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Brian E. Reed[a]; Wei Lin[a]; Chris Dunn[a]; Patrick Carriere[a]; Gary Roark[a]
[a] DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING, WEST VIRGINIA UNIVERSITY, MORGANTOWN, WEST VIRGINIA, USA

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Treatment of an Oil/Grease Wastewater Using Ultrafiltration: Pilot-Scale Results

BRIAN E. REED,* WEI LIN, CHRIS DUNN,
PATRICK CARRIERE, and GARY ROARK
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
WEST VIRGINIA UNIVERSITY
MORGANTOWN, WEST VIRGINIA 26506-6103, USA

ABSTRACT

Wastewater containing about 0.5% oil and grease (O/G) from a metal industry was treated by tubular ultrafiltration using membranes having a molecular weight cutoff (MWCO) of 120,000 and a negative surface charge (P membrane) and of 100,000 and no surface charge (M membrane). Permeate flux decreased dramatically during the first several hours of operation and then leveled-off for the remainder of semibatch operation. The average P membrane flux was significantly higher than the M membrane (38 versus 27 gal/ft^2·d) because of its higher MWCO and negative surface charge. Increasing the transmembrane pressure and crossflow velocity increased the permeate flux for both membranes. O/G concentrations less than 50 mg/L and total suspended solids (TSS) levels less than 25 mg/L were common for both membranes. O/G removal efficiencies (rejections) averaged 98% for the M membrane and 97% for the P membrane. TSS rejections were approximately 97% for both membranes. Effluent O/G concentration and turbidity from the P membrane were slightly higher than the M membrane because of the P membrane's higher MWCO and the larger flux. The average volume reduction and residual production were 97% and 32 gal/1000 gal, respectively. Acid cracking of the concentrate with sulfuric acid was marginally successful.

INTRODUCTION

Wastewater from a metal industry contained oil and grease (O/G) primarily from coolants that were used to dissipate heat during rolling opera-

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* To whom correspondence should be addressed.

tions. Waste coolant (≈ 5% O/G) was mixed with waste from other plant operations and was sent to two lined settling ponds where a large portion of the O/G separated and was removed by skimming. Pond effluent (≈ 0.5% O/G) was applied to a sprayfield where O/G were reduced further by microbial degradation. Groundwater regulations, in the state in which the plant was located, have been modified such that land application of almost all industrial wastes is no longer allowed. These stringent groundwater regulations forced the facility to examine other methods for treating the pond effluent. Five technologies were investigated on the pilot-scale: ultrafiltration, chemical additions–dissolved air flotation, constructed wetlands, land application, and biofilter. In this article, results from the ultrafiltration portion of the study are presented.

BACKGROUND

Ultrafiltration (UF) is a pressure-driven membrane technique that uses porous membranes for the separation of material in the 1 nm to 10 μm size range or compounds with molecular weights in excess of 5000. Collidal material, macromolecules, and micelles are examples of items that can be fractionated. "Clean" water (permeate) is forced through the porous membrane while the waste that is retained by the membrane (concentrate) becomes more concentrated. Numerous researchers have reported on UF's effectiveness in treating oil/grease wastewaters. UF reduces the volume of a waste-cutting oil emulsion by 95 to 98% and concentrated oil and solids as much as 60% (1). Bodzek and Konieczny (2) reported oil reductions of 95 to 99% and COD reductions of 91 to 98% in the UF permeate from a metal industry emulsion. Zaidi et al. (3) reported that the oil content of several oilfield brines was reduced to less than 20 mg/L and the short-term permeate flux was about 80 gal/ft^2·d. Cheryan (4) summarized several case studies in which UF was demonstrated to be an effective treatment method for oily wastes. Treatability studies for individual wastes are required to properly design a UF system.

The performance of UF systems is adversely affected by suspended solids and free oil. Over long periods of time, membrane fouling can reduce the short-term permeate flux by one, or even two, orders of magnitude (3). A decrease in the permeate flux during a treatment run is expected and is attributed to the following phenomena: 1) concentration polarization, 2) gel layer formation, and 3) contaminant adsorption by the membrane. Concentration polarization is defined as the generation of a concentration gradient of rejected particles near the membrane surface. Formation of a gel layer results when the contaminant's solubility is exceeded at the membrane surface. The contaminant may also adsorb on the membrane surface and within the membrane pores. Adsorption is often irreversible, resulting in a permanent decrease in the permeate flux (i.e., flux cannot be recovered by cleaning/backflushing). These three phenomena act to decrease the membrane's permeability. To reduce the thickness of the fouling layer (concentration polarization and gel layer), concentrate is recycled back to the membrane so that large crossflow velocities exist near the membrane surface. The large velocities increase turbulence, which reduces the thickness of the fouling layer by shearing action. Crossflow velocities in the range of 10 to 15 ft/s are typical. As the concentrate thickens during a treatment run, maintenance of high crossflow velocities is problematic because of the difficulty in pumping viscous material at large flow rates. The presence of the fouling layer also increases adsorption because the adsorptive driving force is larger. Membrane fouling can be reduced by using hydrophilic and charged membranes.

