERENCES

1. A. S. Michaels, "New Separation Technique for the CPI." Chem. Eng. Prog., 64, 31-43 (1968).

2. W. F. Blatt, A. Dravid, A. S. Micheals, and L. Nelson, (1970) "Solute Polarization and Cake Formation in Membrane Ultrafiltration: Causes, Consequences, and Control Techniques." Membr. Sci. and Technol. pp 47-97, (1970).

3. R. L. Goldsmith, "Macromolecular Ultrafiltration with Microporous Membranes." Ind. Eng. Chem., 10, 113-120 (1971).

4. M. C. Porter, "Concentration Polarization with Membrane Ultrafiltration." Ind. Eng. Chem. Prod. Res. Dev., 11, 234-248 (1972).

5. D. R. Trettin and M. R. Doshi, "Pressure Independent Ultrafiltration: Is it Gel Limited or Osmotic Pressure Limited?" ACS Symp. Ser. #154, Synthetic Membranes. VII. Hyper- and Ultrafiltration Membranes, pp. 373-409 (1981).

6. M. S. Le and J. A. Howell, "Alternative Model for Ultrafiltration." Chem. Eng. Res. Des., 62, 373-380 (1984).

7. S. Nakao, T. Nomura, and S. Kimura, "Characteristics of Macromolecular Gel Layers Formed on Ultrafiltration Tubular Membranes." AIChE J., 25(4), 615-622 (1979).

8. W. M. Clark, A. Bansal, M. Sontakke, and Y. H. Ma, "Protein Adsorption and Fouling in Ceramic Ultrafiltration Membranes." J. Memb Sci, 55, 21-28 (1991).

9. W. N. Gill, "The Effect of Viscosity on Concentration Polarization in Ultrafiltration." AICHE J, 43, 1563-1567 (1988).

10. E. F. Leonard and C. S. Vassilieff, "The Deposition of Rejected Matter in Membrane Separation Processes." Chem. Eng. Commun., 30, 209-217 (1984).

11. C. Rosen and C. Tragardh, "Computer Simulations of Mass Transfer in the Concentration Boundary Layer over Ultrafiltration Membranes." J. Memb. Sci., 85, 139-156 (1993).

12. J. L. Gaddis, "Effects of Pressure and Crossflow Velocity on Ultrafiltration Flux." Chem. Eng. Commun., 116, 153-169 (1992).

13. S. Bagchi, "Viscous Interaction in Ultrafiltration" MS Thesis, Clemson Univ. (1994).

14. S. Datta and J. L. Gaddis, "Dynamics and Rheology of Fouling Cakes Formed During Ultrafiltration" Sep. Sci and Technol., 32, 327-353 (1997).

15. T. Galliard, Starch: Properties and Potential, Critical Reports on Applied Chemistry, John Wiley & Sons, Society of Chemical Industry, (1987).

16. A. S. Bakshi and R. P. Singh, "Kinetics of Water Diffusion and Starch Gelatinization during Rice Parboiling." J. Food Sci., 45, 1387-1492 (1980).

17. S. E. Case, D. D. Hamann, and S. J. Schwartz, (1992) "Effect of Starch Gelatinization of Physical Properties of Extruded Wheat and Corn Based Products." Cereal Chem., 69(4), 401-404 (1992).

18. K. D. Dolan and J. F. Steffe, "Modeling Rheological Behavior of Gelatinizing Starch Solutions using Mixer Viscometry Data." J Texture Stud., 21, 265-294 (1990).

19. K. Kubota, Y. Hosokama, K. Suzuki, and H. Hosaka, "Studies on the Gelatinization Rate of Rice and Potato Starches." J. Food Sci., 44, 1394-1397 (1990).

20. S. Lai and J. L. Kokini, "The Effect of Extrusion Operating Conditions on the On-Line Apparent Viscosity of 98% Amylopectin (Amioca) and 70% Amylose (Hylon 7) Corn Starches During Extrusion." J. Rheol., 34 (8), 1245-1266 (1990).

21. D. B. Lund and M. Wirakartakusumah, "A Model for Starch Gelatinization Phenomenon." *Engineering and Food v. 1, Engineering Sciences in the Food Industry.* (B. M. McKenna, Ed) Elsevier 42 , 425-432 (1981).

22. K. Suzuki, K. Kubota, M. Omichi, and H. Hosaka, "Kinetic Studies on the Cooking of Rice." J. Food Sci., 41, 1180-1183 (1976).

23. J. B. Kim, S. Y. Lee, and S. K. Him, "Rheological Characteristics of Thermal Gelatinized Corn Starch Solutions." Korean J Food Sci Technol, 24(1), 54-58 (1992).

24. I. D. Evans and D. R. Haisman, "Rheology of Gelatinized Starch Suspensions." J Texture Stud., 10, 347-370 (1979).

25. D. D. Christianson and E. B. Bagley, "Apparent Viscosities of Dispersions of Swollen Cornstarch Granules." Cereal Chem., 60(2), 116-121 (1983)

26. K. Dialer. K. Fogler, and F. Patat, "Zur Charakterisierung Fraktionierter Polyvinylalkohole" Helv. Chim Acta, 35, 869-885 (1952).

27. F. T. Wall, P. F. Grieger, and C. W. Childers, "Rapid Method for Measuring Diffusion Coefficients for Solutions." J. Am. Chem. Soc., 74, 3562-3567 (1952).

28. F. T. Wall and C. W. Childers, "Measurement of Ordinary Diffusion Coefficients of Polymers." J. Am. Chem. Soc., 75, 3550-3552 (1953).

29. D. See, via C. Gooding, Department of Chemical Engineering, Clemson University, private communication.