

TREATMENT OF OILY WASTES USING HIGH-SHEAR ROTARY ULTRAFILTRATION

By Brian E. Reed,¹ Member, ASCE, Wei Lin,² Roger Viadero Jr.,³ and Joseph Young⁴

ABSTRACT: The high-shear rotary ultrafiltration (UF) system uses membrane rotation to provide the turbulence required to minimize concentration polarization and flux decline. The high-shear UF system was effective in concentrating oily wastes from about 5% to as high as 65%. The decoupling of turbulence promotion from feed pressurization/recirculation by rotating the membrane was the primary reason for the improvement in performance over that observed with conventional UF systems. Transitional and gel layer oil concentrations (20% and 50–59%, respectively) were higher than values reported in the literature. Permeate flux was dependent on the temperature and rotational speed. Flux increased by about 45% when the temperature was increased from 43 to 60°C. A larger decrease in waste viscosity, over that predicted for water alone, and increased oil droplet diffusivity were hypothesized as reasons for the stronger than expected flux-temperature relationship. The flux-rotational speed (ω) relationship was described by $J = f(\omega)^{0.90}$; however, the gel layer exhibited stability with increasing ω . The ceramic membrane was superior to the polymeric membrane in regards to permeate flux and quality as well as cleaning and durability.

INTRODUCTION

Oily wastes are produced by various metal-working operations (rolling mills, metal cutting, and working). For many companies the oily waste is mixed with other oil or nonoil waste streams and then treated with conventional cross-flow membrane filtration systems (e.g., tubular, spiral wound, etc.). The residual from conventional membrane systems is usually treated further by physical-chemical methods (e.g., chemical addition-settling) prior to disposal or recycling.

The ability of conventional membrane technology to treat a concentrated oily waste directly or the residual from the conventional membrane system is limited because of the low permeate flux observed at high oil concentrations. Conventional cross-flow systems rely on high recirculating velocities (≈ 3 m/s) to scour or clean the membrane surface so that a satisfactory permeate flux is maintained. As the concentration of the feed increases, the maintenance of a high velocity is difficult because of the increase in feed viscosity. The decoupling of the cleaning action from feed recirculation/pressurization can be accomplished by rotating the membrane surface. The rotation of the membrane provides the turbulence required to clean the membrane while the pump is required only to provide transmembrane pressure and a relatively small amount of recirculation (SpinTek, Huntington Beach, Calif.).

The objective of this research was to assess the efficacy of using the high-shear rotary membrane system in the treatment of concentrated oily wastes. Two types of membrane materials, ceramic and polymeric, were evaluated. System performance was measured using the following parameters: (1) Permeate flux; (2) permeate quality; and (3) membrane cleaning and durability. The effects of rotational speed and temperature

were investigated, and values of the mass transfer coefficient, transitional concentration, and gel layer concentration were determined.

BACKGROUND

Ultrafiltration (UF) is a pressure-driven membrane technique that uses porous membranes for the separation of material in the 1 nm-10 μm size range or compounds with molecular weights in excess of 1,000 (Cheryan 1986). Colloidal material, macromolecules, and micelles are examples of items that can be fractionated. "Clean" water (permeate) is forced through the porous membrane while the solute is retained by the membrane, concentrating the feed with time. Numerous researchers have reported on UF's effectiveness in treating oil/grease wastewaters. UF reduced the volume of a waste-cutting oil emulsion by 95–98% and concentrated oil and solids as much as 60% (Pinto 1978). Bodzek and Konieczny (1992) reported oil reductions of 95–99% and COD reductions of 91–98% in the UF permeate from a metal industry emulsion. Zaidi et al. (1992) reported that the oil content of several oil field brines was reduced to less than 20 mg/L and that the short-term permeate flux was about 3.25 $\text{m}^3/\text{m}^2\text{-d}$ (80 gal./ft²-d). Cheryan (1986) summarized several case studies in which UF was demonstrated to be an effective treatment method for oily wastes and stressed the need for waste specific treatability studies in order to properly design a UF system. Treatability studies should be of long enough duration so that temporal changes in membrane behavior (e.g., membrane fouling) can be ascertained.

In all membrane processes, a solute boundary layer will form at the membrane surface due to convective mass transport. This phenomenon is referred to as "concentration polarization" and is shown schematically in Fig. 1 (Cheryan 1986). Concentration polarization is one reason why the permeate flux for a waste is lower than the clean water flux (CWF). The buildup of the solute near the membrane surface is reduced by back diffusion of the solute, and the boundary layer thickness can be reduced through turbulence. If the solute concentration at the membrane is high enough, a "gel layer" can form. The "gel layer" can be an actual gel or the closest-packed arrangement of solute molecules. Additionally, solute can be adsorbed or be forced into the membrane pores resulting in fouling of the membrane.

The high-shear rotary membrane system (Fig. 2) uses a series of flat, round membrane disks set on a hollow rotating shaft inside a cylindrical housing. A very porous cot-

¹Assoc. Prof., Dept. of Civ. and Envir. Engrg., West Virginia Univ., Morgantown, WV 26506-6103.

²Asst. Prof., Dept. of Civ. Engrg., North Dakota State Univ., Fargo, ND 58102-1890.

³Grad. Res. Asst., Dept. of Civ. and Envir. Engrg., West Virginia Univ., Morgantown, WV.

⁴Grad. Res. Asst., Dept. of Civ. and Envir. Engrg., West Virginia Univ., Morgantown, WV.

Note. Associate Editor: J. B. Neethling. Discussion open until May 1, 1998. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on January 2, 1997. This paper is part of the *Journal of Environmental Engineering*, Vol. 123, No. 12, December, 1997. ©ASCE, ISSN 0733-9372/97/0012-1234-1242/\$4.00 + \$.50 per page. Paper No. 14866.

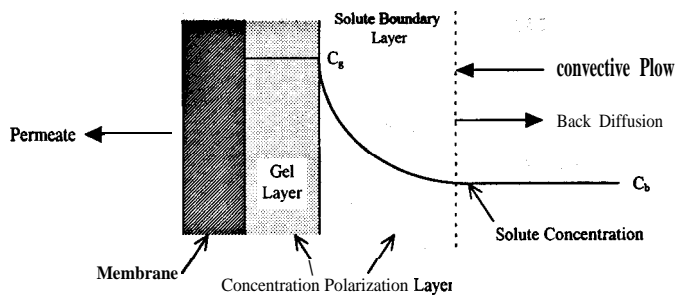


FIG. 1. Schematic of Concentration Polarization at Membrane Surface (after Cheryan 1988)