Permeate flux is influenced by such parameters as: 1) wastewater characteristics (contaminant type, solids content), 2) membrane characteristics (pore size and distribution, material, surface charge, membrane configuration), and 3) operational conditions (transmembrane pressure, temperature, crossflow velocity, run duration, concentration factor). Obviously, the characteristics of the wastewater will affect both UF system design and operation. Membrane material and configuration (e.g., tubular, hollow fiber, etc.) and operational conditions are selected with a specific waste in mind.

Membranes that are used for ultrafiltration are 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 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. As mentioned previously, 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 is also negatively charged. The repulsive force between the membrane surface and contaminant will act to decrease the fouling layer thickness as well as contaminant adsorption on the membrane surface/pores.

Increasing the transmembrane pressure, crossflow velocity, and temperature generally will increase permeate flux. The pressure–flux relationship is linear at low pressures, can level-off as the pressure is raised further, and finally can decrease at high pressures because of compression of the fouling/gel layer (5). Increasing the crossflow velocity decreases the thickness of the fouling layer, leading to an increase in flux. Increasing the temperature decreases the waste's viscosity, making it easier to push water through the membrane. High temperatures are common in UF systems because of the large amount of heat that is transferred from the pump to the waste. In some situations, heat exchangers may be required so that the membrane is not damaged by high temperatures.

UF systems are operated in the batch, semibatch, and continuous mode. In this study the pilot-scale system was operated first in the semibatch and then in the batch mode. In the semibatch mode, the permeate and raw waste flow rates were equalized by maintaining a constant volume in the feed tank. The contaminant concentration in the feed tank increases steadily with operation time. In the batch mode, which normally occurs at the end of semibatch operation, no raw waste is added to the system and the concentrate remaining from semibatch operation is concentrated further ("batch-downed"). Semibatch operation is used to produce permeate, and the batch operation is used to reduce the residual volume.

All membrane technologies are volume reduction technologies because contaminants are not degraded or destroyed. Thus, an important measure of the efficiency of membrane technology is the concentration factor (CF). CFs during semibatch and batch-down operation are calculated using the following equations. Semibatch operation:

$$\mathrm{CF_{SB}} = 1 + V_{\mathrm{perm}}/V_{\mathrm{feed\ tank}}$$

Batch-down operation:

$$\mathrm{CF_{BD}} = \mathrm{CF_{SB}} \times [V_{\mathrm{feed\ tank}}/(V_{\mathrm{feed\ tank}} - V_{\mathrm{perm}})]$$

where $\mathrm{CF_{SB}}$ = concentration factor during semibatch operation
V_{perm} = volume of permeate produced (gal)
$V_{\mathrm{feed\ tank}}$ = volume of the feed tank (gal)
$\mathrm{CF_{BD}}$ = concentration factor during batch-down operation

Concentration factors are expressed as 1×, 2×, etc., and increase with treatment time. During batch-down, CFs in excess of 100× are obtainable.

INVESTIGATIVE APPROACH

Experimental Design

UF experiments were conducted during the summer (eight runs) and winter (four runs) months. Two membrane types, denoted as M and P, were investigated. The M membrane had a molecular weight cut-off

(MWCO) of 100,000 and no net surface charge while the P membrane had a MWCO of 120,000 and a net negative surface charge. Both membranes were constructed of polyvinylidane fluoride. A tubular UF system was supplied by Koch Membrane Systems Inc. (Wilmington, MA). A schematic of the UF system is presented in Fig. 1 (6). Sixteen membrane tubes, eight for each membrane type, were housed on the UF unit. During summer operation, pond effluent was fed directly to the feed tank. During the winter months, an inclined steel plate coalescer was used as a pretreatment step prior to the UF unit. The average transmembrane pressure was held constant at 42 psi unless an excursion experiment was occurring. The UF system was first operated in the semibatch mode. For several summer runs, flow and pressure excursions were conducted during semibatch operation to determine the effect of transmembrane pressure and crossflow velocity on permeate flux. The transmembrane pressure at midlength of the tube is defined by

$$P_{TM} = (P_{in} + P_{out})/2 - P_{perm}$$

where P_{TM} = transmembrane pressure at midlength
P_{in} = pressure at inlet of tube
P_{out} = pressure at outlet of tube
P_{perm} = pressure on the permeate line

P_{perm} is zero for normal operations. The crossflow velocity is controlled by altering ΔP ($P_{in} - P_{out}$) and P_{perm} while P_{TM} is kept constant. ΔP

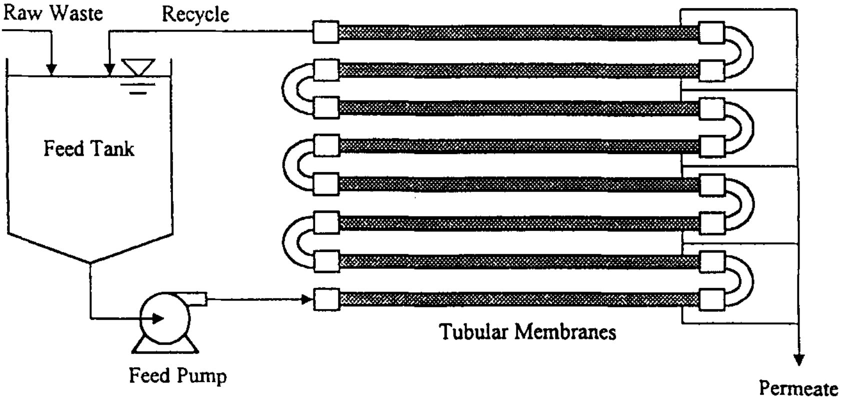

FIG. 1 Schematic of Koch Tubular Ultrafiltration System (6).

was varied between 9 and 29 psi while the transmembrane pressure was kept constant at 42 psi. Transmembrane pressures were varied between 27.5 and 43.5 psi while holding ΔP constant. For all pressure and flow excursions, the concentration factor was held constant by recycling the permeate back to the feed tank. Following semibatch operation, the system was operated in the batch mode. For two winter runs, acid cracking experiments were conducted on the concentrate remaining after the batch operation.

