

Hydrodynamic Resistance and Flux Decline in Asymmetric Cellulose Acetate Reverse Osmosis Membranes

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Synopsis

Long-term flux-versus-time measurements were made on a series of homogeneous, dense cellulose acetate (39.8% acetyl) membranes. All tests were carried out at 1500 psi applied pressure on a 3.5% NaCl feed. These tests show that essentially all the resistance to solvent (water) flow in the typical asymmetric reverse osmosis membrane is concentrated in the thin dense layer. Further, the evidence strongly suggests that the long-term flux decline noted in asymmetric membranes is a result of viscoelastic deformation of the dense layer.

INTRODUCTION

In the 1950's Reid and Breton¹ showed that cellulose acetate membranes had the selectivity necessary to function in a reverse osmosis desalination process. The early membranes suffered from uneconomically low water fluxes, however, and it remained for Loeb and Sourirajan² to develop a procedure for fabricating high-flux asymmetric membranes from cellulose acetate. They reported fluxes in the range of 5 to 11 gallons/ft²·day (gfd) at test pressures of 1500 psi with salt rejections better than 98%. Manjikian³ later simplified the Loeb-Sourirajan process and obtained similar membranes.

Riley et al.⁴ showed that a typical asymmetric cellulose acetate membrane consisted of a dense layer approximately 0.25 microns thick supported on a porous, spongy layer comprising the rest of the 100-micron membrane thickness. The selectivity of the asymmetric membranes is universally attributed to the dense layer, but the question of the resistance of the membrane to solvent flow is not so clear-cut. Even though the dense layer would be expected to have a much higher resistance to solute flow per unit of thickness, it comprises only 0.25% of the total membrane thickness. A clearer understanding of hydrodynamics of asymmetric membranes under actual process conditions is required to point the way to high-flux membranes.

Asymmetric cellulose acetate membranes exhibit a decline in product water flux with time. This flux decline has been variously ascribed to

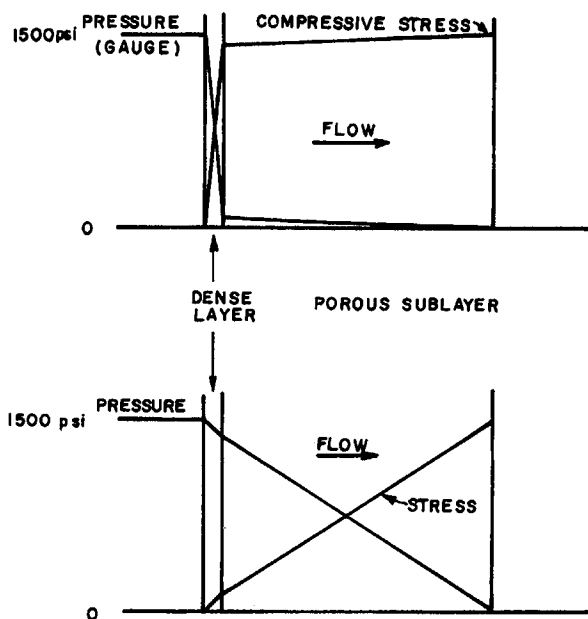


Fig. 1. Schematic pressure and stress profiles in an asymmetric membrane: (a) hydrodynamic resistance concentrated in dense layer; (b) hydrodynamic resistance concentrated in support layer.

compaction of the dense and/or support layer, hydrolysis of the polymer, conversion of support layer to dense layer (accretion), or fouling of the membrane by impurities. If the flux decline is due to a mechanical deformation of the membrane material, an understanding of the membrane hydrodynamics is essential because it fixes the stress distribution within the membrane and thus determines the nature of the deformation process. The pressure and compressive stress distributions are sketched in Figure 1 for two possible extremes: (a) essentially all of the hydrodynamic resistance in the dense layer and (b) essentially all of the hydrodynamic resistance in the support layer.