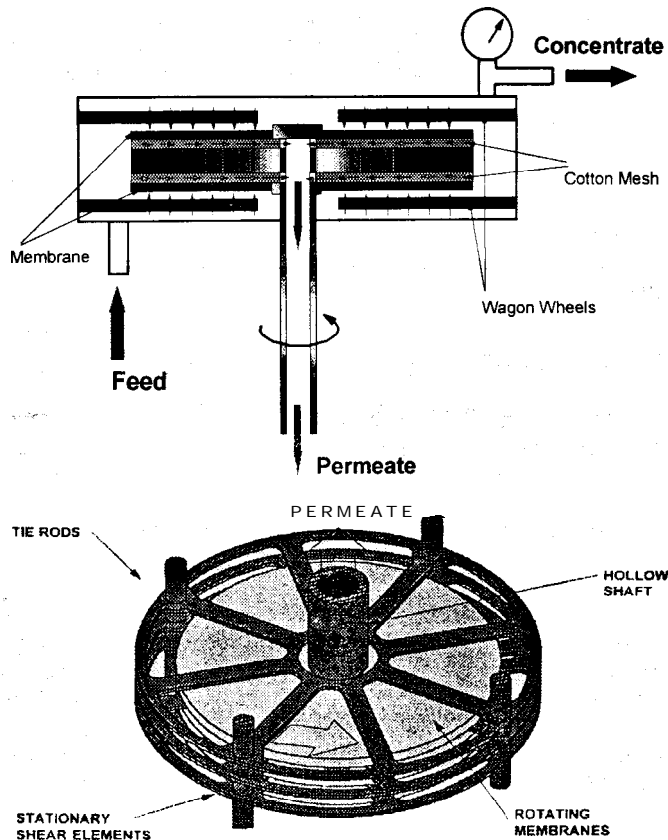


FIG. 2. Schematic of SpinTek High-Shear Rotary Membrane Vessel (Only One Disk Shown) and Turbulence Promoters ("Wagon Wheels")

ton mesh lies between the membrane and solid disk and acts as the flow channel for the permeate. The feed stream enters the membrane chamber under pressure and is distributed across the membrane surface. Permeate is forced through the membrane into the cotton mesh and travels toward the center of the disk where it collects in the hollow shaft and is discharged. The concentrate exits at the edge of the membrane packs. To reduce concentration polarization in conventional UF systems, a large portion ($\approx 98\%$) of the concentrate is recycled back to the membrane unit producing large liquid velocities near the membrane surface. The large velocities increase turbulence, which reduces the thickness of the solute boundary layer. In the high-shear system, the rotation of the membrane disk produces the required turbulence. In addition to the rotational action, turbulence promoters ("wagon wheels") are located on each side of the membrane to prevent rotational flow (vortex formation) from occurring. In conventional UF systems, maximum liquid velocities of about 4.5 m/s are possible, whereas with the high-shear system, liquid velocities of 18 m/s are typical. As the feed thickens with treatment time, a conventional UF system is not able to main-

tain the high cross-flow velocities because of the difficulty in pumping viscous material at high flow rates. Because the high-shear system does not rely on pumping to produce the required liquid velocities, extremely concentrated wastes can be treated.

UF membranes are often characterized by the molecular weight of a compound that is not able to pass through the membrane. In theory a significant amount (90%) of compounds having a molecular weight greater than the membrane's molecular weight cutoff (MWCO) would be retained by the membrane, and compounds with molecular weights less than the MWCO would pass through the membrane and reside in the permeate. It should be noted that the MWCO designation is somewhat misleading because a molecule having a molecular weight less than the membrane's MWCO may still be retained by the membrane because its three-dimensional shape will not allow it to pass through the membrane pores and vice versa. Membranes can also be designed so that the surface is charged. For example, a membrane with a negative surface charge may be chosen for a contaminant that also is negatively charged. The repulsive force between the membrane surface and solute can decrease the solute boundary thickness and density as well as solute adsorption on the membrane surface. Reed et al. (1997) reported that a negatively charged tubular membrane with a MWCO of 120,000 had a higher flux and similar permeate quality in comparison with a membrane having a neutral charge and a MWCO of 100,000 in treating a 0.2–0.5% oil/grease waste.

Modeling Permeate Flux

In Fig. 3 the hypothetical relationship among flux, transmembrane pressure, feed concentration, and cross-flow velocity is presented. For clean water and feeds at low concentrations and pressures, the Hagen-Poiseuille model can be used to predict the permeate flux

$$J = \epsilon r^2 \Delta P / 8 \eta \Delta x \quad (1)$$

where J = permeate flux (volume/membrane area-time); ϵ = surface porosity of membrane; r = mean pore radius; ΔP = transmembrane pressure; η = viscosity of fluid permeating membrane; and Δx = membrane thickness. As pressure or solute concentration is increased, the flux becomes independent of pressure, and film theory model (based on mass transfer considerations) is used to predict the limiting flux (Lipp et al. 1984)

$$J = k_s \ln(C_b/C_m) \quad (2)$$

where k_s = mass transfer coefficient; C_b = solute concentration in bulk solution; and C_m = solute concentration at membrane surface. If the concentration of the solute at the membrane

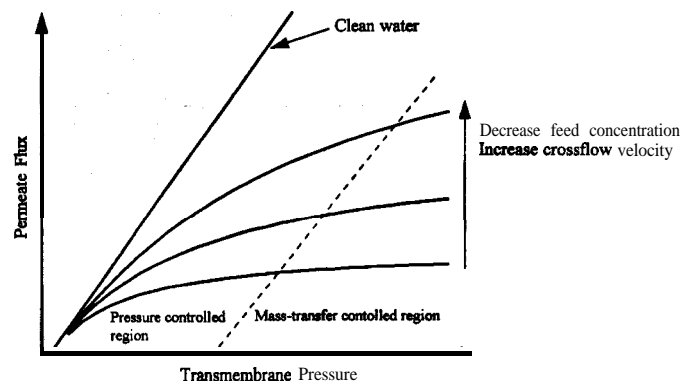


FIG. 3. Hypothetical Relationship between Permeate Flux and Transmembrane Pressure, Feed Concentration and Cross-Flow Velocity (after Cheryan 1988)

surface is high enough, a gel layer can form. For this case (2) becomes

$$J = k_s \ln(C_r/C_b) \quad (3)$$

where C_r = gel layer concentration. Prior to the formation of the gel layer, the flux is a weak function of C_b because C_m increases with increasing C_b . When the gel layer has formed, J will decrease exponentially with C_b .

The film theory model predicts that the limiting flux is dependent on the concentration of the solute at the membrane surface and k_s but independent of pressure. Increasing the transmembrane pressure momentarily increases the flux, but the thickness of the solute boundary layer will also increase, which reduces the flux to its previous level. In the mass transfer controlled region (i.e., pressure independent), the flux can only be increased by increasing the mass transfer coefficient (k_s):

$$k_s = D/\delta \quad (4)$$

where D = solute diffusion coefficient; and δ = thickness of concentration polarization layer. Decreasing δ by increasing the turbulence at the membrane surface and increasing D by increasing the operational temperature are two ways of increasing the mass transfer coefficient. Cheryan (1986) reported the following general relationship:

$$k_s d_h / D = A(R)^\alpha (S)^\beta \quad (5)$$

where d_h = hydraulic diameter; R = Reynolds number; and S = Schmidt number. For turbulent flow ($R > 4,000$), $A = 0.023$, $\alpha = 0.8$, and $\beta = 0.33$.

The Wilkes modification of the Stokes-Einstein equation can be used to estimate the increase in diffusivity with temperature

$$D_1 = D_2 \eta_2 T_1 / T_2 \eta_1 \quad (6)$$

where T = absolute temperature. A power-law relationship can be used to ascertain the effect of cross-flow velocity (or rotation) on the flux

$$J = f(\text{velocity})^\alpha \quad (7)$$

Values of α ranging from 0.3 to 0.6 for laminar conditions and from 0.8 to 1.2 for turbulent conditions have been reported (Cheryan 1986).