Data collected during the research included influent and effluent water quality parameters (O/G, TSS, turbidity, pH, temperature) and process performance parameters (flux, concentration factor, residual production). O/G, TSS, and pH data were collected because these parameters were of concern to the regulatory community. The effectiveness of UF technology was based primarily on the magnitude of the permeate flux and the removal of O/G. Turbidity data were used as a real-time indicator of process effectiveness as well as to determine if there is a correlation between turbidity and O/G.

Materials and Methods

Preparation for operating the UF system in the semibatch mode included filling two large holding tanks with wastewater from one of the two settling ponds. Influent wastewater was sampled for O/G, TSS, temperature, and pH. The influent wastewater was pumped to the 225 gallon feed tank located on the UF unit. Wastewater was periodically introduced into the feed tank via a level control/solenoid system. During semibatch operation, wastewater temperature was monitored using an in-line thermometer. Inlet and outlet pressures were monitored with in-line pressure gages. Samples of influent and UF concentrate and permeate were taken periodically and analyzed for turbidity, O/G, TSS, and pH. Turbidity on a given sample was monitored with time and no significant change was observed, thus the initial turbidity was reported. Permeate flux was monitored using a graduated cylinder and stopwatch. Data collected during batch operation were basically the same as those reported for semibatch operation except that the volume and quality of the residual at the end of batch-down was determined.

At the conclusion of batch operation a 45 to 50 gallon supply of 0.5% solution of a proprietary detergent [Koch Liquid Detergent (KLD)] and tap water was prepared in the cleaning tank. The membranes were cleaned for a total of 60 minutes with the concentrate and permeate being routed into the cleaning tank. Toward the middle of the cleaning period, sponge balls were inserted into the membrane tubes and were pumped through the membranes and retrieved in the cleaning tank. Spongeball cleaning was repeated and then the unit was allowed to continue with KLD cleaning for an additional 30 minutes. At the end of the cleaning, the KLD solution was removed from the cleaning tank and purged wastewater was removed from the feed tank with a submersible pump. Fresh tap water was fed into the cleaning tank, and the contents of the membranes were purged into the feed tank. Tap water was circulated through the membranes and the clean water flux (CWF) was determined. The CWF after each cleaning was compared to the CWF determined with virgin membranes. If the CWF was not close to the virgin CWF, then the cleaning procedure was repeated.

Acid cracking experiments were conducted on the residual remaining after batch-down was completed. The residual was completely mixed, and a sample was taken and placed in a graduated beaker. Known quantities of concentrated sulfuric acid were added followed by rapid mix and settling periods. Observations were made after each acid addition/mixing/settling effort to determine if the sample had broken. Once the sample broke, the volume of the broken phase free oil was recorded and the water content (burnability) determined.

Analytical Methods and Quality Assurance/Quality Control

O/G was determined using Standard Methods 413.1, Liquid Partition Gravimetric Method. TSS was determined by Standard Methods 160.2. Turbidity and pH were determined using a Nephlometric Turbidimeter and an Omega pH meter, respectively. Temperatures were determined with a mercury thermometer. Water content was determined using an facility-specified method that utilized hexane to separate oil and water from the broken phase. After oil and water separation, the water content was determined by measuring the volume of water separated from the sample. Ten percent of the analyses were duplicated, and results were generally within 10%.

RESULTS AND DISCUSSION

Results are presented under the following headings: permeate flux; permeate quality; flow and pressure excursions; and batch-down and residual production/treatment. A preliminary design of the membrane systems is also provided.

Permeate Flux

In Figs. 2 and 3 the permeate flux and concentration factor during semibatch operation for summer run 1 (S1) and for winter run 3 (W3) are presented, respectively. The horizontal line represents the average per-