EXPERIMENTAL

A series of "dense" cellulose acetate membranes was cast from acetone solutions. Dried cellulose acetate (Eastman organic chemicals, E-398-3) was dissolved at 5 or 10 wt-% in dried and redistilled acetone. The resulting casting solutions were spread on a carefully cleaned glass plate with a Gardner adjustable film-casting knife. The membranes were allowed to air dry for 4 hr in a dust-free environment, after which they were transferred to a vacuum oven for 12 hr at 50°C and full pump vacuum (about 30 in. Hg). Membrane thicknesses were estimated by weighing a membrane section of known area and assuming a density of 1.3 g/cc for the dense cellulose acetate.

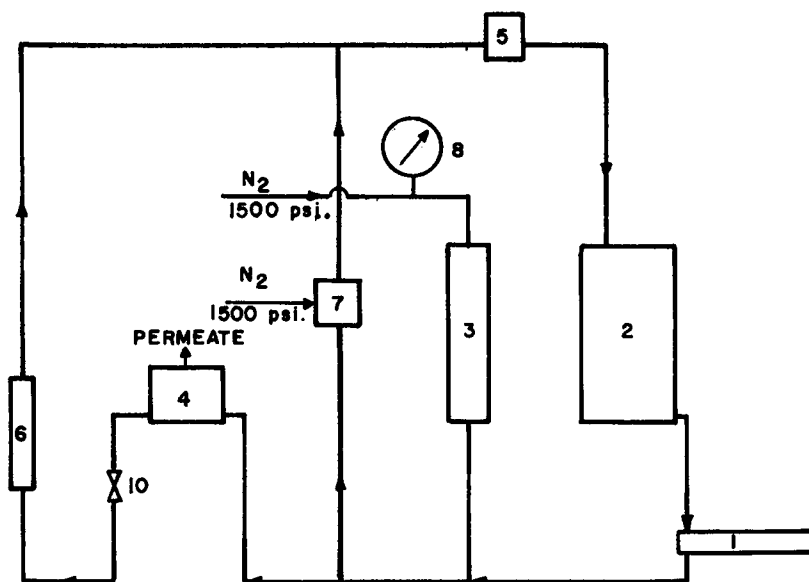


Fig. 2. Reverse osmosis test loop: (1) pump; (2) reservoir; (3) surge tank; (4) test cell; (5) filter; (6) flowmeter; (7) back-pressure regulator; (8) pressure gauge.

A flow diagram of the reverse osmosis test loop is shown in Figure 2. The individual components are: (1) pump (Sprague Engineering Model S-216—S-35); (2) brine reservoir; (3) 1-gal surge tank (Hoke 8401-G); (4) test cell; (5) filter; (6) flowmeter; (7) back-pressure regulator (Victor Controls, BPR-21); (8) pressure gage.

A diagram of the test cell is given in Figure 3. During tests, the membranes were supported on Millipore RAWPO4700 membranes (nominal pore size, 1.2 micron) and then on sintered stainless-steel disks. The manufacturer's literature (catalog MF-68) indicates that at the fluxes observed in this work (5.4×10^{-3} to 2.6×10^{-4} ml/cm²·min), the pressure drop across the Millipore filter is approx. 10^{-3} cm Hg, totally negligible under all experimental circumstances. Simple experiments confirmed the fact that the hydrodynamic resistance of the membrane supports was negligible.

All tests were carried out on a 3.5% NaCl solution at 1500 psi, $27 \pm 0.1^\circ\text{C}$. The feed solution pH was maintained at 5–6 to minimize membrane hydrolysis.

Fluxes were measured by feeding the product stream to a precision 1-ml burette and timing the rate of accumulation. Salt rejections were obtained for the thinner membranes by conductance measurements. For the thicker membranes, product fluxes were so low that the piping downstream from the membrane had to be filled with distilled water at the beginning of a run to obtain flux data. It would have taken months, in some cases, for the product water to displace the distilled water and reach a