MATERIALS AND METHODS

A total of six runs was completed using coolants/lubricants from an aluminum rolling mill operation. Three runs were conducted using polymeric membranes (PV-1 OOK), and three were completed using a ceramic membrane. Characteristics of the two membranes are presented in Table 1. The coolants/lubricants had an initial oil content between 4.2 and 4.6% and were taken directly from the milling process at different points in their "batch life." Both coolants contained surfactants, film strength additives, and antifoaming agents, but specific contents of the mixtures cannot be disclosed for proprietary reasons.

A schematic of the experimental apparatus is presented in Fig. 4. The pilot-scale high shear unit contained one 20-cm (8-in.) diameter membrane disk. The disk had a membrane on each side for a total membrane area of 492 cm² (0.53 ft²). Membrane rotational speed could be varied between 100 and 1,750 rpm. A heat exchanger was located in the feed tank to control system temperature. The volumes of the feed and waste storage tanks were 57 L (15 gal.) and 227 L (60 gal.), respectively. A centrifugal pump was used to transfer the waste from the feed tank to the membrane vessel as well as to provide the required transmembrane pressure. A bypass valve was used to control the transmembrane pressure. After

TABLE 1. Characteristics of Membranes

Characteristic (1)	PV-1 OOK (2)	Ceramic (3)
Manufacturer	Advanced membrane technology	TRUMEM
Material	Polyvinylidene fluoride	TiO ₂ -Al ₂ O ₃
Area	492 cm ²	492 cm ²
Average pore size	100,000 MWCO*	0.11 μm
Maximum operating pressure	150 psi	z-150 psi
Maximum operating temperature	-50°C	>70°C

*Molecular weight cutoff. A MWCO of 100,000 ≈ 0.05 μm.

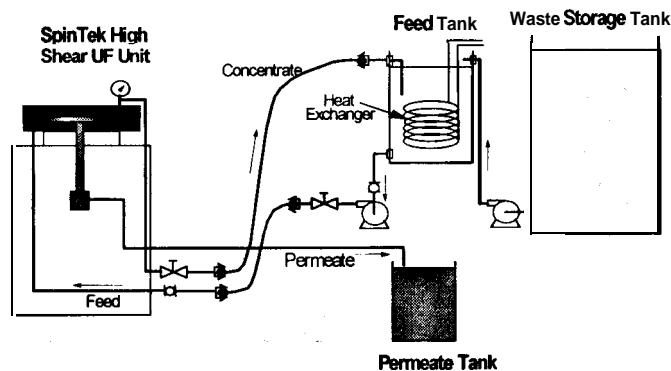


FIG. 4. Schematic of Experimental Pilot-Scale Setup

leaving the membrane chamber, the concentrated waste ("concentrate") was returned to the feed tank. The flow rate from feed tank to membrane vessel is referred to as the recirculating flow rate. The feed tank waste volume was controlled by pumping waste from the waste storage tank to the feed tank using a peristaltic pump.

Prior to the start of a run, the system was filled with deionized water and the CWF was measured under the following conditions: (1) Pressure = 42 psi; (2) rotational speed = 1,750 rpm; (3) recirculating flow rate = 4.5 L/min (1.2 gal./min); and (4) feed tank temperature = 43°C ± 1°C (110°F ± 2°F). Permeate flux was measured every 5 min until it had stabilized for a 30-min period.

Following the CWF determination, the system was drained and the waste was pumped from the original waste drum(s) through a 100 mesh sieve into the waste storage tank. A predetermined volume of coolant (V_{system}) was then pumped from the waste storage tank to the feed tank. The system was first operated in semibatch mode. During semibatch operation, the feed tank volume was kept constant (V_{system}) by pumping waste from the waste storage tank to the feed tank at the same rate as permeate was removed. When the waste storage tank was empty, batchdown operation began. During batchdown operation the feed tank volume was reduced at the rate that permeate was removed. The run was ended when the lowest possible feed tank volume was reached [≈9.5 L (2.5 gal.)]. For two runs (PV-100K runs 2 and 3), the system was cleaned in midrun because the permeate turbidity increased significantly. Based on earlier research, turbidity was a good real-time indicator of oil in the permeate (Reed et al. 1997; Lin and Reed 1996). The operational conditions for waste treatment were the same as those presented earlier for the CWF determination. Permeate flow rate and turbidity, feed tank temperature, and vessel pressure were measured every 30 min.

Volumetrically based waste concentration factors (CFs) were calculated by measuring the volume of permeate produced (V_{perm}) and the following equations:

$$CF_{SB} = 1 + V_{\text{perm}}/V_{\text{system}} \quad (8)$$

$$CF_{BD} = CF_{SB} \times [V_{\text{system}}/(V_{\text{system}} - V_{\text{perm}})] \quad (9)$$

where CF_{SB} = concentration factor during semibatch operation;

V_{perm} = volume of permeate produced; V_{system} = volume of waste in feed tank; and CF_{BD} = concentration factor during batchdown operation. The concentration factor is expressed as nX —raw waste has a $CF = 1X$. If the volume of the waste is halved, the $CF = 2X$ and so on. During semibatch and batchdown operation, the value of CF increases as permeate is removed from the system and oil is retained. The volumetrically based waste CF is equivalent to the solute based CF if the amount of solute in the permeate is small relative to the amount of solute that is retained. At whole number values of CF (i.e., $1X$, $2X$, $3X$, etc.), the permeate was sampled for oil/grease (O/G), total suspended solids (TSS), COD (PV-100K runs 1 and 2 only) and pH and analyzed according to Standard (1992).

At the conclusion of batchdown operation, all concentrate was drained from the system and its volume was measured. The system was first flushed using tap water ($\approx 57^\circ\text{C}$) until the liquid from the return hose was clear, and then was washed. For all the polymeric runs and ceramic run 1, the washing solution consisted of 181 g of a commercial laundry detergent and -30 mL of a commercial dishwashing liquid in 19 L of hot tap water ($\approx 57^\circ\text{C}$). The pH of the washing solution was 10.3. For ceramic runs 2 and 3, the washing solution was changed because a white substance, believed to be detergent, had deposited on the inner portion of the membrane. A new washing solution, consisting of 30 mL of the dishwashing liquid, pH = 10 (adjusted with NaOH), was used. Following washing, the system was flushed with tap water (43°C) and then the CWF was determined. After determining the CWF, the membrane was visually inspected. If, after visual observation, it was determined that the membrane was permanently fouled/damaged or the CWF was not close to the CWF taken prior to the run, the membrane was replaced.

Deviations from the previously mentioned procedure were as follows: (1) For ceramic runs 2 and 3, the system was operated in the recycle mode at whole number values of CF to assess long-term performance of the system (routing the permeate back to feed tank kept the CF and oil content in the feed tank constant); and (2) for ceramic run 3, temperature and rotational speed excursions were conducted at $CF = 4X$. Temperature was increased to 60°C (140°F) for about 20 h during the course of the run, and the rotational speed was 1,750 rpm. After the temperature excursion, the rotational speed was changed from 1,750–1,000 rpm to 1,250–1,500 rpm and then finally back to 1,750 rpm. The system temperature was 43°C (110°F) during the rotational excursions and each excursion lasted about 5 h.