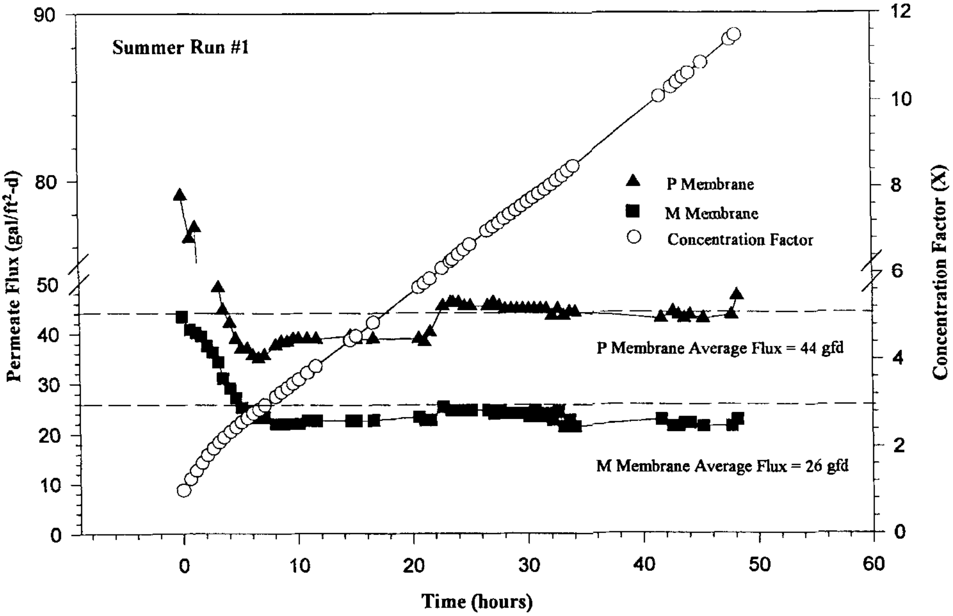

FIG. 2 Permeate flux and concentration factor during semibatch operation for summer run 1.

meate flux over the duration of the run. Initially, the initial portion of the permeate flux graph was neglected when calculating the average flux. However, based on recommendations from the UF manufacturer, this portion was later included in the average flux calculation because while the high flux may only occur for several hours, a substantial amount of permeate can be produced. The permeate flux versus time for the other UF runs were similar in shape except for summer run 4 which had to be ended early because of low fluxes for both membranes. For all runs, the permeate flux decreased dramatically during the first several hours of operation and then leveled-off for the remainder of semibatch operation. The decrease in flux with time can be attributed to concentration polarization and the possible development of an oily gel layer at the membrane surface. Lee et al. (7) reported that a gel layer can form when the O/G concentration is between 0.5 and 3%. Thus, at the larger concentration factors observed toward the end of the semibatch operation, gel layer formation may have occurred. Regardless of the fouling mechanism, the membrane permeability decreased, causing a decrease in flux with time. This result was expected and is common in membrane applications.

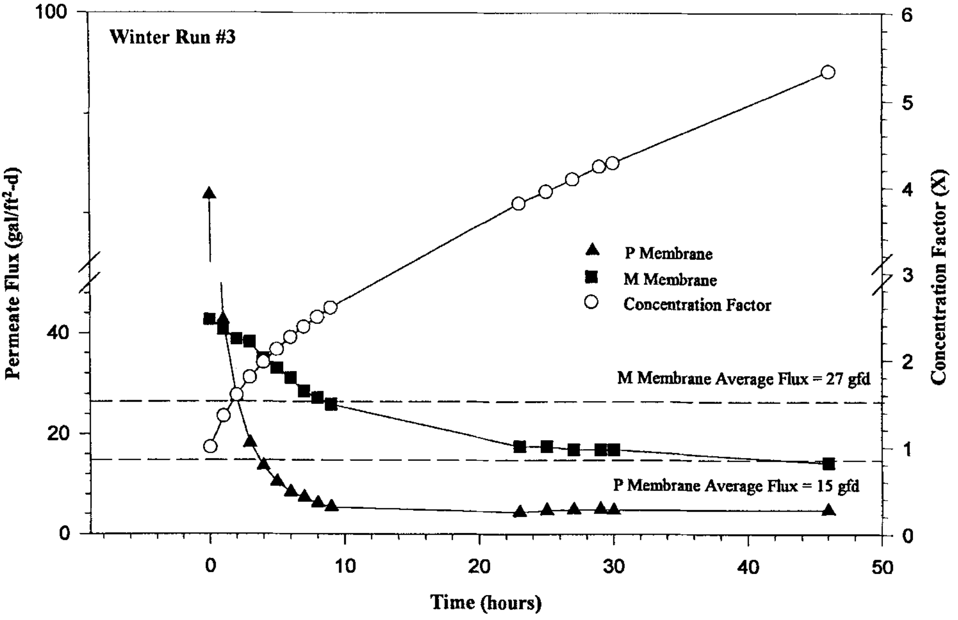

FIG. 3 Permeate flux and concentration factor during semibatch operation for winter run 3.

In Table 1 a summary of permeate flux and temperature results is presented for summer and winter operation. Run S4 was omitted because the flux decreased to almost zero after only 2 hours of operation. In a full-scale operation, waste that is processed at such a low flux would be returned to the facility's separation ponds for a longer opportunity to separate and homogenize.

The overall average P membrane flux was significantly higher than the M membrane flux (38 versus 27 gal/ft^2·d) as well as the flux observed during both summer and winter operations. On an individual run basis, the P membrane flux was greater than or equal to the M membrane flux for all runs except W3 and W4. The higher flux for the P membrane can be attributed to its higher MWCO (120,000 compared to 100,000) and negative surface charge. The larger the MWCO, the higher the membrane's permeability. The repulsion of the negatively charged O/G droplets by the P membrane surface decreased the fouling layer thickness.