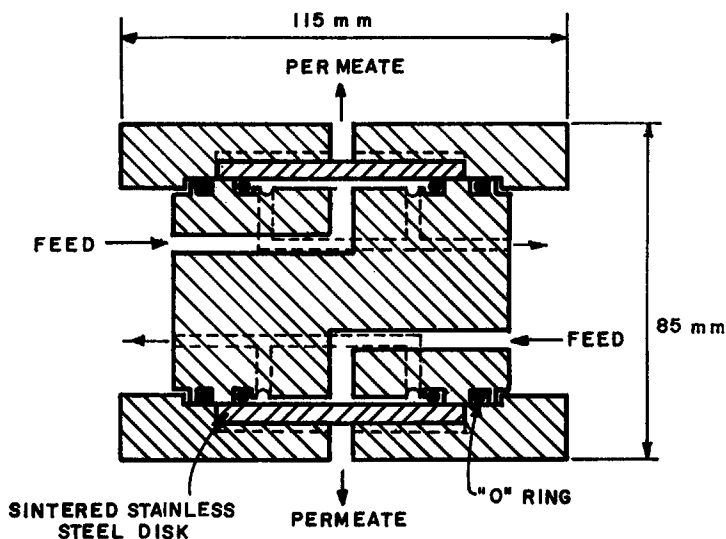


Fig. 3. Membrane test cell.

steady state, hence no rejection measurements were possible with the thick membranes.

RESULTS AND DISCUSSION

The solute flux J through a reverse osmosis membrane is given by

$$J = \frac{K(\Delta P - \Delta \pi)}{x} \quad (1)$$

where ΔP is the applied hydrostatic pressure difference across the membrane, $\Delta \pi$ is the difference in osmotic pressures between feed and product solutions, x is the membrane thickness, and K is the intrinsic permeability of the membrane material to solute. If K is truly a property of the membrane material, a plot of $1/J$ versus x should be linear for a series of experiments such as these in which only x was varied. (Measured rejections are shown in Table I. Slight variation in product stream π due to differences in rejection from membrane to membrane are negligible.) Such a plot is shown in Figure 4 for fluxes at 1 hr. The slope is $0.55 (\text{gfd} \cdot \mu)^{-1}$. Using a $\Delta \pi$ of 25 atm gives a K for E-398-3 of $0.0016 \text{ gfd} \cdot \mu / \text{psi}$.

For a dense layer of 0.25μ in thickness (the observed thickness of the dense layer in an asymmetric membrane), the predicted flux is then 7.3 gfd. This is just the magnitude of flux noted in asymmetric membranes, so it may be concluded that the hydrodynamic resistance of the typical asymmetric cellulose acetate membrane is confined essentially to the dense "skin."

TABLE I
Membrane Performance

Thickness, μ	Flux at 1 hr, gfd	Compaction slope	Salt rejection, %	
			Initial	Final
1.26	1.82	-0.075	97.7	98.6
1.60	1.34	-0.075	99.2	99.4
1.76	1.06	-0.062	96.5	—
2.26	0.78	-0.062	98.5	99.5
2.68	0.74	-0.062	99.6	99.7
2.76	0.55	-0.034	95.1	—
5.5	0.29	-0.110	93.5	96.8
6.0	0.31	-0.044	95.6	99.0
6.1	0.29	-0.017	—	—
7.3	0.25	-0.037	—	—
8.6	0.20	-0.012	—	—
8.6	0.21	—	—	—
10.1	0.17	-0.035	—	—
11.1	0.17	—	—	—
12.2	0.15	-0.052	—	—