RESULTS

Permeate Flux

Polymeric Membrane

In Fig. 5 the permeate flux and concentration factor (CF) versus time are presented for polymeric runs 1-3. After the temperature had stabilized at 43°C (110°F), the flux during semibatch operation was relatively stable in run P1 but declined in runs P2 and P3. In conventional cross-flow UF systems, flux decline at the start of a run is much larger than what was observed in Fig. 5. For example, Lin and Reed (1996) and Reed et al. (1997) reported that for a 0.5% oil waste the flux declined by as much as 50% from its initial value to the flux observed several hours into the run. The decline in flux was attributed to concentration polarization. While concentration polarization is also operative in the high-shear rotary system, the rotationally induced turbulence kept the flux decline to a minimum, despite the waste having an oil content that was an order of magnitude larger. The highest flux was observed in run P2, and the high flux could be the cause of the

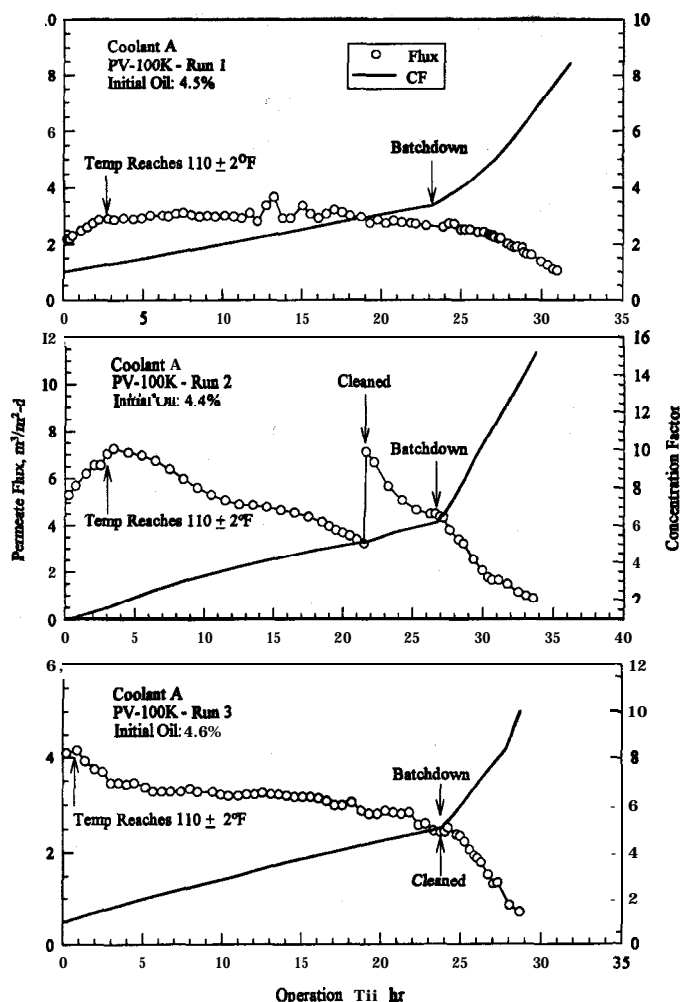


FIG. 5. Permeate Flux and Concentration Factor (CF) versus Operation Time for PV-100K Membrane Runs 1, 2, and 3

most obvious flux decline. The higher the flux, the more solute is transported to the membrane surface and the larger the concentration polarization effect. The more obvious flux decline in run P2 could also be due to waste variations. For run P2 the system required cleaning at 21.5 h because of high turbidity levels in the permeate. After cleaning, the flux increased to approximately the value that was observed at the beginning of the run ($-6.9 \text{ m}^3/\text{m}^2\text{-d}$), but then decreased sharply. For run P3 the system was cleaned prior to the start of the batchdown operation, but no increase in flux was observed following cleaning, indicating that the membrane had not been fouled as was the case in run P2. For all runs the flux decreased sharply during batchdown operation as the CF (oil content of feed) increased rapidly.

Ceramic Membrane

In Fig. 6 the permeate flux and concentration factor (CF) versus operation time are presented for ceramic runs 1-3. For runs C2 and C3 the system was operated in the recycle mode at whole number values of CF to determine if the flux was temporally dependent at a given CF . In run C2 (coolant A), the flux decreased during changes in CF but then increased during the subsequent recycle operation to about one-half or more of the value observed at the previous CF . For run C3 (coolant B), this phenomenon was not as apparent and could be due to the differences between coolants A and B. In a full-scale system, V_{system} is often large (40 – 160 m^3), and the system is operated for long periods of time before there is a large change in the CF . For coolant A, if the predesign treatability

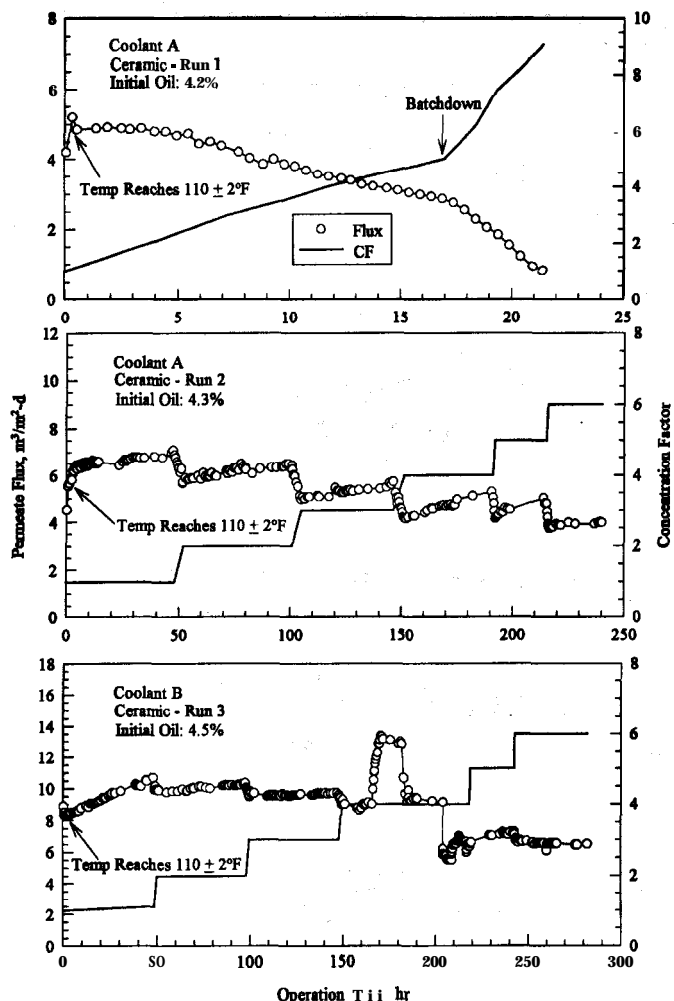


FIG. 6. Permeate Flux and Concentration Factor (CF) versus Operation Time for Ceramic Membrane Runs 1, 2, and 3

study was conducted without recycling the permeate at predetermined *CFs* (as was done in ceramic run C1), the design flux would be underestimated. Cheryan (1986) has suggested that the flux versus *CF* relationship be determined using discrete membrane tests (i.e., make up samples of the waste at predetermined concentrations and then run the membrane system in the recycle mode). After each discrete test, the system would be cleaned and the CWF measured to ascertain if fouling has occurred. While this approach is useful when dealing with synthetic wastes, it is not feasible when actual wastes are studied.