In Table 1 the influent temperature represents the temperature of the pond effluent when it first arrived in the treatment facility's holding tanks. The lower value of the concentrate temperature represents the tempera-

TABLE 1
Summary of Average Permeate Fluxes and Temperatures

Run	Permeate flux (gal/ft^2·d) M	P	Temperature (°F) Influent	Concentrate[a]
S1	26	43	78	78–110 (102)
S2	30	63	72	72–100 (86)
S3	58	58	70	70–94 (86)
S5	16	25	77	76–110 (98)
S6	17	20	77	73–111 (92)
S7	26	31	76	75–106 (94)
S8	32	69	77	79–102 (93)
W1	25	29	67	65–92 (79)
W2	22	47	62	68–82 (75)
W3	26	15	64	61–100 (90)
W4	17	16	63	56–100 (87)
Average summer	29	44	75	93
Average winter	22	26	64	83
Overall average[b]	27	38	—	—

[a] Range, average value is given in parentheses.

[b] Average of summer and winter data.

ture of the feed tank contents at the start of the run while the high value represents the temperature toward the end of the run. The average concentrate temperature during semibatch operation is included in parentheses. The ability of the pump to increase the temperature of the concentrate is apparent during both summer and months. In one sense, the increase in temperature is welcomed since the flux increases with the decrease in viscosity. However, during one period in the summer when ambient temperatures rose to over a 100°F, the temperature of the membranes increased to such an extent that the membrane housings had to be hosed down with tap water to prevent damage. Following these episodes, a heat exchange was installed but was not needed in subsequent runs.

The average temperature of the UF influent and concentrate was about 10 degrees lower in the winter than in the summer. The difference in flux based on viscosity differences at 83 and 93°F (average concentrate temperatures for winter and summer months, respectively), is only 12% while the actual fluxes were 25 and 40% lower in the winter months for the M and P membranes, respectively. As will be discussed in the next section, the O/G and TSS content of the influent was higher in the summer months. Thus, the lower winter flux is not attributable to O/G and TSS content although the nature of the waste may be quite different.

Permeate Quality

In Table 2 the UF influent and effluent quality results are presented. The influent O/G ranged from 920 to 5600 mg/L and averaged 2460 mg/L, while the TSS ranged from 150 to 2100 and averaged 645. Summer influent concentrations of O/G and TSS were slightly higher than those observed during winter operations. Waste variability over the course of the entire project as well as within a given run was large and demonstrates the complex nature of the waste in the settling ponds. In some cases, influent quality changed noticeably within a matter of minutes. The influent TSS was primarily made up of O/G. Following filtration onto a

TABLE 2
Summary of Influent and Effluent Quality Results[a]

			Permeate					
	Influent (mg/L)		O/G (mg/L)		TSS (mg/L)		Turbidity (NTU)	
Run	O/G	TSS	M	P	M	P	M	P
S1	2300–2600 (2500)	600–630 (615)	3–105 (39)	6–97 (45)	NA	NA	NA	NA
S2	2000–3700 (2600)	950	7–12 (9)	10–13 (11)	NA	NA	NA	NA
S3	2100–5600 (3900)	1000–1500 (1240)	5–21 (9)	9–26 (15)	9–13 (10)	5–23 (11)	1.8–21 (7)	1.6–27 (9)
S5	2300–3500 (3030)	930–1300 (1090)	8–590 (245)	18–1060 (470)	9–87 (39)	6–92 (43)	23–32 (26)	25–134 (73)
S6	2350–4600 (3200)	930–2100 (1500)	7–63 (25)	9–160 (55)	NA	NA	4.5–44 (22)	20–75 (46)
S7	1500–2500 (2000)	440–1200 (820)	5–43 (23)	6–68 (30)	5–9 (6.3)	5–8 (6.0)	0.6–16 (7.8)	4–42 (20)
S8	920–1700 (1110)	290–910 (450)	6–15 (14)	8–19 (15)	NA	NA	13–36 (19)	22–38 (33)
W1	1280–3080 (2350)	150–1460 (310)	15–43 (26)	18–61 (34)	14–17 (15)	18–22 (19)	0.7–1.1 (1)	5.2–18 (9.8)
W2	1610–2080 (1850)	560–800 (700)	34–45 (40)	29–36 (33)	5–10 (7.5)	5–6 (5.5)	2.6–4.5 (3.5)	4.9–8.3 (6.6)
W3	2440–3550 (2930)	730–1180 (890)	28–126 (87)	5–300 (115)	25–170 (93)	32–52 (43)	6.3–17 (11)	3–37 (31)
W4	900–3230 (2080)	190–1130 (650)	27–93 (55)	16–142 (82)	5–26 (14)	5–18 (18)	18–35 (25)	12–46 (26)
Average summer	2620	950	40	67	18	20	18	36
Average winter	2300	640	52	66	32	21	10	18
Overall average[b]	2460	645	46	66	20	20	14	27

[a] Range, average value is given in parentheses. NA: Not available.

[b] Average of summer and winter data.

0.8-μm filter, the filter was washed with Freon. The weight of the filter after drying was significantly less than the weight of a duplicate sample that was not washed with Freon. The influent pH averaged 6.2 in the summer and 6.5 in the winter.