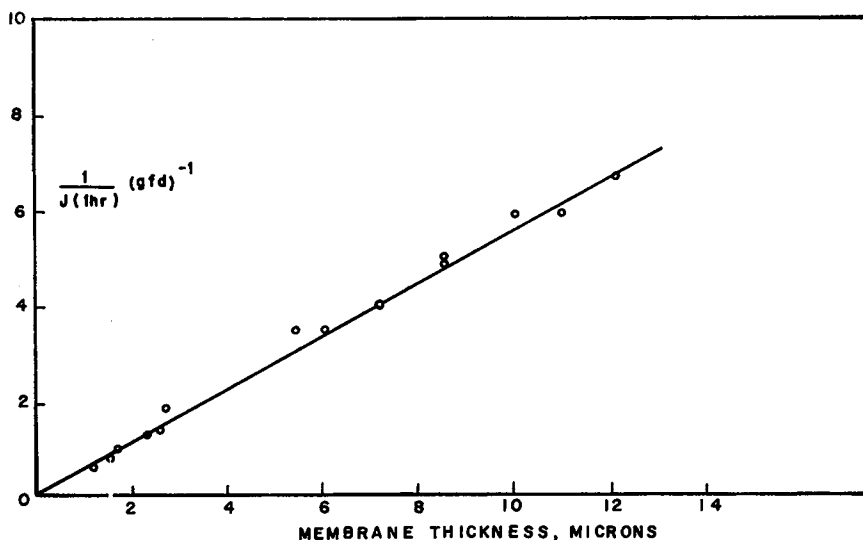


Fig. 4. Reciprocal of 7-hr product flux vs. membrane thickness.

Figure 5 shows some of the log-log flux-versus-time curves for the dense membranes. As is the case for asymmetric membranes, they are adequately represented by a power law relation

$$J = J(1) t^n \tag{2}$$

where $J(1)$ is the flux at 1 hr and t is the time in hours. The compaction slopes n for the various membranes are given in Table I. Although there is considerable scatter, the magnitude of n appears to decrease with in-

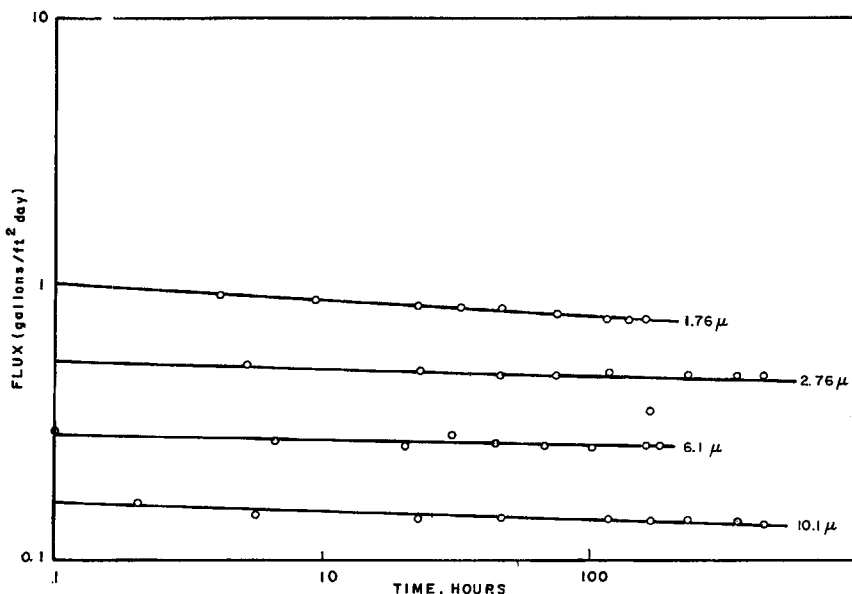


Fig. 5. Flux vs. time for membranes of various thickness.

creasing thickness. At a thickness of 0.25μ , the compaction slope would be about -0.10 , comparable to what has been observed⁵ (-0.08 to -0.14) for Manjikian-type asymmetric membranes at 27°C . While not conclusive evidence, this strongly suggests that the observed flux decline in asymmetric membranes is exclusively a matter of compaction of the dense layer, i.e., a decrease in its permeability.

Several other flux-decline mechanisms may be ruled out definitely, however. Consider the "accretion" model in which the thickness of the dense layer is postulated to increase with time at the expense of the support layer, its permeability assumed constant. Since the stress situation at the dense layer-support layer interface does not change with time, the increase in dense layer thickness must be linear with time, i.e.,

$$x(t) = x(0) + at \quad (3)$$

where $x(0)$ is the initial membrane thickness and a is the rate of dense layer accretion. Equation (1) then becomes

$$J = \frac{K(\Delta P - \Delta\pi)}{x(0) + at} \quad (4)$$

It is immediately apparent that eq. (4) is inconsistent with the observed flux decline, eq. (2). It might be argued, however, that eq. (2) is simply an empirical approximation to eq. (4) valid over a limited time span. Figure 6 compares a typical flux decline response for an asymmetric membrane, $J(1) = 7.3$ gfd, $n = -0.10$, with that predicted by eq. (4), with parameters evaluated to fit at 1 hr and 100 hr. There is no way eq. (4)