Permeate Quality

In Table 2 a summary of the permeate quality parameters for both membranes for the entire run, between *CF* = 1X to 6X and *CF* > 6X is presented. Results from each membrane will be discussed separately.

Polymeric Membrane

In Fig. 7 permeate turbidity and O/G versus operation time are presented for PV-100K runs 1-3. The permeate TSS followed the same trend as the turbidity and O/G; thus, a summary of TSS data is presented in table form only (see Table 2). For all runs the permeate turbidity, O/G, and TSS increased with operation time with the largest increase taking place at high *CFs*. In run P1 the turbidity decreased from about 5 to 20 h and could be due to the formation of a solute boundary layer that acted as a second membrane. In run P2 the system

was cleaned at 21.5 h; however, turbidity and O/G were lowered only for a short time, after which both rose sharply. Permeate COD was measured for runs P1 and P2 and followed the same trends as permeate turbidity, O/G, and TSS. Initially, the permeate COD was approximately 2,600–2,800 mg/L and was a measure of the low molecular weight additives (free surfactant, antifoaming agents, biocides, etc.) that were not retained by the membrane. As the feed thickened, the COD increased to as high as 15,000 mg/L. The high COD at higher *CFs* is attributed to oil droplets that were not retained by the membrane and an increased amount of low molecular weight additives in the aqueous phase due to an increase in oil droplet size (as the oil content increased, oil droplets coalesced, allowing surfactant to be transferred to the aqueous phase—a larger oil droplet requires less surfactant to remain emulsified). For all runs there was a good correlation among permeate turbidity, O/G, and TSS; thus, the use of turbidity as a real-time indicator of permeate quality is feasible.

Ceramic Membrane

In Fig. 8 permeate turbidity and O/G versus operational time are presented for ceramic membrane runs 1-3. In run C1 the turbidity and O/G followed the same trend as observed with the polymeric membranes. However, in runs C2 and C3 the turbidity was very low throughout the run and the O/G was always below 45 mg/L. Differences in oil content of the feed between run C1 and runs C2 and C3 do not account for the difference in membrane performance as the permeate quality in the common *CF* range (1X to 6X) was better for runs C2 and C3 compared with run C1 (see Table 2). Additionally, in over nine additional runs on a variety of oily wastes, the same ceramic membrane always produced permeate that was similar in quality to that observed in runs C2 and C3. It is not clear why the membrane performed better in runs C2 and C3 (and in other subsequent runs) compared with run C1 (virgin membrane). With use a membrane may be compressed, producing a tighter membrane for later runs. However, this phenomenon has been reported for polymeric membranes but not for ceramic membranes. The physical/chemical nature of the membrane may also have been altered, for the better, by additives found in the coolant or by the first washing. In future research, the physical/chemical nature (e.g., oil and water contact angles and surface tensions) of the membrane should be compared after each run to determine the effect of the waste on membrane behavior. Waste differences between runs could also account for the difference in permeate quality. However, as was mentioned previously, in numerous subsequent run the permeate was of similar quality to that observed in runs C2 and C3. For runs C2 and C3 the system produced permeate of excellent quality while being operated for extended periods of time (between 250 and 300 h); thus, long-term operation of the system should not affect permeate quality significantly.

DISCUSSION

Lipp et al. (1984) reported that extrapolating the flux to 0 on the *J* versus log concentrate concentration plot provides an estimate of the value of *C_g*. In Fig. 9, *J*-log oil content (OC) data are presented for PV-100K runs 1-3 and for ceramic run 1. The transitional OC (oil content at which *J* decreases linearly with log OC-transition between pressure dependent and mass transfer control regions) for ceramic run 1 was 19.0% and for PV-100K runs 1 and 3 was 20.6 and 20.7%, respectively. *C_g* was calculated by linearly extrapolating the OC data, which was greater than *OC_{transition}* to *J* = 0. *OC_g* for ceramic run 1 was 50.4% and for PV-100K runs 1 and 3 was 58 and 59%, respectively. Lipp et al. (1984) reported a transitional oil content of about 15% and a *C_g* of 35% for a coolant/lubricant

TABLE 2. Summary of Permeate Water Quality Results

Parameter (1)	Mean Value (Range)			Removal (%) (5)
	Entire run (2)	CF: 1X to 6X (3)	CF > 6X (4)	
Turbidity, NTU				
PV-1&K				
Run 1	74 (1.7-1,210)	4.8 (1.7-123)	453 (151-1,213)	NA ^b
Run 2 ^a	183 (0.9-1,510)	74 (0.9-237)	554 (162-1,510)	
Run 3	144 (0.6-1,380)	12.5 (0.6-245)	876 (347-1,380)	
Ceramic				
Run 1	81 (2.1-760)	11.6 (2.1-92)	436 (131-760)	NA ^b
Run 2	—	1.2 (0.7-9.0)	—	
Run 3 ^c	—	0.2 (0.1-0.3)	—	
O/G, mg/L				
PV-100K				
Run 1	221 (87.5-1,190)	105 (87.5-117)	647 (242-1,190)	98.8
Run 2 ^c	831 (81-4,390)	426 (81-1,540)	1,480 (241-4,390)	94.8
Run 3	945 (76-9,660)	111 (76-257)	3,730 (463-9,660)	99.6
Ceramic				
Run 1	187 (106-464)	130 (106-176)	300 (194-464)	99.4
Run 2	—	37.4 (32.4-42.3)	—	99.9
Run 3	—	10.8 (<1-20.7)	—	99.9
TSS, mg/L				
PV-100K				
Run 1	55.6 (11.1-251)	36.2 (11.1-94.9)	126 (29.0-251)	99.3
Run 2 ^c	120 (1-329)	82.1 (1-329)	161 (31.0-296)	99.0
Run 3	53.6 (cl -401)	11.0 (<1-73)	217 (99-296)	99.5
Ceramic				
Run 1	12.3 (<1-49)	3.4 (<1-10.0)	32.3 (26.0-49.0)	99.5
Run 2	—	8.8 (cl -32.0)	—	99.7
Run 3 ^c	—	1.2 (<1-4.0)	—	99.7
COD, mg/L				
PV-100K				
Run 1	4,100 (2,820-5,560)	3,790 (2,830-4,590)	4,820 (4,670-5,100)	NA ^b
Run 2	6,550 (2,610-15,000)	5,230 (2,610-9,760)	7,870 (3,120-15,000)	

^cIncludes period after cleaning.

^bNot applicable-initial value too high to be measured.