While there were some effluent samples with high O/G and TSS concentrations, the vast majority of the samples had O/G concentrations less than 50 mg/L and TSS levels less than 25 mg/L. O/G removal efficiencies (rejections) averaged 98% for the M membrane and 97% for the P membrane. TSS rejections were approximately 97% for both membranes. The discharge permit for this facility has not been finalized but it is likely that a tertiary treatment system that is capable of lowering O/G concentrations to less than 15 to 25 mg/L will be required. It is envisioned that a land-based system, such as constructed wetlands, will be chosen, and the influent O/G to the tertiary system should be on average less than 100 mg/L. Given these criteria, UF meets the requirements of a secondary treatment system.

For all runs the effluent O/G concentration and turbidity from the P membrane were higher than from the M membrane. Effluent TSS was greater for the P membrane for all runs except W3 and S7 (TSS for run S7 was almost equal). Given the larger MWCO of the P membrane (120,000 compared with 100,000), the effluent should be better for the M membrane. In addition, O/G was transported to and possibly through the P membrane at a higher rate/force because the flux for the P membrane was usually higher. The negative charge of the P membrane counteracted the increase in advective transport. Effluent quality during the winter months was slightly better than that observed during the summer months, possibly due to the lower influent contaminant concentrations and lower fluxes. Effluent pH averaged 6.3 and 6.75 for the M and P membranes, respectively, well within the range (6–9) the facility would be required to meet under its discharge permit.

Because of the time required for an O/G analysis, it cannot be used as a real-time indicator of process performance. Effluent turbidities were measured for all samples in which O/G analyses were performed to determine if there was a relationship between the two parameters. It was hoped that turbidity could be used as a real-time indicator of effluent quality. However, there was not a statistically significant relationship between O/G and turbidity (data not presented). Thus, the use of turbidity as an indicator of O/G rejection is not possible.

Flow and Pressure Excursions

In Figs. 4 and 5 the results from transmembrane pressure and crossflow (ΔP) excursions for summer run 1 are presented, respectively. Results

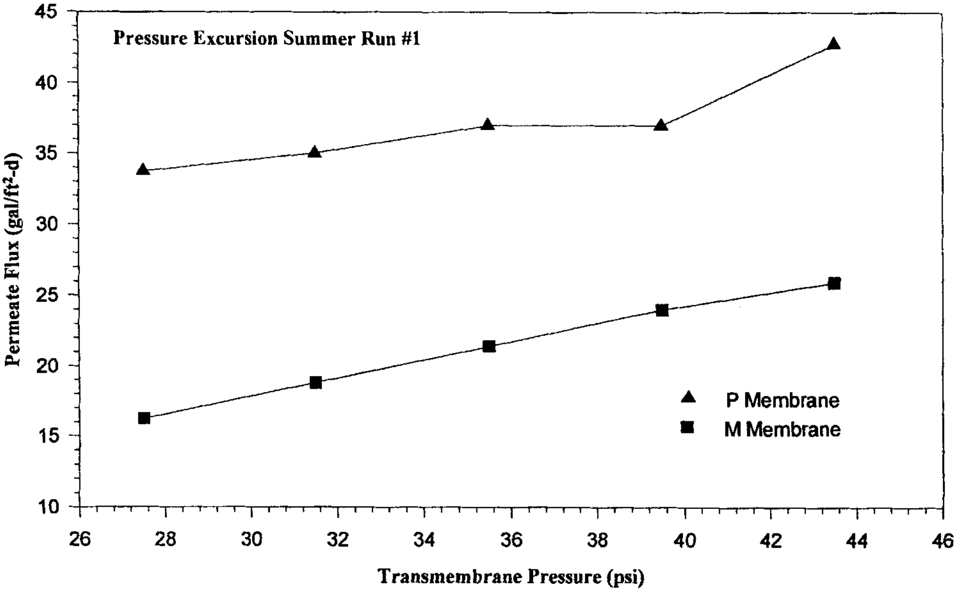

FIG. 4 Permeate flux versus transmembrane pressure for summer run 1.

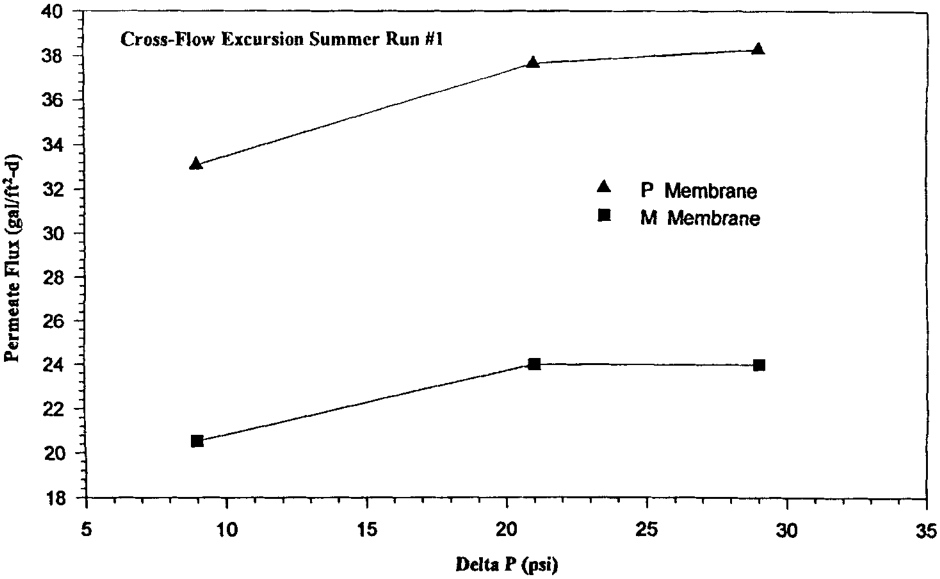

FIG. 5 Permeate flux versus ΔP for summer run 1.