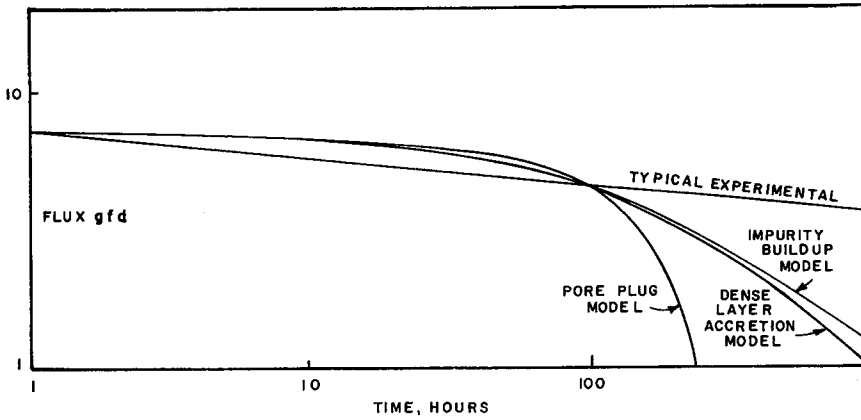


Fig. 6. Comparison of typical experimental flux vs. time results with the predictions of various models.

can fit the flux decline data obtained over two to three orders of magnitude, hence an accretion mechanism may be ruled out.

If it is postulated that the flux decline is due only to an accumulating layer of impurities on the membrane surface, the flux is given by

$$J = \frac{\Delta P - \Delta \pi}{(x/K) - x'(t)/K'} \tag{5}$$

where x and K are properties of the membrane material, here assumed constant, K' is the permeability of the impurity layer (also constant), and $x'(t)$ is the time-varying thickness of the impurity layer.

It is logical to assume that the amount of impurity deposited on the membrane is proportional to q , the total volume of fluid per unit area which has passed through the membrane since the beginning of the test, i.e.,

$$q(t) = \int_0^t J(t) dt = J(1) \int_0^t t^n dt = J(1) \left[\frac{t^{n+1}}{n+1} \right] \tag{6}$$

and

$$x'(t) = b \cdot q(t). \tag{7}$$

Therefore,

$$J = \frac{(\Delta P - \Delta \pi) K}{x - \{b J(1)/[K'(n+1)]\} t^{n+1}}. \tag{8}$$

Using the experimentally observed value of $n = -0.10$, and fitting eq. (8) at $t = 1$ and 100 hr, Figure 6 illustrates that this model cannot explain the facts either.

If a pore model for membrane structure is adopted, it may be argued that flux decline is due to a plugging of the pores at the membrane surface

by particles. In this case, the permeability K is proportional to the number of open pores present, or

$$K(t) = K(0) \left(1 - \frac{n_b(t)}{n(0)} \right)$$

where $n_b(t)$ represents the number of pores *blocked* at time t . It is reasonable to assume that the number of blocked pores is proportional to the volume of fluid which has passed through the membrane,

$$n_b(t) = c \cdot J(1) \left[\frac{t^{n+1}}{n+1} \right] \quad (9)$$

and

$$J = \frac{K(0) (1 - [c \cdot J(1)/(n+1)]t^{n+1})}{x} \quad (10)$$

Again, using $n = -0.10$ and fitting at $t = 1$ and 100 hr, Figure 6 shows that eq. (10) is unable to explain the data.

Since the three models examined all fail in the same fashion (slopes too small at short time, too large at long times), no combination of them could prove adequate, further supporting the contention that flux decline is a result of viscoelastic compression of the dense layer.

CONCLUSIONS

Essentially all the hydrodynamic resistance to the flow of solvent in an asymmetric cellulose acetate membrane is concentrated in the thin, dense, salt-rejecting layer. The evidence strongly suggests that flux decline in such membranes results from viscoelastic creep of the dense layer. Thus, future work attempting to improve flux and flux decline properties of such membranes need concentrate on the dense layer only.

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