^cIncludes data up to CF = 4X prior to temperature excursion.

waste. Lee et al. (1984) reported a C_g of 40% for a mineral oil-based coolant. The absolute value of the slope of the log J versus log OC plot (for OCs data $> OC_{transition}$) is equal to k_s (Cheryan 1986). k_s was $1.86 \text{ m}^3/\text{m}^2\text{-d}$ for ceramic run 1 and 1.41, 1.85, and $1.73 \text{ m}^3/\text{m}^2\text{-d}$ for PV-100K runs 1, 2 (after cleaning), and 3, respectively. The value of k_s should not vary with membrane type [see (4) and (5)] unless the membranes differ significantly in their behavior toward oil. For ceramic runs 2 and 3, the coolant was concentrated to $CF = 6X$, and no estimation of C_g and k_s could be made (final OC not sufficiently beyond $OC_{transition}$).

In both the Lipp et al. (1984) and Lee et al. (1984) studies, a batch UF cell stirred at 300 rpm was used. Under these conditions, laminar conditions prevailed and a gel layer thickness of about $100 \mu\text{m}$ at 25% oil was calculated (Lipp et al. 1984). The thickness of the gel layer in this study in the region of high shear should be much smaller given the high rotational speed and the presence of the turbulence promoters. Since the rotational speed decreases with membrane radius, the thickness of the gel layer should be greatest near the center. In fact, when viewing the polymeric membranes after a run, an oil stain was observed in the region $r = 1.9\text{-}7 \text{ cm}$ (the region $r = 0\text{-}1.9 \text{ cm}$ constituted the hollow shaft, i.e., no membrane) indicating that the oil may have coalesced in this region. The membrane from $r = 7$ to 10.15 cm retained its original whitish color. Thus, a portion of the flux decline can be attributed to a decrease in effective membrane area. Given that the rotationally induced cleaning action varies radially in the rotary membrane system, the value of C_g may be overestimated because a nonzero flux at high CF s may exist due to the presence of a relatively clean membrane surface at the outer ring. Ex-

periments are currently being conducted to investigate this phenomenon.

For PV-100K run 2 the system was cleaned at a CF of 5.14. The flux increased after cleaning (but at the same CF), indicating that the flux decline was due in part to membrane fouling in addition to concentration polarization. By contrast, for PV-100K run 3 the system was cleaned at a $CF = 5$, but the flux before and after cleaning was the same. A constant flux before/after cleaning indicates that concentration polarization is primarily responsible for the flux decline. The fouling of the membrane during PV-100K run 2 may have been bacterial in nature. The aluminum manufacturer has reported in the past the presence of a large population of bacteria that degrades the emulsifying additives. The degradation of the emulsifying packaging could also explain the higher flux observed in PV-100K run 2. As the emulsifier concentration is lowered, the oil droplet size increases, resulting in a larger flux. This phenomenon has been reported by other researchers (Lipp et al. 1984). Also, as the size of the oil droplets increases, the emulsion is more likely to "break" (free oil formation). Free oil formation on the PV-100K membrane surface may have been the cause of the decrease in permeate quality at high CF s.

The effect of temperature and rotational speed on permeate flux was determined during ceramic run 3 and the results are presented in Fig. 10. At 166 h and $CF = 4X$, the feed tank temperature was increased from 43 to 60°C (110 to 140°F), resulting in an increase in flux from 8.96 to $13.0 \text{ m}^3/\text{m}^2\text{-d}$. The viscosity of water, which decreases by 24% over the temperature range investigated, accounts for only a portion of the flux increase. The additional increase in flux was due to changes in the waste viscosity and the diffusivity of the oil

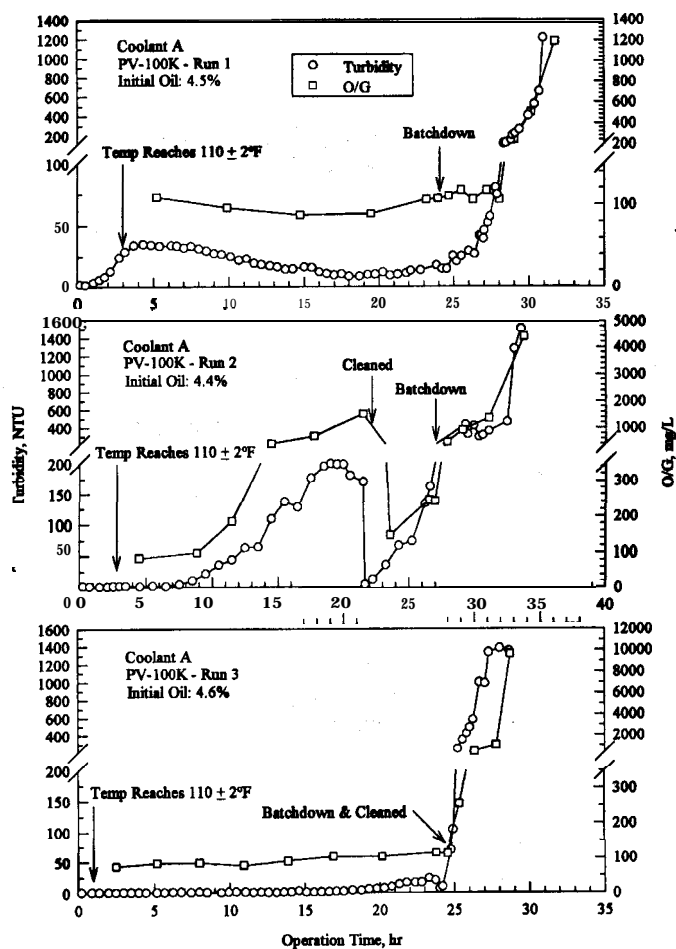


FIG. 7. Permeate Turbidity and O/G versus Operation Time for PV-100K Membrane Runs 1, 2, and 3

droplets. Coolant B's viscosity-temperature relationship was determined at a $CF = 4X$ ($\approx 20\%$ oil; data cannot be presented for proprietary reasons). The coolant viscosity decreased more sharply with temperature compared to what is predicted for water. In addition, oil droplet diffusivity increases with increasing temperature, which causes an increase in the mass transfer coefficient [see (4)], and ultimately the flux. Because the flux-temperature relationship was so strong, a full-scale system should be operated at the highest temperature possible. Thus, the ceramic membrane, which has a maximum operating temperature of about 70°C (160°F), has a distinct advantage over the polymeric membrane [maximum temperature of about 50°C (120°F)].