from other excursions were similar to those in Figs. 4 and 5. Increasing the transmembrane pressure from 27.5 to 43.5 increased the P and M membrane fluxes from 34 to 43 gal/ft^2·d and from 16 to 26 gal/ft^2·d, respectively. There was no leveling-off of the flux at higher pressures, indicating that gel formation had not yet become a major factor. Additional increases in transmembrane pressure were not possible because of pump limitations. Increasing ΔP (crossflow velocity) from 9 to 21 increased the P and M membrane fluxes from 33 to 38 gal/ft^2·d and from 20.5 to 24 gal/ft^2·d, respectively For both membranes, the flux plateaued at higher values of ΔP but more so for the M membrane. Less material was transported to the surface for the M membrane because of the lower flux. Thus, concentration polarization and gel layer formation would not occur to the extent it would with the P membrane. Therefore, changes in crossflow velocity would have less of an effect on the M membrane compared to the P membrane.

Batch-down and Residual Production/Treatment

In Table 3 a summary of the results from batch-down operations is presented. Batch-down was not conducted for runs S4, S5, S7, W1 and W2. For runs S7 and W2, the feed tank overflowed due to a faulty solenoid valve. High temperatures prevented batch-down during run S5 while low fluxes at the end of the semibatch portion of runs S4 and W1 necessitated membrane cleaning. If batch-down was not possible in full-scale operation, the concentrate at the end of semibatch operation would be sent back into the separation ponds to allow for free oil separation and for a more homogeneous mixture of wastes to be introduced to the UF unit.

TABLE 3
Summary of Batchdown Results

Run	Concentration factor[a]	Volume reduction (%)	Residuals (gal/1000 gal)	Temperature (°F)	Average flux (gal/ft^2·d) M	Average flux (gal/ft^2·d) P	Average permeate O/G (mg/L) M	Average permeate O/G (mg/L) P
S1	27 ×	95.6	44	106	22	34	112	14
S2	23 ×	95.6	44	100	25	52	15	14
S3	16 ×[b]	94.2	58	112	NA	NA	11	46
S6	60 ×	96.6	30	117	16	20	26	24
S8	116 ×	98.3	18	111	30	63	8	10
W3	42 ×	97.8	23	107	6	15	98	33
W4	104 ×	99	10	103	9	7	93	43

[a] At end of batch-down.

[b] Batch-down was ended prematurely because of high temperature.

Concentration factors (CF) between 16 and 116× and volume reductions between about 94 and 99% were observed at the end of batch-down. Residual production ranged from 10 to 58 gal/1000 gal of wastewater treated. Batch-down for run S3 ended prematurely because of high temperatures producing the lowest CF and the highest residual production (16× and 58 gal/1000 gal). The average volume reduction and residual production for the entire project were 97% and 32 gal/1000 gal, respectively. The summer batch-down permeate fluxes were similar to the average fluxes observed during semibatch operation while the winter batch-down fluxes were lower. The maintenance of the flux during batch-down despite the increase in feed tank O/G and TSS concentrations can be attributed to the system being operated at a high temperature for the duration of batch-down operation.

During batch-down for runs S7, S8, W1, W3, and W4, free oil appeared in the feed tank. The free oil was periodically removed and later analyzed for water content. In Table 4 the free oil production rates and water contents are presented. Free oil production ranged from 2.5 to 7.3 gal/1000 gal of wastewater treated. All samples had a trace amount of water associated with the free oil (<5%). The facility in question conducted burnability tests and reported that the free oil was suitable for burning in on-site boilers.

In Table 5 the results from H_2SO_4 cracking experiments performed on concentrate taken at the end of batch-down for runs W3 and W4 are presented. Increasing the volume of concentrated H_2SO_4 from 140 to 180 mL (per 1000 mL concentrate) for run W3 caused the emulsion to go from a partial break to a complete break. The turbidity from the sample that broke completely was relatively low. However, the volume of residual was about the same as the amount of acid added. Thus, little volume reduction occurred. In addition, the supernatant had a very low pH and

TABLE 4
Free Oil Production and Water Content

Run	Water content	Free oil production (gal/1000 gal)
S7	Trace	7.3
S8	Trace	3.8
W1	Trace	3.7
W3	Trace	2.5
W4	Trace	4.7
Average	Trace	4.4

TABLE 5
Results of Acid Cracking Experiments

Run	CF	H_2SO_4 added (mL)	Residual volume (mL/L)	Supernatant pH	Supernatant turbidity NTU	Comments
W3	42×	140	60	<1	>200	Partial break
W3	42×	180	175	<1	124	Break
W4	104×	280	50	<1	>200	Partial break

would require adjustment prior to discharge to the settling ponds. The broken phase also had a very low pH and would be considered a hazardous waste. The facility in question decided not to pursue acid cracking further because of regulatory and health/safety concerns.