At 204 h rotational speed excursions were started. Rotational speeds were varied in the following sequence: $1,750 \rightarrow 1,000 \rightarrow 1,500 \rightarrow 1,250 \rightarrow 1,750$ rpm. The temperature for the rotational excursions was maintained at 43°C (110°F) and each excursion lasted about 5 h. In Fig. 11 $\log J$ versus \log rotational speed is presented. The open symbols represent the data from the first excursion, where the rotational speed was decreased from 1,750 rpm (\circ) to 1,000 rpm (\square)—the flux decreased from 9.36 to $5.70 \text{ m}^3/\text{m}^2\text{-d}$. For this rotational change, the flux-velocity relationship is $J = f(\omega)^{0.90}$. This value of α is within the range reported by Cheryan (1986) for turbulent conditions (0.8–1.2). When the rotational speed was increased from 1,000 to 1,500 rpm, the flux (\blacksquare) did not fully recover to its value predicted by $J = f(\omega)^{0.90}$. However, when the rotation speed was decreased to 1,250 rpm, the flux (\bullet) increased to the value predicted by $J = f(\omega)^{0.90}$. It is hypothesized that the flux did not have sufficient time to rebound when the rotation speed was increased from 1,000 to 1,500 rpm, but with additional time it did increase to its predicted

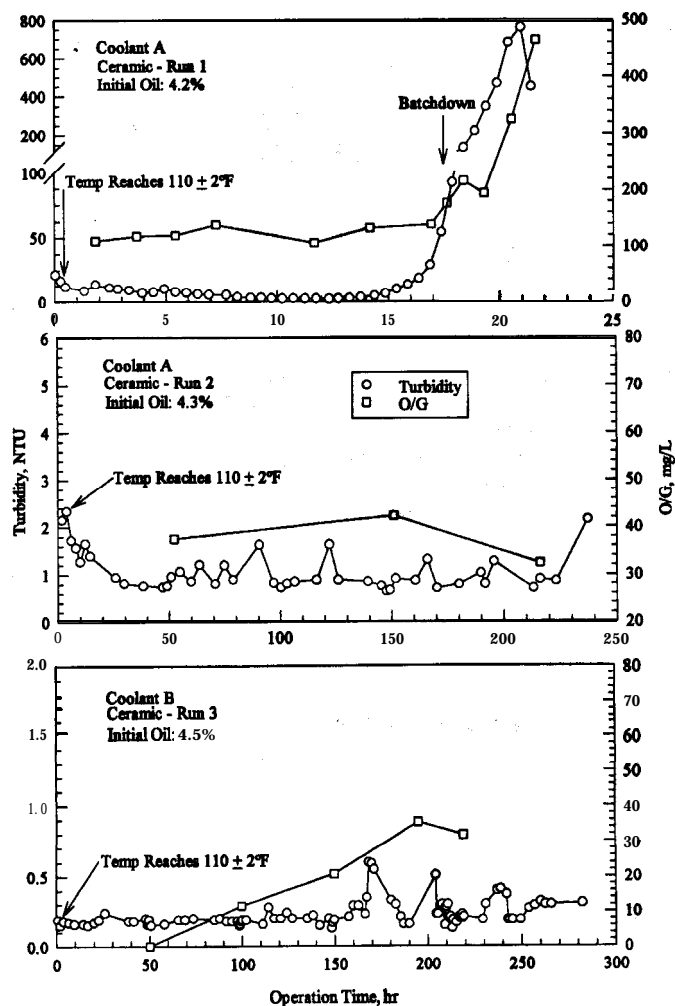


FIG. 8. Permeate Turbidity and O/G versus Operation Time for Ceramic Membrane Runs 1, 2, and 3

value. When ω was increased to 1,750 rpm (\blacklozenge), the flux increased, but not to the prerotational excursion value of $9.36 \text{ m}^3/\text{m}^2\text{-d}$. Lipp et al. (1984) reported the gel layer, once formed, may be sufficiently stable to withstand increases in turbulence. It is hypothesized that this phenomenon was operative during the rotational excursion portion of ceramic run 3. Given the large increase in permeate flux and decrease in membrane fouling potential with increasing rotational speed, the highest possible rotational speed should be used in actual operations. Permeate turbidity, O/G, and TSS were not adversely affected by temperature or rotational speed changes.

In Table 3 a summary of permeate flux results is presented for the six runs. A similar table was presented earlier for permeate quality results (see Table 2). The ceramic membrane had a larger flux compared with the PV-100K membrane. This was most likely due to the larger pore size of the ceramic membrane [$0.1 \mu\text{m}$ compared to $100,000 \text{ MWCO}$ (about $0.05 \mu\text{m}$)]. However, the use of a membrane with a larger pore diameter does not guarantee a higher flux. If the solute size is about the size of the pore, the solute can easily plug the pore opening. The ceramic membrane also produced a permeate that was generally of better quality, despite having the larger pore size. A tighter membrane does not guarantee a better quality effluent. For example, the particle size of the oil droplets in this study were between 1 and $10 \mu\text{m}$. Given that pore size of both membranes (0.1 and $0.05 \mu\text{m}$) were smaller than the diameter of the oil droplet, both membranes should reject the oil droplets in similar quantities. The fact that the ceramic membrane produced a better quality permeate indicates that other surface phenomena were operative. For example, the ce-

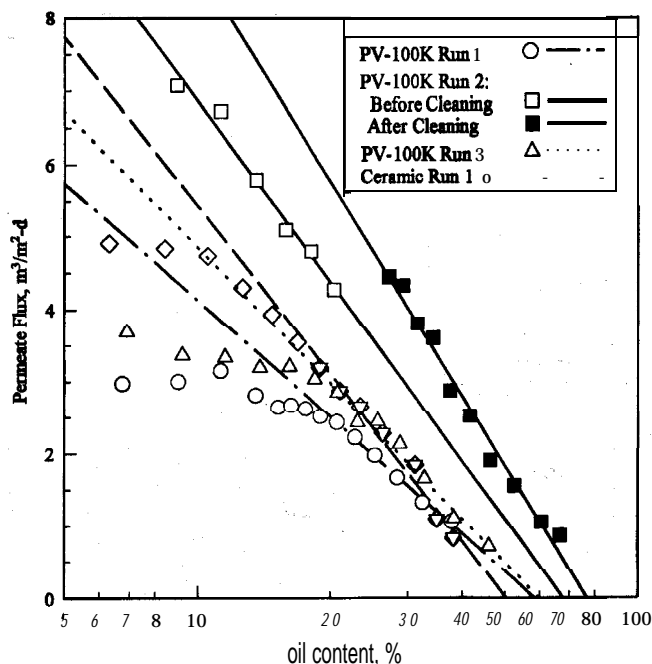


FIG. 9. Permeate Flux versus Log Oil Content for PV-100K Runs 1, 2, and 3 and for Ceramic Run 1

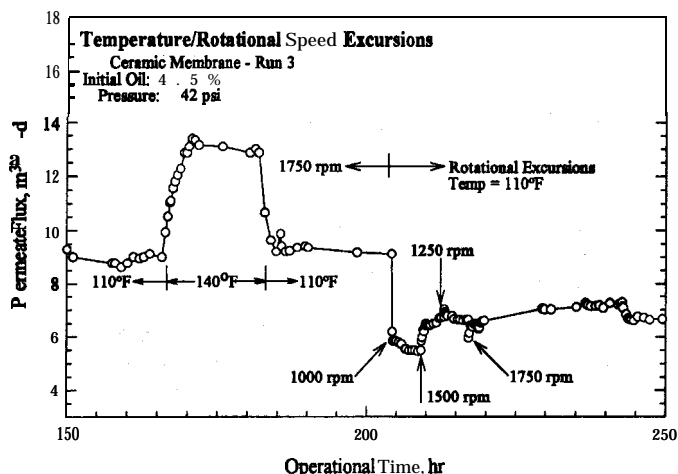


FIG. 10. Permeate Flux versus Operation Time for Ceramic Run 3 Temperature and Rotational Excursions

ceramic membrane may be more hydrophilic than the polymeric membrane. Oil is less likely to reside near the surface of a hydrophilic membrane surface, decreasing the potential for an oil droplet to be pushed through a membrane pore.

For the polymeric membrane a new membrane was required for each run. There was a noticeable layer of free oil on the polymeric membranes for all runs. Additionally, in runs P2 and P3 the CWF was never restored to near its original value. In contrast, the same ceramic membrane was used for all runs. These observations indicate that the polymeric membrane may be less hydrophilic than the ceramic membrane. Between ceramic runs 1 and 2, the washing solution was altered (no detergent). During ceramic run 1 cleaning, the flux was high but eventually decreased to 0. The membrane vessel was opened and a white deposit, believed to be commercial detergent, was observed on the membrane. After removing the deposit and sponging the ceramic membrane with $\approx 1\%$ sulfuric acid solution, the CWF was restored above its initial value.

CONCLUSION

The high-shear rotary UF system was effective in concentrating oily wastes from about 5% to as high as 65% while

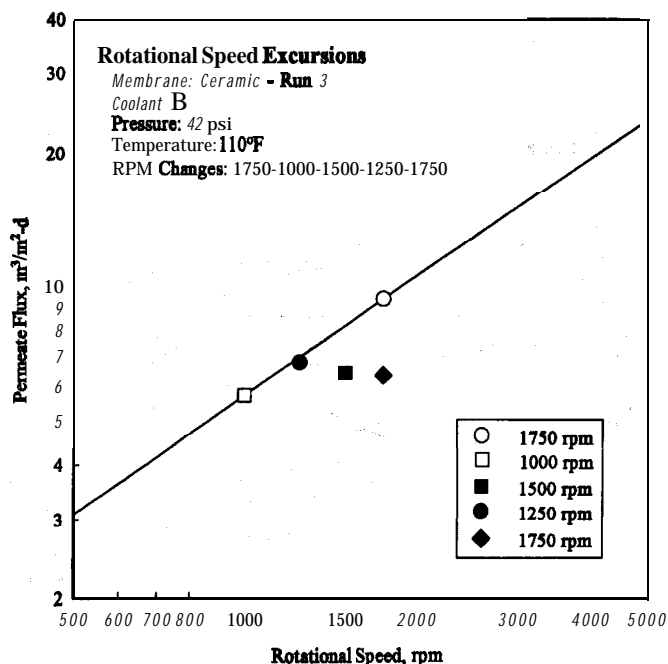


FIG. 11. Log Permeate Flux versus Log Rotational Speed for Ceramic Run 3 Rotational Excursion

TABLE 3. Summary of Permeate Flux Results

Run ID (1)	Mean Flux ^a (Range), m ³ /m ² -d			CWF, m ³ /m ² -d	
	Entire run (2)	CF: 1X to 6X (3)	CF > 6 X (4)	Before: (5)	After (6)
PV-100K					
Run 1	2.58 (1.05-3.65)	2.76 (1.92-3.65)	1.92 (1.06-1.90)	4.80	4.80
Run 2	4.47 (0.85-7.25)	5.34 (3.21-7.25)	2.50 (0.85-4.50)	24.0	7.00
Run 3	2.85 (0.70-4.15)	3.18 (2.42-4.15)	1.80 (0.70-2.52)	29.2	4.69
Ceramic					
Run 1	3.56 (0.82-5.20)	3.94 (2.54-5.20)	1.53 (0.82-2.29)	13.0	6.47
Run 2	—	5.51 (3.75-7.08)	—	20.9	17.5
Run 3 ^c	—	9.66 (9.52-10.7)	—	17.5	19.6

^aAt 43°C \pm 1°C (110°F \pm 2°F).

^bClean water flux.

^cIncludes data up to CF = 4X prior to temperature excursion.

maintaining a high permeate flux. The decoupling of turbulence promotion from feed pressurization/recirculation by rotating the membrane was hypothesized to be the primary reason for the increase in system performance over that observed with conventional cross-flow UF systems. The following specific conclusions can be forwarded:

1. Transitional and gel layer oil concentrations (20% and 50-59%, respectively) were much higher than values reported in the literature. Possible reasons include the higher level of turbulence and the variation in the thickness of the concentration polarization layer with membrane radius. The mass transfer coefficient, predicted by the film theory model, varied between 1.41 and 1.85 m³/m²-d for the two membranes tested.
2. Permeate flux was dependent on the feed temperature and rotational speed. Flux increased by about 45% when the temperature was increased from 43 to 60°C (110 to 140°F). A larger decrease in waste viscosity, over that predicted for water alone, and an increase in oil droplet diffusivity were hypothesized as reasons for the stronger than expected flux-temperature relationship. The flux-rotational speed (ω) relationship was described by $J = f(\omega)^{0.90}$; however, the gel layer did exhibit stability when ω was increased from its lowest value. Given the large increase in permeate flux and decrease in membrane

fouling potential with increased rotation, the highest possible rotational speed should be used in actual operations. Permeate water quality was not affected by temperature or rotational speed excursions.

3. The ceramic membrane was superior to the **PV-100K** polymeric membrane in regard to flux quantity and quality as well as membrane cleaning/durability. In addition, because of the higher operating temperature of the ceramic membrane ($>70^{\circ}\text{C}$ compared with 50°C for the **PV-100K** membrane), its use in full-scale operations is recommended.
4. Permeate turbidity is a satisfactory real-time indicator of permeate TSS and **O/G** concentrations. Turbidity and flux can be used to judge when the system should be cleaned

APPENDIX. REFERENCES

Bodzek, M., and Konieczny, K. (1992). "The use of ultrafiltration membranes made of various polymers in the treatment of oil-emulsions wastewaters." *Waste Mgmt.*, 12, 75-84.

- Cheryan, M. (1986). *Ultrafiltration handbook*. Technomic Publishing Co., Lancaster, Pa.
- Lee, S., Yves, A., and Roques, H. (1984). "Concentration polarization, membrane fouling and cleaning in ultrafiltration of soluble oil." *J. of Membrane Sci.*, 19, 23-38.
- Lin, W., and Reed, B. E. (1996). "Comparison of cross-flow ultrafiltration and centrifugal membrane technology in treating an oil/grease wastewater." *Proc., 28th Mid-Atlantic Industrial and Hazardous Waste Conf.*, A. Scott Weber, Ed., Technomic Publishing Co., Lancaster, Pa., 278-285.
- Lipp, P., Lee, C. H., Fane, A. G., and Fell, C. J. D. (1984). "A fundamental study of the ultrafiltration of oil-water emulsions." *J. of Membrane Sci.*, 36, 161 - 177.
- Pinto, S. D. (1978). "Ultrafiltration for dewatering of waste emulsified oils." *Lubrication challenges in metalworking and processing. Proc., 1st Int. Conf.*, Illinois Institute of Technology Research Institute, Chicago, Ill., 1-4.
- Reed, B. E., Lin, W., Dunn, C., Carriere, P., and Roark, G. (1997). "Treatment of an oil/grease wastewater using ultrafiltration." *Separation Science and Technology*, 32(9), 1493-1511.
- Standard methods for the examination of water and wastewater.* (1992). American Public Health Association (APHA), Washington, D.C.
- Zaidi, A., Simms, A., and Kok, S. (1992). "The use of micro/ultrafiltration for the removal of oil and suspended solids from oilfield brines." *Water Sci. and Technol.*, 25(10), 163 - 173.