Membrane Cleaning

Membrane cleaning is an integral part of a successful UF system. One measure of how well a membrane is cleaned is the clean water flux (CWF). In Table 6, clean water fluxes and run durations are presented. For all runs, cleaning the membrane resulted in a CWF in excess of the virgin CWF. Thus, membrane fouling was not apparent. CWFs larger than the virgin CWF are most likely due to the presence of residual cleaning solution in the system. Another measure used to determine if a membrane is fouled is to compare the flux during treatment from one run to the next (see Table 1). There was no discernible trend of lower permeate fluxes with an increase in run number.

Runs S4 and W1 were ended because of low flux during semibatch operation. However, cleaning restored the membrane's CWF. Two cleanings were required for runs S5, S6, and W3. It does not appear that run duration was the reason that a second cleaning was needed. Runs of considerably longer duration (runs S6 and W4) required only one cleaning. The implications of a second cleaning are an additional half to one hour of labor and the use and generation of additional cleaning solution.

Preliminary Design of Full-Scale UF System

In Table 7 the preliminary design information for a full-scale UF system that utilizes the P membrane is presented for summer and winter conditions. The P membrane was chosen because during winter and summer testing the P membrane flux was consistently higher than that of the M

TABLE 6
Clean Water Flux and Run Duration

Run	Run duration (h)	Clean water flux ($gal/ft^2 \cdot d$)	
		M	P
Virgin	—	98	206
S1	57	99	274
S2	48	112	434
S3	50	156	362
S4[a]	2	146	386
S5[b]	32	111	426
S6[b]	123	103	361
S7	52	152	370
S8	83	126	369
W1[a]	22	105	257
W2	29	246	510
W3[b]	63	130	255
W4	208	189	446

[a] Two cleanings were required to reach stated CWF.
[b] Run was ended early because of low flux.

membrane while the effluent quality for the P membrane was not significantly different than that observed for the M membrane. The design flow rate is 80,000 gal/d. The require membrane area for winter conditions assuming a 5% expansion capability is 3240 ft^2. During summer months the system will be able to process more waste than the daily flow, which is attractive for the facility because the settling ponds can be drawn down, creating additional storage space for periods of inclement weather (it is

TABLE 7
Preliminary Design of Full-Scale UF System

Design parameter	Summer	Winter
Number of tubes	922	1,472
Membrane area/tube, ft^2	2.2	2.2
Total membrane area, ft^2	2,030	3,240
Average flux, $gal/ft^2 \cdot d$	44	26
Capacity, gal/d	89,232	84,188
Estimated tube life, yr	5	5
Membrane tube cost, $	250	250

envisioned that a land-based tertiary treatment system will also be used). Provisions have been made in the full-scale design to include heat exchangers and submersible heaters for high and low temperature control, respectively, as well as the use of parallel UF units. The estimated life of the membranes was provided by the UF manufacturer and was verified by discussions with several membranes users.

CONCLUSIONS

Wastewater containing about 0.5% oil and grease (O/G) from a metal industry was treated by tubular ultrafiltration using membranes having a molecular weight cutoff (MWCO) of 120,000 and a negative surface charge (P membrane) and of 100,000 and no surface charge (M membrane). Eight runs were conducted during summer months and four runs were conducted during winter months.

For all runs the permeate flux decreased dramatically during the first several hours of operation and then leveled-off for the remainder of semi-batch operation. The flux decrease can be attributed to concentration polarization and the possible development of an oily gel layer at the membrane surface. The average P membrane flux was significantly higher than the M membrane flux (38 versus 27 gal/ft^2·d) because of its higher MWCO and negative surface charge. The average temperature of the waste was about 10 degrees lower in the winter than in the summer while the fluxes were 25 and 40% lower in the winter months for the M and P membranes, respectively. Viscosity effects due to temperature differences could only account for 12% of the differences in permeate fluxes between winter/summer operation. Increasing the transmembrane pressure increased the permeate flux for both membranes, and leveling-off of the flux was not observed. The effect of ΔP (crossflow velocity) on permeate flux was similar except a flux plateau occurred at higher values of ΔP.

O/G concentrations less than 50 mg/L and TSS levels less than 25 mg/L were common for both membranes. O/G removal efficiencies (rejections) averaged 98% for the M membrane and 97% for the P membrane. TSS rejections were approximately 97% for both membranes. Effluent O/G concentration and turbidity from the P membrane were slightly higher than the M membrane because of the P membrane's higher MWCO and the larger flux. There was no correlation between effluent turbidity and O/G. Thus, the use of turbidity as a real-time indicator of O/G removal is not possible.

Concentration factors (CF) between 16 and 116× and volume reductions between about 94 and 99% were observed at the end of batch-down. Residual production ranged from 10 to 58 gal/1000 gal of wastewater treated. The average volume reduction and residual production were 97% and 32 gal/1000 gal, respectively. Free oil separated out from the waste in the feed tank at a rate that ranged from 2.5 to 7.3 gal/1000 gal of wastewater treated. All free oil samples contained trace amounts of water and could be burned at the facility's boilers. Acid cracking of the concentrate with sulfuric acid was marginally successful. While the waste was broken, the large amount of acid required negated any volume reduction benefits and produced two very low pH phases.

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